

Conclusions

In a previous report,⁸ we proposed that the binding of ligands to ferrous porphyrins should be described by a three-state mechanism. Here, we report the studies of the bimolecular association rates under applied solution pressure. The positive volumes of activation for the bimolecular association of MeNC, *t*-BuNC, and 1MeIm to five-coordinate model heme complexes indicate that the rate-controlling transition state occurs as the ligand enters the "contact pair". The large negative volume of activation for the bimolecular association of CO to MCPH indicates that the transition state for binding occurs in the bond-making process. The smaller negative value for O₂ suggests an intermediate case.

The bimolecular association of ligands to sperm whale myoglobin, as well as the escape of the ligands from the protein, has been studied under pressure. Isocyanide ligands and O₂ have a positive volume of activation in which the overall transition state for ligation is attributed to the ligand entering the protein. The transition state for the bimolecular association of CO to deoxy-

myoglobin is assigned to the bond-making process on account of its negative volume of activation.

The volumes of activation for the escape of ligands from the protein to the solvent are all positive. This can be attributed to a conformational change of the protein that is required as the ligand leaves the heme pocket.

These pressure studies are well understood within the three- and four-state models previously proposed. They add support for the basic concept and behavior of the intermediates postulated.

Acknowledgment. This research was supported in part by National Institutes of Health Grants HL13581 (T.G.T.) and RR02353-01 and National Science Foundation Grant CHE-8715561 (D.M.). Support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged (R.v.E.).

Registry No. (MeNC)PHDME, 128218-29-1; (*t*-BuNC)PHDME, 128218-30-4; CO, 630-08-0; O₂, 7782-44-7; MeNC, 593-75-9; *t*-BuNC, 7188-38-7.

Hydrogen Atom Transfer Reactions of Transition-Metal Hydrides. Kinetics and Mechanism of the Hydrogenation of α -Cyclopropylstyrene by Metal Carbonyl Hydrides

R. Morris Bullock* and Edward G. Samsel

Contribution from the Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973. Received January 8, 1990

Abstract: The hydrogenation of α -cyclopropylstyrene (CPS) by a series of metal carbonyl hydrides (MH) gives a mixture of the unrearranged hydrogenation product Ph(CH₃)(c-C₃H₅)CH (UN) and the rearranged hydrogenation product (*E*)-Ph(CH₃)C=CHCH₂CH₃ (RE). With the exception of HCr(CO)₃Cp, second-order kinetics are found, conforming to the rate law $-d[\text{CPS}]/dt = k[\text{CPS}][\text{MH}]$. The proposed mechanism involves hydrogenation by sequential hydrogen atom transfers from the metal hydride to the organic substrate. The rate-determining step is the first hydrogen atom transfer in which a carbon-centered radical and a metal-centered radical are formed. In the case of HCr(CO)₃Cp at 22 °C, the equilibrium constant for this step is $K \sim 10^{-12}$. The effect of the significant amount of 17-electron *Cr(CO)₃Cp radical formed in the hydrogenation of CPS by HCr(CO)₃Cp is accommodated by the kinetic analysis. Since the initially formed carbon-centered radical undergoes first-order ring-opening rearrangement in competition with second-order trapping by MH, analysis of the product ratio as a function of [MH] concentration provides relative rates of hydrogen atom transfer from metal hydrides to a carbon-centered radical. Relative rates of hydrogen atom transfer at 60 °C from MH to 1 are as follows: $k_{\text{rel}} = 1$ for HMn(CO)₅PPh₃, $k_{\text{rel}} = 4$ for HMo(CO)₃(C₅Me₅), $k_{\text{rel}} = 93$ for HMo(CO)₃Cp, $k_{\text{rel}} = 94$ for HFe(CO)₂(C₅Me₅). Comparison of the hydrogenation of CPS by HW(CO)₃Cp and DW(CO)₃Cp indicates that the kinetic isotope effect is inverse ($k_{\text{HW}}/k_{\text{DW}} = 0.55$) for the first hydrogen atom transfer but normal ($k_{\text{HW}}/k_{\text{DW}} = 1.8-2.2$) for the second hydrogen atom transfer. The first hydrogen atom transfer is endothermic, and its rate is largely influenced by the strength of the M-H bond. Steric effects appear to exert a dominant influence on the rate of the second hydrogen atom transfer, which is exothermic. Kinetic and mechanistic experiments indicate that hydrogenation of 2-cyclopropylpropene by HCr(CO)₃Cp also occurs by a radical pathway.

Organometallic reactions involving odd-electron pathways and free-radical intermediates have become increasingly well-recognized.¹ A prominent example is the homolytic cleavage of the M-H bond of a metal hydride, resulting in hydrogen atom transfer reactions. A seminal study by Sweany and Halpern² provided definitive evidence that the hydrogenation of α -methylstyrene by HMn(CO)₅ proceeds by a free-radical mechanism. Several lines of evidence, including the observation of an inverse kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} \approx 0.4$) and CIDNP effects in the NMR, were

consistent with a mechanism involving sequential hydrogen atom transfers from the metal hydride to the organic substrate. Similar hydrogen atom transfer reactions have been proposed to occur in the hydrogenation of substituted styrenes,³ anthracenes,⁴ all-

(1) For reviews treating various aspects of free radical mechanisms, metal radicals, and hydrogen atom transfer, see: (a) Halpern, J. *Pure Appl. Chem.* **1986**, *58*, 575-584; **1979**, *51*, 2171-2182. (b) Brown, T. L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 80-89. (c) Tyler, D. R. *Prog. Inorg. Chem.* **1988**, *36*, 125-194. (d) Troglor, W. C. *Int. J. Chem. Kinet.* **1987**, *19*, 1025-1047. (e) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217-1227. (f) Eisenberg, D. C.; Norton, J. R. *Isr. J. Chem.*, in press.

(2) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335-8337.

(3) (a) Sweany, R. L.; Comberrel, D. S.; Dombourian, M. F.; Peters, N. A. *J. Organomet. Chem.* **1981**, *216*, 57-63. (b) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *182*, 299-311. (c) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1980**, *199*, 265-269. (d) Nalesnik, T. E.; Freudenberger, J. H.; Orchin, M. *J. Organomet. Chem.* **1981**, *221*, 193-197; *J. Mol. Catal.* **1982**, *16*, 43-49; *J. Organomet. Chem.* **1981**, *236*, 95-100. (e) Nalesnik, T. E.; Orchin, M. *Organometallics* **1982**, *1*, 222-223. (f) Matsui, Y.; Orchin, M. *J. Organomet. Chem.* **1983**, *244*, 369-373. (g) Ungváry, F.; Markó, L. *Organometallics* **1982**, *1*, 1120-1125; *J. Organomet. Chem.* **1983**, *249*, 411-414. (h) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1981**, *222*, C5-C8. (i) Bockman, T. M.; Garst, J. F.; King, R. B.; Markó, L.; Ungváry, F. *J. Organomet. Chem.* **1985**, *279*, 165-169. (j) Roth, J. A.; Wiseman, P. *J. Organomet. Chem.* **1981**, *217*, 231-234. (k) Roth, J. A.; Wiseman, P.; Ruzsala, L. *J. Organomet. Chem.* **1983**, *240*, 271-275.

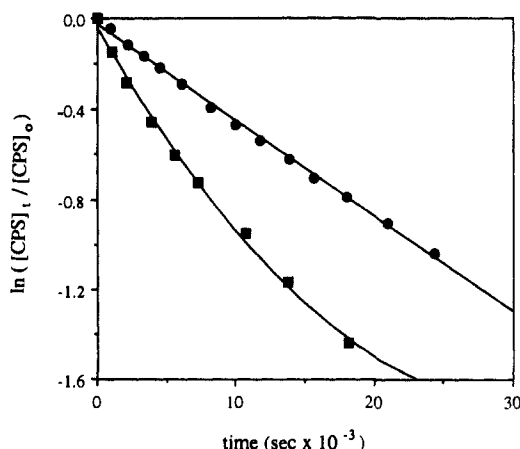
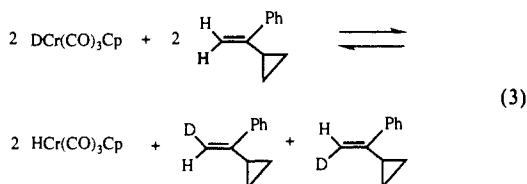


Figure 2. Plot of $\ln ([CPS]_t/[CPS]_0)$ vs time for the reaction of $HCr(CO)_3Cp$ (0.058 M) with CPS (0.0053 M) at 22 °C. ■, no added $[Cr(CO)_3Cp]_2$; ●, solution saturated with $[Cr(CO)_3Cp]_2$.

Reversibility of the First Hydrogen Atom Transfer Step. As indicated by the proposed mechanism (Scheme I), the initial hydrogen atom transfer is reversible. The reversibility of this hydrogen atom transfer was demonstrated experimentally by the observation of deuterium incorporation into the vinyl positions of the CPS (and concomitant formation of the metal hydride) when metal deuterides are allowed to react with CPS. This exchange process is shown in eq 3; note that two isomers of $CPS-d_1$



are formed since D can occupy either of the two vinyl positions. Figure 1 shows the vinyl region of the 300-MHz 1H NMR spectrum from the reaction of $DCr(CO)_3Cp$ with CPS in C_6D_6 at ambient temperature. The two largest peaks in the lower spectrum are due to the two vinyl protons of undeuterated CPS. The smaller resonances that appear ~ 0.015 ppm upfield¹³ of the large resonances are due to the protons of $CPS-d_1$. The upper spectrum of Figure 1 was recorded after 18 min of total reaction time. At this time the hydrogenation of CPS was only $\sim 29\%$ complete, but it is clear that a substantial amount of isotopic exchange has taken place.

Much less isotopic exchange was observed with certain other metal deuterides. For example, when a C_6D_6 solution of $DW(CO)_3Cp$ (0.24 M, 97% D) and CPS (0.025 M) was heated in a sealed tube at 100 °C for 12.5 h, a 68% combined yield of UN and RE was formed. However, the amount of $CPS-d_1$ formed was no more than the amount shown in the lower spectrum of Figure 1, which corresponded to $<5\%$ reaction in the Cr case.

Kinetic Studies. The kinetics of these reactions were studied in toluene at five different concentrations of metal hydride, using an excess of metal hydride concentration over the cyclopropylstyrene. The concentration of metal hydride in these experiments was varied over a factor of 10. The rate of change of the CPS concentration was monitored by using gas chromatography with an internal standard. The combined yields of UN and RE were generally 90–95%.¹⁴

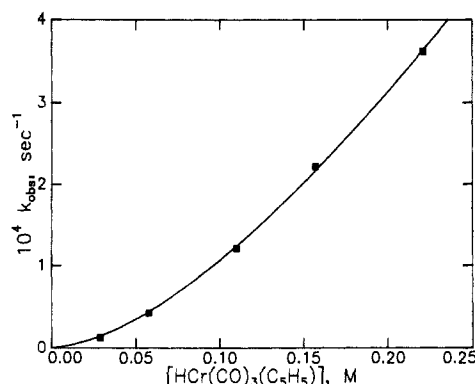


Figure 3. Plot of k_{obs} vs $[HCr(CO)_3Cp]$ for reaction of CPS with $HCr(CO)_3Cp$ at 22 °C in solutions saturated with $[Cr(CO)_3Cp]_2$.

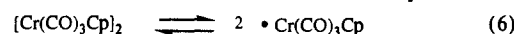
The rate law derived (see Appendix) for the mechanism shown in Scheme I is

$$-\frac{d[CPS]}{dt} = k_{obs}[CPS] \quad (4)$$

where

$$k_{obs} = k_1[MH] \frac{k_2 + k_3[MH]}{k_{-1}[M^*] + k_2 + k_3[MH]} \quad (5)$$

Figure 2 shows plots of $\ln ([CPS]_t/[CPS]_0)$ vs time for the reaction of $HCr(CO)_3Cp$ with CPS at 22 °C. Unlike the other metal dimers, which are the organometallic products from reactions involving the other metal hydrides examined in this study, the chromium dimer exists in equilibrium with a significant amount of the 17-electron chromium radical. McLain has recently reported¹⁵ that $\Delta H^\circ = 15.8 \pm 0.4$ kcal/mol and $\Delta S^\circ = 37.1 \pm 1.4$ cal/K mol for the chromium dimer/radical equilibrium shown in eq 6. These data indicate that at 22 °C, the equilibrium



constant for eq 6 is $K_{eq} = 2.5 \times 10^{-4}$ M. Thus, the curvature shown by the squares in Figure 2 is in accord with the fact that the value of the $k_{-1}[M^*]$ term in the denominator of eq 5 is not constant but increases as the reaction proceeds.

Confirming this conclusion is the behavior observed when the reaction of $HCr(CO)_3Cp$ and CPS is carried out in a solution that is saturated with the chromium dimer $[Cr(CO)_3Cp]_2$. Plots of $\ln ([CPS]_t/[CPS]_0)$ vs time are now linear, as shown by the circles in Figure 2. Saturation of the solution with chromium dimer keeps the concentration of the chromium radical constant. The kinetics of the hydrogenation of CPS by $HCr(CO)_3Cp$ were studied at 22 °C in toluene solutions saturated with $[Cr(CO)_3Cp]_2$; in each case the initial $HCr(CO)_3Cp$ concentration was 10 times as large as the initial CPS concentration. Figure 3 shows a plot of k_{obs} vs $[HCr(CO)_3Cp]$. We have determined the solubility of $[Cr(CO)_3Cp]_2$ in toluene- d_8 to be 0.011(1) M. The curvature in Figure 3 indicates that the $k_{-1}[Cr(CO)_3Cp]$ term in eq 5 is not negligible. Since the values of $[Cr(CO)_3Cp]$, k_2 , and k_3 (vide infra) are known, the values of k_1 and k_{-1} can be determined by using the experimental data shown in Figure 3 and a computer program that calculates the best fit of the experimental points to eq 5 by using a nonlinear least-squares analysis.¹⁶ The solid curve drawn in Figure 3 is in excellent agreement with eq 5, which predicts more curvature at low $[HCr(CO)_3Cp]$. The rate constants obtained from the data analysis are $k_1 = 3.4 (\pm 0.3) \times 10^{-3} M^{-1} s^{-1}$ and $k_{-1} = 3.1 (\pm 1.9) \times 10^9 M^{-1} s^{-1}$. The confidence limits were estimated by a Monte Carlo¹⁷ simulation of the sensitivity

(13) For a review of isotopic effects on chemical shifts, see: Hanson, P. E. *Annu. Rep. NMR Spectrosc.* 1983, 15, 105–234.

(14) In some cases, small amounts of (*Z*)-2-phenyl-2-pentene (the geometric isomer of RE) and 2-phenylpentane were observed by gas chromatography (and confirmed by comparison of their GC retention times and GC/MS with authentic samples), but the combined amounts of these two minor products was $<5\%$.

(15) McLain, S. J. *J. Am. Chem. Soc.* 1988, 110, 643–644, and references therein.

(16) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; pp 204–247.

(17) (a) Kalos, M. H.; Whitlock, P. A. *Monte Carlo Methods, Volume I: Basics*; Wiley: New York, 1986. (b) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes; The Art of Scientific Computing*; Cambridge University Press: Cambridge, 1986; pp 529–532.

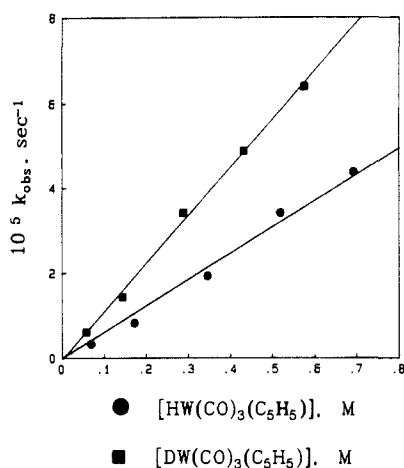


Figure 4. Plot of k_{obs} vs tungsten hydride and deuteride concentrations (M), for reaction with CPS at 100 °C. ■, $\text{DW}(\text{CO})_3\text{Cp}$; ●, $\text{HW}(\text{CO})_3\text{Cp}$.

of k_1 and k_{-1} to the uncertainties in the input values of $[\text{*Cr}(\text{CO})_3\text{Cp}]$, k_2 , and k_3 . Our estimated uncertainty of 50% for $[\text{*Cr}(\text{CO})_3\text{Cp}]$ takes account of our errors in the determination of the concentration of a saturated toluene solution of $[\text{Cr}(\text{CO})_3\text{Cp}]_2$, as well as the errors in K_{eq} for eq 6 [K_{eq} at our experimental temperature of 22 °C was determined by using the values (and uncertainties) of ΔH° and ΔS° for eq 6 reported by McLain].¹⁵ The k_3/k_2 ratio (from the slope of Figure 6, vide infra) is known to a significantly higher precision than the actual value of k_2 , which has an uncertainty of at least 25%. The resultant 10% uncertainty in the value of k_1 is dominated by the scatter in Figure 3; it is essentially independent of the uncertainties in either $[\text{*Cr}(\text{CO})_3\text{Cp}]$ or k_2 . The comparatively large uncertainty in k_{-1} is dominated by the 50% uncertainty in $[\text{*Cr}(\text{CO})_3\text{Cp}]$. The equilibrium constant (k_1/k_{-1}) for hydrogen atom transfer from $\text{HCr}(\text{CO})_3\text{Cp}$ to CPS is $K_{\text{eq}} = 1.1 (\pm 0.6) \times 10^{-12}$. This corresponds to $\Delta G^\circ = 16.1 (\pm 0.4)$ kcal/mol for this endothermic hydrogen atom transfer.

In the case of $\text{HCr}(\text{CO})_3\text{Cp}$, the nonnegligible amount of $\text{*Cr}(\text{CO})_3\text{Cp}$ present in solution required that the rigorous expression for k_{obs} given in eq 5 had to be used. However, in cases where $(k_2 + k_3[\text{MH}]) \gg k_{-1}[\text{M}^*]$, eq 5 simplifies to $k_{\text{obs}} = k_1[\text{MH}]$. Accordingly, we have found that plots of $\ln([\text{CPS}]_t/[\text{CPS}]_0)$ vs time are linear (in the absence of added dimer) for all of the metal hydrides that we have studied except $\text{HCr}(\text{CO})_3\text{Cp}$. Pseudo-first-order rate constants were obtained from the slopes of plots of $\ln([\text{CPS}]_t/[\text{CPS}]_0)$ vs time. In some cases the reaction was followed to >90% completion, and linear plots of $\ln([\text{CPS}]_t/[\text{CPS}]_0)$ vs time were obtained for up to 6 half-lives. In other cases the rate constants were obtained from reactions that were only followed for 2–3 half-lives. In all of these cases, the reactions are first order in CPS and first order in metal hydride and conform to the rate law $-d[\text{CPS}]/dt = k_1[\text{CPS}][\text{MH}]$. Second-order rate constants were determined from the slopes of plots of the observed pseudo-first-order rate constants vs the excess $[\text{MH}]$. Comparison of the slope obtained for $\text{HW}(\text{CO})_3\text{Cp}$ and the deuteride $\text{DW}(\text{CO})_3\text{Cp}$ (see Figure 4) gives an inverse isotope effect, $k_{\text{HW}}/k_{\text{DW}} = 0.55 \pm 0.1$. The rate of the reaction of CPS with $\text{HFe}(\text{CO})_2\text{Cp}$ was determined by monitoring the rate of disappearance of the IR bands due to the iron hydride in experiments using an excess of CPS. Table I gives the second-order rate constants and the temperatures at which they were determined for all of the metal hydrides studied. The same experiments used to determine the kinetics of disappearance of CPS also provide a measure of the $[\text{UN}]/[\text{RE}]$ product ratio.

Two metal hydrides were essentially unreactive toward CPS. A C_6D_6 solution of $\text{HRe}(\text{CO})_5$ (1.1 M) and CPS (0.4 M) showed little reaction after 18 h at 54 °C. After the solution was heated at 105 °C for 5 h, nearly all of the $\text{HRe}(\text{CO})_5$ was consumed, and $\text{Re}_2(\text{CO})_{10}$ precipitated from the solution when it was cooled to room temperature. An ^1H NMR spectrum indicated that only

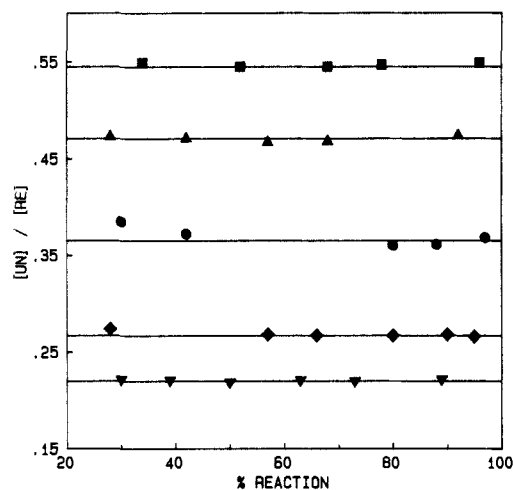


Figure 5. Plot of the $[\text{UN}]/[\text{RE}]$ product ratio as a function of percent reaction, for reaction of CPS at 100 °C with different concentrations of $[\text{HW}(\text{CO})_3\text{Cp}]$. ■, 0.69 M; ▲, 0.52 M; ●, 0.35 M; ◆, 0.17 M; ▼, 0.069 M.

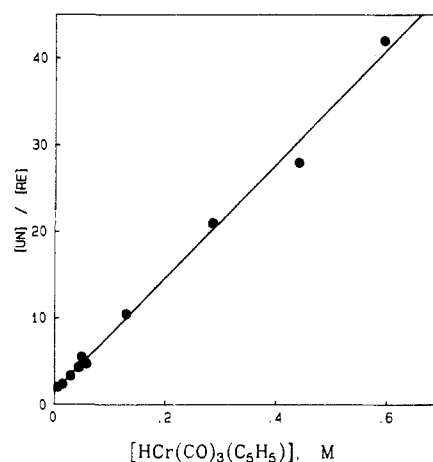
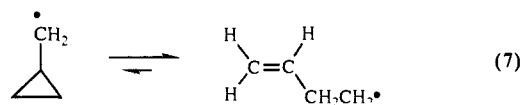


Figure 6. Plot of the $[\text{UN}]/[\text{RE}]$ product ratio vs $[\text{HCr}(\text{CO})_3(\text{C}_5\text{H}_5)]$ at 22 °C.

~10% of the CPS had been consumed, and a small amount of UN had been formed. In contrast to the iron analogue, the ruthenium hydride $\text{HRu}(\text{CO})_2\text{Cp}$ was remarkably unreactive toward CPS. When a solution of $\text{HRu}(\text{CO})_2\text{Cp}$ (0.35 M) and CPS (0.2 M) was heated for 1 week at 100 °C, less than 10% consumption of either the hydride or the CPS was observed.

Utilization of the Radical Rearrangement. Ring opening of the cyclopropylmethyl radical (eq 7) is an intramolecular rear-



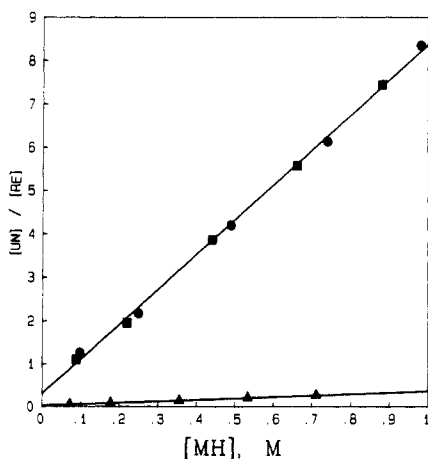
range that has been extensively used as a mechanistic probe and radical clock. The rate constant for this ring-opening rearrangement is $1 \times 10^8 \text{ s}^{-1}$ at 25 °C.¹⁸ In the hydrogenation of CPS, the initially formed carbon-centered radical is 1, which is a substituted cyclopropylmethyl radical. This tertiary benzylic radical enjoys a substantial stabilization relative to the unsubstituted cyclopropylmethyl radical. As expected, the enhanced stability of this radical is reflected in the slower rate of ring-opening

(18) For recent measurements of the kinetics of cyclopropylmethyl radical ring opening, see: (a) Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275–277. (b) Beckwith, A. L. J.; Bowry, V. W. *J. Org. Chem.* **1989**, *54*, 2681–2688. For earlier measurements using different kinetic techniques, see: (c) Mathew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981–7984. (d) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024–7026.

Table I. Second-Order Rate Constants for Reaction with CPS, Bond Dissociation Energies of the M-H Bond, and Relative k_3 Values

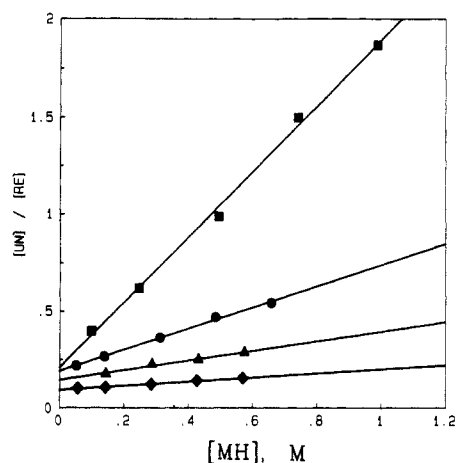
metal hydride	temp, °C	k_1 , ^a M ⁻¹ s ⁻¹	BDE, ^b kcal/mol	k_3 ^c
HCr(CO) ₃ Cp	22	$3.4(3) \times 10^{-3}$	62	1
HFe(CO) ₂ Cp	22	$4.3(3) \times 10^{-4}$	58	5
HMn(CO) ₅	25	$7.4(5) \times 10^{-6}$ ^d	68	7
HFe(CO) ₂ (C ₅ Me ₅)	60	$9.6(5) \times 10^{-4}$		94
HMo(CO) ₃ (C ₅ Me ₅)	60	$6.3(4) \times 10^{-5}$	69	3.8
HMo(CO) ₃ Cp	60	$8.3(1) \times 10^{-5}$	70	93
<i>cis</i> -HMn(CO) ₄ PPh ₃	60	$9.0(2) \times 10^{-5}$	69	1
HMo(CO) ₃ Cp	100	$2.6(1) \times 10^{-3}$	70	16
HMo(CO) ₂ (PMe ₃)Cp	100	$1.2(1) \times 10^{-4}$		1
HW(CO) ₃ Cp	100	$6.2(5) \times 10^{-5}$	73	5
HRu(CO) ₂ Cp	100	<i>e</i>	65	
HRe(CO) ₅	105	<i>f</i>	75	

^aSecond-order rate constant for reaction of the metal hydride with CPS. ^bBond dissociation energy of the metal-hydrogen bond reported in ref 31. ^cRelative k_3 values for comparison of different metal hydrides at the same temperature, with the slowest k_3 at each temperature normalized to 1. Slopes and intercepts of the plots of [UN]/[RE] vs [MH] are tabulated in the Experimental Section. ^dRate constants determined by NMR at 25 °C (ref 21). The [UN]/[RE] product ratios for HMn(CO)₅ were determined in separate experiments at 22 °C. ^e<10% reaction after 1 week at 100 °C. ^fSignificant decomposition of HRe(CO)₅, but little hydrogenation of CPS, after 5 h at 105 °C.

**Figure 7.** Plot of the [UN]/[RE] product ratio at 60 °C vs [MH]. ■, HFe(CO)₂(C₅Me₅); ●, HMo(CO)₃Cp; ▲, HMo(CO)₃(C₅Me₅).

rearrangement ($k_2 = 3.6 \times 10^5$ s⁻¹ at 22 °C)¹⁹ compared to that shown in eq 7.

Hydrogen atom transfer from metal hydride to radical 1 leads to formation of the unrearranged product UN. However, this second-order trapping by metal hydride competes with first-order ring-opening rearrangement to give 2, which then forms RE by reaction with MH. The competition between second-order trapping and first-order rearrangement predicts the formation of more unrearranged product at higher concentrations of MH. If this mechanism (Scheme 1) is correct, the [UN]/[RE] product ratio should be constant throughout the course of the reaction, since under the conditions of our experiments [MH] remains approximately constant. The unrearranged/rearranged product ratio does not change appreciably with the extent of reaction, as shown in Figure 5 for the reaction of CPS with HW(CO)₃Cp at 100 °C. Another important consequence of the proposed mechanism is that plots of the unrearranged/rearranged product ratio vs metal hydride concentration should be linear. Figures 6–8 shows plots of [UN]/[RE] vs [MH] for experiments carried out at 22, 60, and 100 °C. For reaction of CPS with an excess of HCr(CO)₃Cp, a plot of [UN]/[RE] vs [HCr(CO)₃Cp] gave a linear plot when the [HCr(CO)₃Cp] concentration was varied over a

**Figure 8.** Plot of the [UN]/[RE] product ratio at 100 °C vs [MH]. ■, HMo(CO)₃Cp; ●, HW(CO)₃Cp; ▲, DW(CO)₃Cp; ◆, HMo(CO)₂(PMe₃)Cp.

factor of 100. In most other cases the [MH] was varied over a factor of 10. Since the slopes of these plots are k_3/k_2 (see Appendix), use of the k_2 value reported at 22 °C enables the estimation of the rate constants of hydrogen atom transfer (k_3) for the hydrides that react at that temperature. Estimated rate constants are $k_3 = 2.3 \times 10^7$ M⁻¹ s⁻¹ for HCr(CO)₃Cp, $k_3 = 1.2 \times 10^8$ M⁻¹ s⁻¹ for HMn(CO)₅, and $k_3 = 1.7 \times 10^8$ M⁻¹ s⁻¹ for HFe(CO)₂Cp. (See note added in proof.)

The equilibrium constant for reaction 7, in which a primary radical rearranges to a different primary radical, is $\sim 10^4$ at 25 °C.²⁰ We now consider the equilibrium between radicals 1 and 2. While steric considerations may favor the 1 → 2 ring opening, it is nonetheless clear that the equilibrium constant for the 1 → 2 ring opening will be much smaller than K_{eq} for eq 7, since in the 1 → 2 rearrangement a stabilized tertiary benzylic radical is converted to a primary radical. As explained in the Appendix, applying the steady-state treatment to radical 2 and accounting for the reversibility of the radical rearrangement gives a value of k_3/k_2 for the slopes of the plots shown in Figures 6–8. The intercept will be equal to $k_{-2}k_3/k_2k_4$. Plots of [UN]/[RE] vs [MH] for experiments carried out at 60 and 100 °C therefore give the relative rates of hydrogen atom transfer (k_3) to 1, in spite of the fact that precise values of k_2 and k_{-2} are unknown at these temperatures. Since the y intercept for these plots is $k_{-2}k_3/k_2k_4$, the positive values of the y intercepts in these plots clearly indicate that $k_{-2} \neq 0$. Comparison of the slopes for the tungsten hydride and deuteride indicates a normal isotope effect, $k_{HW}/k_{DW} = 2.2 \pm 0.2$, for k_3 , in contrast to the inverse isotope effect observed for the kinetics of the overall reaction.

For the plots of [UN]/[RE] vs [MH], division of the slope by the intercept gives k_4/k_{-2} values, which provide a measure of the relative rates of hydrogen atom transfer from the metal hydrides to the rearranged radical 2. Comparison of these relative k_4 values for HW(CO)₃Cp and DW(CO)₃Cp indicates a normal isotope effect $k_{HW}/k_{DW} = 1.8 \pm 0.3$. In most cases the uncertainties are larger on the relative k_4 values than for the relative k_3 values, due to the somewhat larger experimental uncertainties in the intercepts compared to the slope. Details of the kinetic analysis are given in the Appendix, and slopes and intercepts of the plots of [UN]/[RE] vs [MH] are tabulated in the Experimental Section.

Reactions under CO. The reaction of CPS with HFe(CO)₂Cp was carried out in C₆D₆ in two NMR tubes, one of which was flame-sealed under vacuum and the other of which was sealed under CO (1 atm). ¹H NMR spectra recorded over the course of the reaction were indistinguishable for the two tubes. As we reported earlier,²¹ second-order rate constants obtained for the reaction of HMn(CO)₅ with CPS were equal within experimental

(20) Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734–1736.

(21) Bullock, R. M.; Rappoli, B. J.; Samsel, E. G.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 261–263.

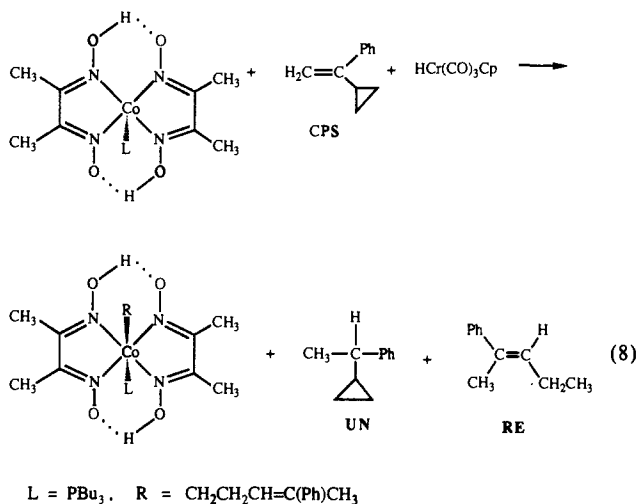
(19) Masnovi, J.; Samsel, E. G.; Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1044–1045.

error for experiments carried out under vacuum compared to experiments under CO. The lack of an effect of CO on the reaction is consistent with the free-radical mechanism, which does not require generation of a vacant coordination site on the metal by loss of CO.

Reactions in Other Solvents. The hydrogenation of CPS by $\text{HCr}(\text{CO})_3\text{Cp}$ in THF or CH_3CN gave unrearranged and rearranged products in yields and ratios similar to those obtained in benzene or toluene, but detailed comparisons of the behavior in these more polar solvents were not made.

Two experiments were carried out to assess whether solvents containing benzylic hydrogens could donate a hydrogen atom to either of the intermediate carbon-centered radicals and thereby influence the product ratio. No difference in the $[\text{UN}]/[\text{RE}]$ product ratio was detected for the reaction of CPS (0.017 M) with $\text{HCr}(\text{CO})_3\text{Cp}$ (0.055 M) when the reaction was carried out in benzene compared to a 1:1 (by volume) mixture of isopropylbenzene and benzene. In another experiment, the reaction of CPS with $\text{HCr}(\text{CO})_3\text{Cp}$ was carried out in ethylbenzene- d_{10} . No deuterium incorporation was detected in either the rearranged or unrearranged product when the reaction products were analyzed by GC/MS. These experiments make it clear that hydrogen atom transfer from hydrocarbons containing benzylic hydrogens to either radical **1** or **2** does not compete with hydrogen atom transfer from metal hydrides to a significant extent.

Radical Trapping by a Co(II) Complex. Attempts to intercept the organic radicals in the reaction of CPS with $\text{HCr}(\text{CO})_3\text{Cp}$ using stable oxygen-centered radicals such as galvinoxyl or an organic nitroxide failed due to reactions with the hydride. Use of a stable metal-centered radical was successful, however. Many Co(II) species containing dimethylglyoxime ligands (dmgH) and related ligands are known to trap organic radicals to produce stable Co(III)-R products. Rate constants reported²² for the combination of organic radicals with various Co(II) complexes are in the range of 10^7 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$. Addition of $(\text{PBU}_3)(\text{dmgH})_2\text{Co}(\text{II})$ to the reaction of CPS with $\text{HCr}(\text{CO})_3\text{Cp}$ led to decreased yields²³ of the hydrogenated products and the concomitant formation of a new complex $(\text{PBU}_3)(\text{dmgH})_2\text{CoCH}_2\text{CH}_2\text{CH}=\text{C}(\text{Ph})\text{CH}_3$ (eq 8).



(22) (a) Roche, T. S.; Endicott, J. F. *Inorg. Chem.* **1974**, *13*, 1575–1580. (b) Mok, C. Y.; Endicott, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 123–129. (c) Endicott, J. F.; Ferraudi, G. J. *J. Am. Chem. Soc.* **1977**, *99*, 243–245. (d) Endicott, J. F.; Netzel, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 4000–4002. (e) Elroi, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1978**, *100*, 5540–5548. (f) Mulac, W. A.; Meyerstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 4124–4128. (g) Baral, S.; Neta, P. *J. Phys. Chem.* **1983**, *87*, 1502–1509. (h) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5179–5202; *Inorg. Chem.* **1989**, *28*, 3901–3904, 4319–4322.

(23) For example, in contrast to the >90% yield of hydrogenated products (UN + RE) obtained from the reaction of $\text{HCr}(\text{CO})_3\text{Cp}$ with CPS in the absence of Co^{II}, the combined yield of hydrogenated products dropped to 53% when $\text{HCr}(\text{CO})_3\text{Cp}$ (0.05 M) and CPS (0.017 M) were allowed to react in the presence of $(\text{PBU}_3)(\text{dmgH})_2\text{Co}^{\text{II}}$ (0.03 M). For a discussion of the influence of competing reactions of radicals, which may occur before their effect is apparent on the material balance of products, see: Wollowitz, S.; Halpern, J. *J. Am. Chem. Soc.* **1988**, *110*, 3112–3120.

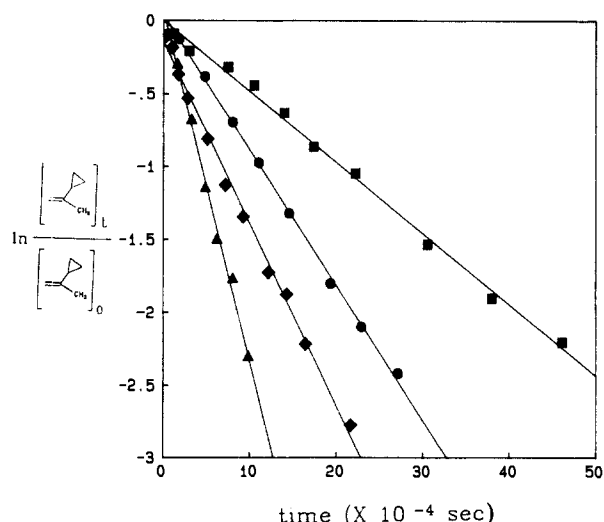


Figure 9. First-order plot for disappearance of 2-cyclopropylpropene in its reaction with excess $\text{HCr}(\text{CO})_3\text{Cp}$ at 68 °C. Concentrations of $\text{HCr}(\text{CO})_3\text{Cp}$: ■, 0.28 M; ●, 0.49 M; ◆, 0.68 M; ▲, 1.06 M.

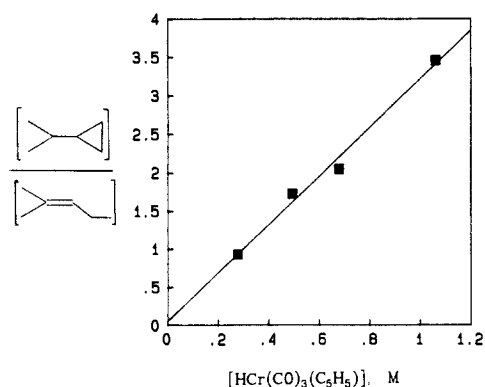
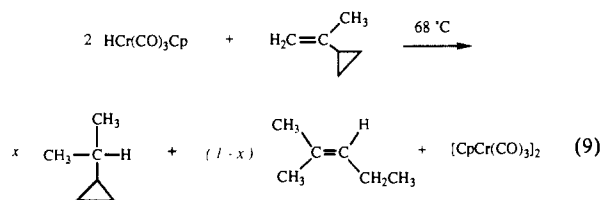


Figure 10. Plot of the unrearranged/rearranged product ratio vs $[\text{HCr}(\text{CO})_3\text{Cp}]$, from reaction of 2-cyclopropylpropene with excess $\text{HCr}(\text{CO})_3\text{Cp}$ at 68 °C.

This cobalt(III) complex has been independently synthesized and was isolated and characterized (see Experimental Section). Several related Co(III) alkyl complexes decompose to give alkenes. For example, Halpern and co-workers have reported²⁴ kinetic and thermodynamic data on the decomposition of $\text{py}(\text{dmgH})_2\text{CoCH}(\text{CH}_3)\text{Ph}$ to give styrene, H_2 , and $\text{py}(\text{dmgH})_2\text{Co}^{\text{II}}$. In the case of our cobalt alkyl complex, an analogous decomposition would give the conjugated diene $\text{Ph}(\text{CH}_3)\text{C}=\text{CHCH}=\text{CH}_2$.²⁵ None of this diene was detected when the reaction mixtures (eq 8) were analyzed by gas chromatography, but we cannot rigorously rule out the possibility that some of the diene formed but underwent further reaction (e.g., polymerization or hydrogenation) prior to GC analysis.

Reactions with 2-Cyclopropylpropene. The reaction of 2-cyclopropylpropene with $\text{HCr}(\text{CO})_3\text{Cp}$ (eq 9) consumes 2 equiv



of $\text{HCr}(\text{CO})_3\text{Cp}$ per alkene and gives a mixture of unrearranged and rearranged products, analogous to the experiments with CPS. The kinetics of this reaction were determined by ^1H NMR at 68

(24) Halpern, J.; Ng, F. T. T.; Rempel, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 7124–7126. (b) Halpern, J. *Pure Appl. Chem.* **1983**, *55*, 1059–1068.

(25) An authentic sample of $\text{Ph}(\text{CH}_3)\text{C}=\text{CHCH}=\text{CH}_2$ was prepared by dehydrohalogenation of $\text{Ph}(\text{CH}_3)\text{C}=\text{CHCH}_2\text{CH}_2\text{Br}$ by 1,4-diazabicyclo[2.2.2]octane (Dabco).

°C using a pseudo-first-order excess of $\text{HCr}(\text{CO})_3\text{Cp}$. First-order plots for disappearance of 2-cyclopropylpropene are shown in Figure 9. The combined yields of unrearranged product (isopropylcyclopropane) and rearranged product (2-methyl-2-pentene) were 77–86%, and Figure 10 shows the linear relationship between the unrearranged/rearranged product ratio and $[\text{HCr}(\text{CO})_3\text{Cp}]$. An experiment carried out in an NMR tube under CO showed no difference from one sealed off under vacuum.

The kinetics were also studied for the reaction of 2-cyclopropylpropene with the deuteride $\text{DCr}(\text{CO})_3\text{Cp}$. As observed in the reactions of $\text{DCr}(\text{CO})_3\text{Cp}$ with CPS, the initial hydrogen atom transfer from the metal hydride to the alkene is reversible, as evidenced by the incorporation of deuterium into the vinyl positions of the alkene and concomitant formation of $\text{HCr}(\text{CO})_3\text{Cp}$ from experiments starting with $\text{DCr}(\text{CO})_3\text{Cp}$. In this case, deuterium is also incorporated into the methyl group of the starting material, since both methyls are equivalent in the radical intermediate. This exchange causes the isotopic purity of the $\text{DCr}(\text{CO})_3\text{Cp}$ to decrease as the reaction proceeds, but an excess of $\text{DCr}(\text{CO})_3\text{Cp}$ (initially 10–20 times as high as the concentration of 2-cyclopropylpropene) was used to decrease errors due to this exchange. The rate of disappearance of the cyclopropyl resonances in the ^1H NMR spectrum was used to determine the kinetics of these experiments with $\text{DCr}(\text{CO})_3\text{Cp}$, since their rate of disappearance is unaffected by deuterium incorporation into the vinyl and methyl positions of the same molecule. The second-order rate constant was obtained from the slope of a plot of the observed pseudo-first-order rate constants vs chromium hydride (and deuteride) concentrations. The rate constant determined at 68 °C for the hydride is $2.0(4) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$; comparison with the rate constant obtained for the deuteride indicates an inverse isotope effect of $k_{\text{HCr}}/k_{\text{DCr}} = 0.45 \pm 0.1$.

The reaction of $\text{HMo}(\text{CO})_3\text{Cp}$ ($\sim 0.8 \text{ M}$ in C_6D_6) with 2-cyclopropylpropene ($\sim 0.1 \text{ M}$) was very slow, and $\sim 15\%$ 2-cyclopropylpropene remained after 120 h at 125 °C. More than 4 equiv of the molybdenum hydride was consumed per equivalent of the alkene, possibly due to thermal decomposition of the hydride at the high temperature employed. While the main products were the same as those observed for the chromium hydride, ^1H NMR and GC/MS spectra also indicated the presence of small amounts of cyclopentene and cyclopentane. These products probably arise from degradation of the cyclopentadienyl ring of $\text{HMo}(\text{CO})_3\text{Cp}$.

Discussion

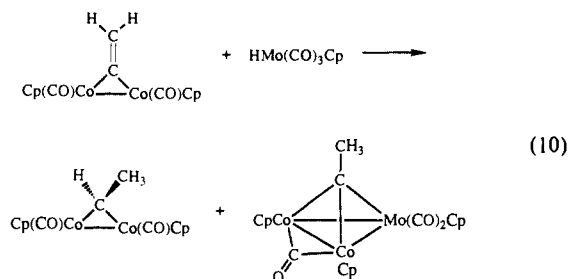
While the free-radical mechanism for hydrogenation of CPS by metal hydrides was expected on the basis of previous work on related systems by others, a unique contribution of this study is that it provides a direct comparison of the relative rates of hydrogen atom transfer from a series of metal hydrides to an alkene (α -cyclopropylstyrene) as well as to the carbon-centered radical (1) formed from it. Clearly there are some differences to be expected in the relative rates of these two hydrogen atom transfer processes, since in one case we are comparing hydrogen atom donation to an alkene to generate a carbon-centered radical, and in the other case hydrogen atom donation to this carbon-centered radical to give the stable hydrogenated product.

Both the first and second hydrogen atom transfers involve rupture of a relatively weak $\text{M}-\text{H}$ bond and formation of a comparatively strong $\text{C}-\text{H}$ bond. The equilibrium constant of $K_{\text{eq}} = k_1/k_{-1} \approx 1 \times 10^{-12}$ for the hydrogen atom transfer from $\text{HCr}(\text{CO})_3\text{Cp}$ to CPS at 22 °C corresponds to $\Delta G^\circ \approx 16 \text{ kcal/mol}$. This ΔG° can be compared to the enthalpy of $\Delta H^\circ \approx 15 \text{ kcal/mol}$ estimated by Halpern¹⁸ for hydrogen atom transfer from a metal hydride (bond dissociation energy of 60 kcal/mol) to styrene. The first hydrogen atom transfer step is endothermic because although a $\text{C}-\text{H}$ bond is formed, an $\text{M}-\text{H}$ bond is broken, and a $\text{C}=\text{C}$ double bond is converted to a $\text{C}-\text{C}$ single bond. The overall reaction proceeds because the favorable energetics of the second hydrogen atom transfer (along with the formation of a metal-metal bond in the organometallic product) compensate for the endothermic first step.

Kinetics of the Free-Radical Hydrogenation and the Influence of Reversibility of the First Hydrogen Atom Transfer. The sec-

ond-order rate law $-\text{d}[\text{CPS}]/\text{d}t = k_1[\text{CPS}][\text{MH}]$ obtained for all of the metal hydrides studied here except $\text{HCr}(\text{CO})_3\text{Cp}$ is analogous to the second-order kinetics reported by others who have previously studied hydrogenations of unsaturated substrates that proceed by sequential hydrogen atom transfers from metal hydrides.^{2–6} More complicated kinetics were found for the reaction of $\text{HCr}(\text{CO})_3\text{Cp}$ with CPS. In this case, the back-reaction of β -hydrogen atom abstraction from carbon-centered radical 1 by $^*\text{Cr}(\text{CO})_3\text{Cp}$ affects the kinetics, due to the fact that the product chromium dimer $[\text{Cr}(\text{CO})_3\text{Cp}]_2$ exists in equilibrium¹⁵ with a significant amount of the 17-electron monomer $^*\text{Cr}(\text{CO})_3\text{Cp}$. While this requires a more complicated treatment of the data in order to obtain an accurate value of k_1 , it does provide additional information not available from the other hydrides studied, since the value of k_{-1} is also obtained.

The observation of isotopic exchange when metal deuterides were used was given as one of the arguments in favor of the free-radical hydrogenation of α -methylstyrene by $\text{HMn}(\text{CO})_3$ reported by Sweany and Halpern.² A remarkably fast rate of hydrogen atom transfer was observed by Jacobsen and Bergman,¹⁰ who studied the reaction of $\text{HMo}(\text{CO})_3\text{Cp}$ and other metal hydrides with a dicobalt complex containing a bridging vinylidene (eq 10). Kinetic and mechanistic information supported a



free-radical reaction leading to hydrogenation of the $\text{C}=\text{C}$ bond of the starting material as well as formation of a Co_2Mo cluster. When $\text{DMo}(\text{CO})_3\text{Cp}$ was reacted with the Co_2 complex, incorporation of D into the vinyl positions of the Co_2 complex was fast, even at -40 °C, and the H/D exchange occurred at least 100 times faster than either the hydrogenation or cluster formation reaction.

A rate constant of $k_{-1} = 3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was determined here for hydrogen atom transfer from 1 to $^*\text{Cr}(\text{CO})_3\text{Cp}$. While the higher bond strengths for most of the other hydrides compared to chromium might lead to the prediction that these other metal radicals would exhibit faster rates of hydrogen atom abstraction, the fact that k_{-1} is close to diffusion-controlled in the reaction of $\text{HCr}(\text{CO})_3\text{Cp}$ means that it cannot be much faster in the cases of the other hydrides. The clean second-order kinetics observed for all the hydrides other than $\text{HCr}(\text{CO})_3\text{Cp}$ indicates that $(k_2 + k_3[\text{MH}]) \gg k_{-1}[\text{M}^*]$. Thus the fact that the $k_{-1}[\text{M}^*]$ term is unimportant in the kinetics of all hydrides except $\text{HCr}(\text{CO})_3\text{Cp}$ is *not* due to the rate constant k_{-1} being small, but is because the concentration of metal radical $[\text{M}^*]$ is extremely small, so that the product $k_{-1}[\text{M}^*]$ is negligible compared to the $(k_2 + k_3[\text{MH}])$ term in the expression for k_{obs} in eq 5. As mentioned above, the equilibrium constant for the chromium dimer/monomer equilibrium (eq 6) is $\sim 2.5 \times 10^{-4} \text{ M}$ at 22 °C. Dimer/monomer equilibrium constants are many orders of magnitude lower for organometallic dimers other than $[\text{Cr}(\text{CO})_3\text{Cp}]_2$. Pugh and Meyer²⁶ have recently determined the equilibrium constants for $\text{Mn}_2(\text{CO})_{10} \rightleftharpoons 2\text{Mn}(\text{CO})_5^*$ ($K = 5.3 \times 10^{-19} \text{ M}$) and for $[\text{Fe}(\text{CO})_2\text{Cp}]_2 \rightleftharpoons 2\text{Fe}(\text{CO})_2\text{Cp}^*$ ($K = 1.7 \times 10^{-17} \text{ M}$). These very small equilibrium constants support the negligible contribution of the $k_{-1}[\text{M}^*]$ term in the kinetics of all of the metal hydrides besides $\text{HCr}(\text{CO})_3\text{Cp}$.

Reactions of two radicals with each other generally exhibit low activation energies, so the large value of k_{-1} obtained in this study is not surprising. Radical combination is another commonly observed reaction that can occur from caged radicals, and products resulting from this pathway have been observed in several reactions

established to proceed by an initial hydrogen atom transfer from a metal hydride to an unsaturated substrate. The Co_2Mo cluster shown in eq 10 was observed by Jacobsen and Bergman¹⁰ as a product of cage combination. Orchin and co-workers have proposed^{3d,f,h} that the competition between cage escape and caged radical combination influences the amount of hydrogenation vs hydroformylation in stoichiometric reactions of $\text{HMn}(\text{CO})_5$ with substituted cyclopropenes; Ungváry and Markó have made similar observations in reactions of $\text{HCo}(\text{CO})_4$ with styrene.^{3b} Baird and co-workers found radical coupling products from reactions of $\text{HMn}(\text{CO})_5$ and $\text{HFe}(\text{CO})_2\text{Cp}$ with conjugated dienes;⁶ for example, $(\text{CO})_5\text{MnCH}_2\text{CH}=\text{C}(\text{CH}_3)_2$ was the major product resulting from reaction of $\text{HMn}(\text{CO})_5$ with isoprene. However, we see no evidence of the metal alkyl complex that would result from combination of M^* with **1**.²⁷ The product that would result from this reaction would have a tertiary carbon center directly bonded to the metal, so it seems likely that if this compound formed it might readily homolyze to regenerate M^* and **1**.

Isotope Effects. The significant differences in the first and second hydrogen atom transfer steps are also reflected in the kinetic isotope effects. We have previously reported²¹ that the reaction of $\text{HMn}(\text{CO})_5$ with CPS exhibits an inverse isotope effect, i.e., the metal deuteride reacts faster than the metal hydride. For the reaction of CPS with $\text{HMn}(\text{CO})_5$ [and $\text{DMn}(\text{CO})_5$] at 25 °C, the isotope effect was found to be $k_{\text{HMn}}/k_{\text{DMn}} \approx 0.5$, which is similar to the inverse isotope effects observed in several related systems.^{2-4,6} The observation of an inverse isotope effect ($k_{\text{HCr}}/k_{\text{DCr}} = 0.45 \pm 0.10$) in the reaction of $\text{HCr}(\text{CO})_3\text{Cp}$ with 2-cyclopropylpropene also provides strong support for the free-radical hydrogenation mechanism. For the experiments on $\text{HW}(\text{CO})_3\text{Cp}$ and $\text{DW}(\text{CO})_3\text{Cp}$, the observed kinetic isotope effect of $k_{\text{HW}}/k_{\text{DW}} = 0.55 \pm 0.1$ is similar to the $k_{\text{HW}}/k_{\text{DW}} = 0.65$ found by Sweany and co-workers^{3a} for the reaction of the same hydride with α -methylstyrene.

In the hydrogen atom transfer from metal hydrides to CPS, a relatively weak M–H bond is ruptured and a comparatively strong C–H bond is formed. The difference in zero-point energy between M–H and M–D is less than the difference in zero-point energy between C–H and C–D. As a result, the reversible formation of the caged radical pair (eq 2) is more favorable for the deuteride than for the hydride. The observed kinetic isotope effect may therefore be controlled by the inverse *equilibrium* isotope effect on the equilibrium constant ($K_{\text{eq}} = k_{1A}/k_{-1A}$).

In many cases it can be difficult to unambiguously distinguish between an inverse isotope effect on an elementary step (which is theoretically possible²⁸) and an inverse isotope effect that results from an inverse *equilibrium* isotope effect on a reversible pre-equilibrium that occurs prior to the rate-determining step. In eq 2, if it were true that $k_{1B} \gg k_{-1A}$, then the pre-equilibrium (k_{1A}/k_{-1A}) would not be established, and the isotope effect would then be properly interpreted as an inverse kinetic isotope effect on an elementary step. Inverse isotope effects observed in several other organometallic reactions (such as reductive elimination of alkanes from alkyl hydride complexes²⁹ and certain α -elimination reactions³⁰) have been interpreted in terms of an equilibrium

isotope effect on a pre-equilibrium, rather than an inverse isotope effect on an elementary step.

Of particular interest here is a comparison of the *inverse* isotope effect observed for the overall kinetics of the reaction compared to the *normal* isotope effects of $k_{\text{HW}}/k_{\text{DW}} = 2.2 \pm 0.2$ for k_3 and $k_{\text{HW}}/k_{\text{DW}} = 1.8 \pm 0.3$ for k_4 . In contrast to the first hydrogen atom transfer, the second hydrogen atom transfer (from the metal hydride to the carbon-centered radical) is exothermic, exhibits a normal isotope effect, and accordingly is expected to have a relatively early transition state.

Relative Rates of Hydrogen Atom Transfer from Metal Hydrides to CPS. The values of the second-order rate constants (k_1) determined in this study are listed in Table I. As defined in Scheme I, k_1 represents the overall rate constant for production of the metal radical and the organic free radical (**1**). As shown in eq 2, a caged pair is an intermediate in this reaction, so k_1 is not an elementary step. While the individual rate constants for k_{1A} , k_{1B} , k_{-1A} , or k_{-1B} are not determined by our experiments, a consideration of all of the results of our study now allows us to make some general comments about the relative values of these rate constants. First, the wide range of values of k_1 undoubtedly manifests itself almost entirely in k_{1A} , which is the most endothermic step of the entire reaction. Diffusive cage escape (k_{1B}) is probably similar for the different metal systems employed here. Second, $k_{1B} < k_{-1A}$, consistent with the H/D exchange observed in reactions of metal deuterides, and with the pre-equilibrium formation of the caged radical pair. Finally, while diffusive cage escape (k_{1B}) is often depicted as irreversible, it is clear (at least in the case of the reaction of $\text{HCr}(\text{CO})_3\text{Cp}$ with CPS) that $k_{-1B} \neq 0$, as demonstrated by the effect of added $\text{CpCr}(\text{CO})_3^*$ (added in the form of the chromium dimer) on the kinetics.

Tilset and Parker³¹ have recently reported the homolytic bond dissociation energies of most of the metal hydrides utilized in this study; these bond energies are also listed in Table I. Even before detailed comparisons of rate constants are made it is immediately clear that a considerable range of rates exists for the hydrogen atom transfer, as evidenced by the different temperatures employed. It is well-established that third row metal hydrides generally undergo reactions slower than their first row counterparts, and this is also found here, since $\text{HW}(\text{CO})_3\text{Cp}$ reacts over 10 times more slowly at 100 °C than does $\text{HCr}(\text{CO})_3\text{Cp}$ at 22 °C. Similar rate constants were obtained for three of the hydrides studied at 60 °C, $\text{HMo}(\text{CO})_3\text{Cp}$, $\text{HMo}(\text{CO})_3(\text{C}_5\text{Me}_5)$, and *cis*- $\text{HMn}(\text{CO})_4\text{PPh}_3$, and all of these have similar bond strengths. The other hydride studied at 60 °C, $\text{HFe}(\text{CO})_2(\text{C}_5\text{Me}_5)$, reacts considerably faster. While the bond strength of this iron hydride is unknown, it may be similar to the 58 kcal/mol found for $\text{HFe}(\text{CO})_2\text{Cp}$ since permethylation of the C_5H_5 ring of $\text{HMo}(\text{CO})_3\text{Cp}$ has a negligible effect on the bond strength.³¹

Substitution of one of the carbonyl ligands of $\text{HMo}(\text{CO})_3\text{Cp}$ by PMe_3 decreases the rate of the reaction of this hydride with CPS. The opposite effect was noted by Jacobsen and Bergman,¹⁰ who found that $\text{HMo}(\text{CO})_2(\text{PMe}_3)\text{Cp}$ reacts ~5 times faster than $\text{HMo}(\text{CO})_3\text{Cp}$ in the hydrogen atom transfer reaction shown in eq 10.

The fact that $\text{HMo}(\text{CO})_3\text{Cp}$ reacts ~40 times faster than the tungsten analogue is also in agreement with the relative bond strengths. Sweany and co-workers^{3a} reported activation parameters for free-radical hydrogenation of α -methylstyrene, and they found that ΔH^\ddagger was ~2 kcal/mol greater for the W hydride than for the Mo hydride.

While the overall trends in these relative rates seem to agree well with the reported bond strengths, such comparisons are perhaps best used for general qualitative purposes, since some anomalies are apparent. For example, the rate constant for $\text{HCr}(\text{CO})_3\text{Cp}$ is faster than that for $\text{HFe}(\text{CO})_2\text{Cp}$, despite a higher

(27) The manganese alkyl complex $(\text{CO})_5\text{MnCH}_2\text{CH}_2\text{CH}=\text{C}(\text{Ph})\text{CH}_3$ is observed as an intermediate in the ring-opening hydroformylation of CPS by $\text{HMn}(\text{CO})_5$ (see eq 12 and ref 21). This complex has been independently synthesized, isolated, and characterized. However, while this compound would formally result from combination of $(\text{CO})_5\text{Mn}^*$ with rearranged radical **2**, it is not clear that it does in fact form in this way in that reaction, and analogous products are not observed for any of the other metals in the well-behaved hydrogenations reported in this paper.

(28) (a) Bigeleisen, J. *Pure Appl. Chem.* **1964**, *8*, 217–223. (b) Melander, L. *Acta Chem. Scand.* **1971**, *25*, 3821–3826.

(29) (a) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897–3908. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550. (c) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332–7346. (d) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172–1179. (e) Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502–5504.

(30) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21–39.

(31) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711–6717; **1990**, *112*, 2843. Recent calorimetric measurements (Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Roper, G. C. *J. Am. Chem. Soc.* **1990**, *112*, 5657–5658) of the Cr–H bond dissociation energy of $\text{HCr}(\text{CO})_3\text{Cp}$ (61.5 kcal/mol) and several substituted derivatives, are in good agreement with the work of Tilset and Parker.

reported bond strength for the Cr vs Fe hydride. While the very low reactivity of $\text{HRe}(\text{CO})_5$ may be understood in terms of its strong (75 kcal/mol) Re-H bond, the very low reactivity that we find for $\text{HRu}(\text{CO})_2\text{Cp}$ is difficult to reconcile with its reported bond strength³¹ of 65 kcal/mol.

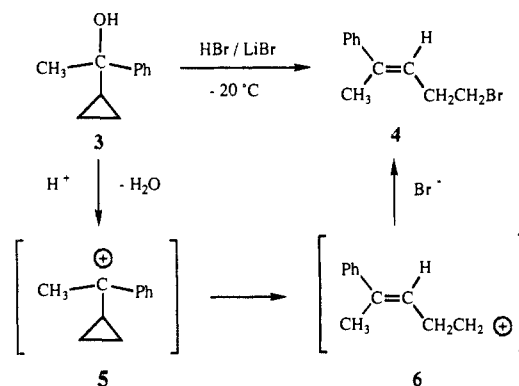
We have not yet carefully examined the reaction of CPS with $\text{HCo}(\text{CO})_4$, but comparative rate data for this hydride vs $\text{HMn}(\text{CO})_5$ are available from the work of Orchin and co-workers.^{3d} The rate constants obtained for free-radical hydrogenation of $\text{Ph}_2\text{C}=\text{CH}_2$ and related olefins were 2–3 orders of magnitude higher for the Co compared to the Mn hydride.

Relative Rates of Hydrogen Atom Transfer from Metal Hydrides to a Carbon-Centered Radical. The relative rate constants of hydrogen atom transfer from the different metal hydrides to the same carbon-centered radical are obtained from the slopes of the plots of $[\text{UN}]/[\text{RE}]$ vs $[\text{MH}]$. Relative k_3 values are tabulated in Table I. The slopes and intercepts are provided in the Experimental Section. The observation that the relative k_3 values are indistinguishable in this experiment for $\text{HMo}(\text{CO})_3\text{Cp}$ vs $\text{HFe}(\text{CO})_2(\text{C}_5\text{Me}_5)$ may be fortuitous, since the two hydrides are from different rows of the periodic table, have different numbers of carbonyls, and have C_5H_5 on Mo but C_5Me_5 on Fe. Another possible explanation is that hydrogen atom transfer from either of these metal hydrides to **1** occurs at the same rate because the actual rate is at the diffusion-controlled limit. Note that while these two hydrides undergo hydrogen atom transfer to **1** at equal rates, their relative rates of hydrogen atom donation to cyclopropylstyrene differ by an order of magnitude. The relative rates of hydrogen atom transfer to **1** are significantly influenced by steric effects, as evidenced by the fact that k_3 is over 20 times lower for $\text{HMo}(\text{CO})_3(\text{C}_5\text{Me}_5)$ compared to $\text{HMo}(\text{CO})_3\text{Cp}$. The relative rate of k_3 for *cis*- $\text{HMn}(\text{CO})_4\text{PPh}_3$ is very low compared to the other hydrides, presumably due to the steric demands of the PPh_3 ligand.

The estimates of the absolute rate constants for k_3 add to the small but growing amount of such data available for transition-metal hydrides. Bergman and co-workers³² estimated a rate constant of $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for hydrogen atom transfer from $\text{HV}(\text{CO})_2\text{Cp}^-$ to *n*-alkyl radicals. A related study by Darensbourg, Newcomb, and co-workers established a radical chain mechanism for reduction of alkyl bromides. Their study³³ resulted in the measurement of the rate constant for hydrogen atom transfer from $\text{HCr}(\text{CO})_5^-$ to $\text{CH}_2=\text{CHCMe}_2\text{CH}_2^\cdot$ as $1.81 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. Norton and co-workers have recently measured the rates of hydrogen abstraction from several metal hydrides by tris(*p*-*tert*-butylphenyl)methyl radical in toluene. The rate constant for reaction of this radical with $\text{HMn}(\text{CO})_5$ was $6.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C.³⁴ This value is many orders of magnitude slower than those we have obtained and is a reflection both of the severe steric constraints for reaction of metal hydrides with this triaryl radical and of the relatively weak C–H bond being formed.

The relative paucity of absolute rate data for hydrogen atom transfers from transition-metal hydrides to carbon-centered radicals contrasts sharply with the data available for other hydrogen atom donors. Tributyltin hydride was found widespread use in organic synthesis³⁵ for many years, often in radical chain reactions as opposed to the nonchain radical reactions reported here. Ingold and co-workers³⁶ have found that the rate constants for hydrogen atom transfer from *n*- Bu_3SnH to ethyl, isopropyl, *n*-butyl, or

Scheme II



tert-butyl radical span the narrow range of $(1.5\text{--}2.4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 27 °C. In contrast, the rate constant for reaction of benzyl radical with *n*- Bu_3SnH is much lower, $3.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C.³⁷ Franz and co-workers have reported Arrhenius parameters for hydrogen atom abstraction from thiophenol by alkyl radicals. As in the case of *n*- Bu_3SnH , rates of hydrogen atom transfer from PhSH to alkyl radicals³⁸ are relatively insensitive to steric effects, and the rate constants were all $\sim 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, ~ 2 orders of magnitude higher than for *n*- Bu_3SnH .

If it is assumed that metal hydrides follow the same trend as that found for tin hydrides and thiols, with lower rate constants found for hydrogen atom donation to benzylic radicals compared to alkyl radicals, then the rate constants for hydrogen atom transfer from metal hydrides to the alkyl radical **2** should exceed those for hydrogen atom donation to the tertiary benzylic radical **1**. Our experiments do not provide an absolute value for k_4 , but as mentioned above, approximate relative values for k_4 may be obtained by dividing the slopes by the intercepts in the plots of $[\text{UN}]/[\text{RE}]$ vs $[\text{MH}]$. Using this crude approximation gives the following relative k_4 values at 60 °C: *cis*- $\text{HMn}(\text{CO})_4\text{PPh}_3$, $k_{\text{rel}} = 1$; $\text{HMo}(\text{CO})_3(\text{C}_5\text{Me}_5)$, $k_{\text{rel}} = 8$; $\text{HMo}(\text{CO})_3\text{Cp}$, $k_{\text{rel}} = 18$; $\text{HFe}(\text{CO})_2(\text{C}_5\text{Me}_5)$, $k_{\text{rel}} = 19$. The accuracy of these relative k_4 values is lower than the relative k_3 values, but they follow the same trend, with $\text{HMn}(\text{CO})_4\text{PPh}_3$ exhibiting a significantly slower rate of hydrogen atom donation to either radical, compared to the other hydrides studied at 60 °C. Furthermore these relative k_4 values span a smaller range than the relative k_3 values, consistent with the relatively low selectivity of **2** for the different metal hydrides in this exothermic hydrogen atom transfer. Franz and co-workers have reported the temperature-dependent rates of hydrogen atom transfer from $\text{HMo}(\text{CO})_3(\text{C}_5\text{Me}_5)$ to the 5-hexenyl radical,³⁹ which gives $k = 2.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 60 °C. Given the similarity of the 5-hexenyl radical to **2**, we suggest that the rate of hydrogen atom transfer from $\text{HMo}(\text{CO})_3(\text{C}_5\text{Me}_5)$ to **2** is probably similar.

Consideration of a Proton Transfer Mechanism. Studies of the kinetic and thermodynamic acidities of metal hydrides by Norton and co-workers⁴⁰ have shown that some of the hydrides used in this study are reasonably strong acids. For example the $\text{p}K_{\text{a}}$ of $\text{HCr}(\text{CO})_3\text{Cp}$ in CH_3CN is 13.3 (compared to $\text{p}K_{\text{a}}$ of acetic acid of 22.3 in CH_3CN). In view of the importance of proton transfer reactions of metal hydrides in other systems,^{40–42} it was important

(37) Franz, J. A.; Suleman, N. K.; Alnajjar, M. S. *J. Org. Chem.* **1986**, *51*, 19–25.

(38) Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 268–275.

(39) (a) Lineham, J. C.; Alnajjar, M. S.; Franz, J. A. *Abstracts of Papers*, 195th National Meeting of the American Society, Toronto, Canada, June 5–19, 1988; American Chemical Society: Washington, DC, 1988; ORGN 411. (b) The rate expression for reaction of $\text{HMo}(\text{CO})_3(\text{C}_5\text{Me}_5)$ with the 5-hexenyl radical is given in footnote 29 of ref 38.

(40) (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255–1263. (b) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257–2263. (c) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945–3953. (d) Kristjansson, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983–1987.

(41) (a) Walker, H. M.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179–1186. (b) Pearson, R. G.; Ford, P. C. *Comments Inorg. Chem.* **1982**, *1*, 279–289. (c) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41–49.

(42) Bullock, R. M. *J. Am. Chem. Soc.* **1987**, *109*, 8087–8089.

(32) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902–7915.

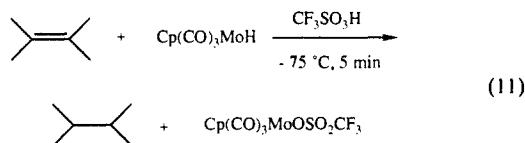
(33) Ash, C. E.; Hurd, P. W.; Darensbourg, M. Y.; Newcomb, M. *J. Am. Chem. Soc.* **1987**, *109*, 3313–3317.

(34) (a) Eisenberg, D. C.; Kristjansson, S. S.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *Abstracts of Papers*, 198th National Meeting of the American Chemical Society, Miami Beach, FL, September 10–15, 1989; American Chemical Society: Washington, DC, 1988; INOR 128. (b) Moody, A. E. Ph.D. Dissertation, Colorado State University, 1989.

(35) (a) Curran, D. P. *Synthesis* **1988**, 417–438, 489–513. (b) Neumann, W. P. *Synthesis* **1987**, 665–683. (c) Giese, G. *Angew. Chem., Int. Ed. Engl.* **1985**, 553–565. (d) Kuivila, H. G. *Synthesis* **1970**, 499–509. (e) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299–305.

(36) Chatgililoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.

to consider the possibility that these reactions might involve proton transfer. This was especially crucial since the carbocationic intermediate that would form by protonation of CPS (i.e., **5**) would undergo a cationic ring-opening rearrangement⁴³ analogous to the radical rearrangement used here. In fact the cationic ring opening can be synthetically useful, and we have found that the reaction of the tertiary alcohol **3** with HBr (in the presence of LiBr)⁴⁴ provides a good synthetic route to the alkyl bromide **4** (Scheme II). The mechanism of this reaction involves ring opening of the carbocation **5** to give carbocation **6**. Trapping of cation **6** by Br⁻ gives the alkyl bromide **4**. If any of the metal hydrides were acidic enough to protonate CPS, the resulting carbocation would be **5**. This carbocation (or its rearranged form **6**) could then abstract a hydride (H⁻) from the metal hydride to give the hydrogenation product. The overall result would be an ionic hydrogenation with metal hydride sequentially serving as H⁺ and H⁻ donors. We have recently demonstrated⁴⁵ that some metal hydrides can serve as stoichiometric hydride donors to carbocations generated by protonation of alkenes with strong acids, resulting in a remarkably facile low-temperature ionic hydrogenation of hindered alkenes (eq 11). The possibility of rate-determining proton transfer in



the hydrogenation of CPS by these metal hydrides is ruled out, however, by the lack of any correlation of the rate constants given in Table I with the known acidities⁴⁰ of the metal hydrides. For example, the fact that HFe(CO)₂(C₅Me₅) (pK_a = 26.6) reacts faster than HMo(CO)₃Cp (pK_a = 13.9) makes it clear that proton transfer mechanisms can be ruled out.

Potential Generality of the Free-Radical Hydrogenation of Alkenes. The results presented above for hydrogenation of CPS by sequential hydrogen atom transfers from metal hydrides indicate that the reaction proceeds through initial formation of a tertiary, benzylic carbon-centered radical. Previous work by others²⁻⁶ has demonstrated analogous mechanisms for free-radical hydrogenation of substituted styrenes, anthracenes, allenes, and dienes. All of these share the common feature that the initially formed carbon-centered radical is stabilized by being either benzylic or allylic. The ~10 kcal/mol stabilization of benzylic radicals⁴⁶ relative to normal alkyl radicals suggests that a free-radical hydrogenation of an alkene that is incapable of forming a benzylic or allylic radical would have a considerably higher activation energy. Accordingly, the hydrogenation of 2-cyclopropylpropene requires significantly higher temperatures for hydrogenation by HCr(CO)₃Cp, compared to hydrogenation of CPS by the same chromium hydride.

The second-order kinetics, inverse isotope effect, and dependence of the product ratio on metal hydride concentration provide strong evidence that the reaction of HCr(CO)₃Cp with 2-cyclopropylpropene proceeds by a free-radical mechanism analogous to that established for the other metal hydrides with CPS (Scheme I). To our knowledge this is the only evidence for this type of hydrogenation mechanism for an alkene that cannot form a stabilized (benzylic or allylic) carbon-centered radical. It might be questioned whether the cyclopropyl group exerts a stabilizing influence on the (c-C₃H₅)(CH₃)₂C[•] radical, similar to the resonance stabilization of benzylic radicals, but smaller in magnitude. However,

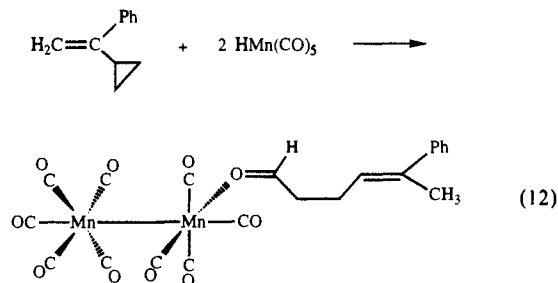
recent evidence⁴⁷ suggests that no significant resonance interaction exists in the unsubstituted cyclopropylmethyl radical.

While it does give the same products, the reaction of the analogous Mo hydride requires harsh conditions and apparently involves competitive decomposition of the hydride. No definitive conclusions can be made regarding the mechanism of the reaction of 2-cyclopropylpropene with HMo(CO)₃Cp. On the basis of the limited data available now [and in view of the fact that HCr(CO)₃Cp had the highest rate constant for reaction with CPS], it at least appears reasonable to suggest that only the most reactive hydrides will be able to hydrogenate simple alkenes by this type of odd-electron pathway.

The second-order kinetics found for the reaction of 2-cyclopropylpropene with HCr(CO)₃Cp contrasts with the more complicated kinetic behavior for the reaction of the same hydride with CPS. Unlike the curved plots of ln([CPS]_t/[CPS]₀) vs time obtained from the reaction of HCr(CO)₃Cp and CPS in the absence of added [Cr(CO)₃Cp]₂ (see Figure 2), no curvature is evident in the plots shown in Figure 9. Although we do not know the rate constant for ring opening of the (c-C₃H₅)(CH₃)₂C[•] radical, both *k*₂ and *k*₃ are expected to be higher for this radical compared to **1**, due to benzylic stabilization of **1**. Accordingly, the second-order kinetics found for hydrogenation of 2-cyclopropylpropene by HCr(CO)₃Cp indicate that (*k*₂ + *k*₃[HCr(CO)₃Cp]) ≫ *k*₋₁[*Cr(CO)₃Cp].

Certain hydrogenations and hydroformylations of alkenes by HCo(CO)₄ have been proposed⁴⁸ to proceed by mechanisms involving chain reactions of the Co(CO)₄[•] radical with unsaturated organic substrates. In view of the substantial amounts of *Cr(CO)₃Cp present in these reactions, we considered the possibility that a direct reaction of the chromium radical with either CPS or 2-cyclopropylpropene could be occurring here. Such a mechanism would be subject to autocatalysis by the chromium radical as the reaction proceeds, so the kinetic behavior observed here is not consistent with a chain reaction involving the chromium radical.

The results of this study and of others provide convincing evidence that a variety of metal carbonyl hydrides can hydrogenate alkenes (and related species) by sequential hydrogen atom transfers, especially when the initially formed carbon-centered radical is stabilized by virtue of being benzylic or allylic. In spite of the apparent generality of this mechanism for these substrates, other unexpected reactions have been observed to occur under some conditions. For example, while thoroughly purified HMn(CO)₅ behaves similarly to the other hydrides in this study, we have found that samples of HMn(CO)₅ that have not been exhaustively purified with P₂O₅ react with CPS to give a ring-opening hydroformylation reaction resulting in the formation of an Mn₂(CO)₉(η¹-aldehyde) complex²¹ (eq 12).



Summary and Conclusion

The hydrogenation of α-cyclopropylstyrene by several metal carbonyl hydrides has been shown to proceed by a radical mechanism involving sequential hydrogen atom transfers from

(43) The carbocationic **5** → **6** rearrangement has been previously demonstrated: (a) Sarel, S.; Ben-Shoshan, R. *Tetrahedron Lett.* **1965**, 1053-1058. (b) Sarel, S.; Breuer, E.; Ertag, S.; Salamon, R. *Isr. J. Chem.* **1963**, *1*, 451-459. (c) Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 577-588.

(44) Masada, H.; Murotani, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1181-1182.

(45) Bullock, R. M.; Rappoli, B. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1447-1448.

(46) (a) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1230-1235. (b) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493-532.

(47) See ref 38 (particularly footnote 30) and footnote 12 of ref 18a, for further discussion of the experimental evidence pertaining to the possible resonance stabilization of radicals by cyclopropyl substituents.

(48) (a) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1981**, *219*, 397-400; *Organometallics* **1986**, *5*, 2341-2345. (b) Ungváry, F.; Markó, L.; Bockman, T. M.; Garst, J. F.; King, R. B. *Isr. J. Chem.* **1986**, *27*, 262-266. (c) Palyi, G.; Ungváry, F.; Galamb, V.; Markó, L. *Coord. Chem. Rev.* **1984**, *53*, 37-53.

the metal hydrides to the organic substrate. The first hydrogen atom transfer is an endothermic reaction, which generates a carbon-centered radical and a metal-centered radical. This step is the rate-determining step of the overall reaction, and it shows an inverse kinetic isotope effect. On the basis of reported M-H bond strengths, it appears that the rate of this reaction is largely influenced by enthalpic considerations. The second step of the reaction is exothermic and involves the donation of a hydrogen atom from the metal hydride to the carbon-centered radical to produce the hydrogenated product. Normal isotope effects and a sensitivity to steric effects were observed for this step. The differing requirements for these two steps means that the relative rates of these two steps need not be the same for different hydrides. For example, at room temperature HCr(CO)₃Cp donates a hydrogen atom to CPS over 100 times faster than HMn(CO)₅, but the Mn hydride is faster at donation of a hydrogen atom to the carbon-centered radical. At 100 °C, HMo(CO)₃Cp is ~40 times faster than the analogous W hydride at the first step, but only 3 times faster at the second step. The amount of data available for rates of hydrogen atom transfer from metal hydrides, while increasing, is still significantly less than the considerable amount of temperature-dependent data that has been published for other hydrogen atom donors, notably *n*-Bu₃SnH and PhSH. The available data do indicate, however, that metal hydrides can exceed either of these in their rates of hydrogen atom donation.

Experimental Section

All manipulations were carried out under a nitrogen or argon atmosphere using Schlenk techniques or in a Vacuum Atmospheres drybox. NMR spectra were recorded on a Bruker AM-300 spectrometer. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer using CaF₂ cells. Toluene was stirred over H₂SO₄ and then distilled under nitrogen from Na/benzophenone. Initial gas chromatography experiments⁷ (and preparative GC of 2-cyclopropylpropene) was carried out using a Perkin-Elmer Sigma 3B gas chromatograph, but most of the experiments reported in this paper were carried out on a Hewlett-Packard 5890A gas chromatograph using helium carrier gas and a flame ionization detector. The column used was a 25 m × 0.32 mm i.d. 5% phenyl methyl silicone with 1-μm film thickness. The injector and detector were held at 250 °C and oven temperatures of 140–175 °C were employed. Data collection was carried out on a Hewlett-Packard 5895A workstation. Dodecane was used as an internal standard, and response factors for all components were calibrated with authentic materials. α-Cyclopropylstyrene (CPS) was prepared from cyclopropyl phenyl ketone and Ph₃P=CH₂ by a published procedure.⁴⁹ 2-Cyclopropylpropene⁵⁰ was prepared similarly from cyclopropyl methyl ketone and Ph₃P=CH₂ in DMSO; it was isolated by bulb-to-bulb distillation on a vacuum line and further purified by preparative GC (7 ft × 3/8 in. column, 20% Carbowax on Chromosorb, helium carrier gas). Metal hydrides were prepared as described below and stored under argon at -20 °C in the dark. HM(CO)₃Cp⁵¹ (M = Cr, Mo, W) were prepared by reduction of the dimers [CpMo(CO)₃]₂⁵² by NaK⁵³ or KH,⁵⁴ followed by protonation by H₃PO₄ to give the hydrides, which were purified by sublimation. The deuterides DM(CO)₃Cp were prepared similarly by using D₃PO₄. HRe(CO)₅ and HMn(CO)₅ were prepared by a published procedure⁵⁵ and dried over P₂O₅. The HMn(CO)₅ was purified several times by vacuum transferring it from P₂O₅ as well as passing it through a U-tube on a vacuum line containing P₂O₅ and glass beads, in order to avoid the ring-opening hydroformylation²¹ of CPS. HMo(CO)₂(PMe₃)Cp⁵⁶ and HMn(CO)₄PPh₃⁵⁷ were prepared by using minor modifications of published procedures. HMo(CO)₃(C₅Me₅) was prepared by a published method⁵⁸ and further purified by sublimation at 50 °C.

HFe(CO)₂(C₅Me₅).⁵⁹ A mixture of [(C₅Me₅)Fe(CO)₂]₂ (2.00 g, 4.05 mmol) and NaK (0.68 g) in THF (80 mL) was stirred for 2 h at room temperature to give a deep red solution of KFe(CO)₂(C₅Me₅),⁶⁰ which was filtered through Celite, cooled to -78 °C, and treated with CH₃C-O₂H (1.0 mL, 16 mmol). The solution was stirred for 10 min at -78 °C, then warmed to room temperature, and stirred for 1 h. The solvent was evaporated and the residue was extracted with hexane (4 × 20 mL). The hexane was evaporated and the iron hydride was isolated by sublimation at 40 °C to give a yellow powder (1.91 g, 7.70 mmol, 95%). ¹H NMR (C₆D₆): δ -11.44 (s, 1 H, FeH), 1.57 (s, 15 H, CH₃). IR (THF) 1994, 1932 cm⁻¹.

HFe(CO)₂Cp.⁶¹ A suspension of KFe(CO)₂Cp⁶² (232 mg, 1.07 mmol) in toluene (10 mL) was cooled to -78 °C and treated with CH₃CO₂H (55 μL, 0.89 mmol, 0.83 equiv). After warming to room temperature and stirring for 5 min, the volatile components were collected at -196 °C in a U-tube on a vacuum line. After most of the toluene had vacuum transferred, the HFe(CO)₂Cp was observed as a yellow oil, which slowly distilled into the U-tube. The U-tube was removed from the vacuum line and taken into the drybox. The product was obtained as a yellow solution (0.060 M in toluene, 68% yield). The yield was determined by quantitative IR spectroscopy. IR (1-cm⁻¹ resolution) of HFe(CO)₂Cp in toluene: 2015 (ε = 2900), 1955 cm⁻¹ (ε = 3200 M⁻¹ cm⁻¹). These ε values for the IR bands of HFe(CO)₂Cp were determined after conversion of the HFe(CO)₂Cp to ClFe(CO)₂Cp by reaction with CCl₄ (a reaction assumed to proceed in quantitative yield) followed by determination of the concentration of ClFe(CO)₂Cp by IR. IR bands of ClFe(CO)₂Cp in toluene: 2049 cm⁻¹ (ε = 2300 M⁻¹ cm⁻¹), 2003 (ε = 2400 M⁻¹ cm⁻¹). HFe(CO)₂Cp can be prepared by this method in C₆D₆ for use in NMR experiments. ¹H NMR of HFe(CO)₂Cp in C₆D₆: δ 4.12 (s, 5 H, C₅H₅), -11.72 (br s, FeH).

HRu(CO)₂Cp.⁶³ A colorless C₆D₆ solution of HRu(CO)₂Cp was prepared by protonation of KRu(CO)₂Cp⁶⁴ with CF₃CO₂H. Isolation of this extremely air sensitive solution was carried out as described above for the Fe analogue. NMR of HRu(CO)₂Cp in C₆D₆: δ -10.66 (s, RuH), 4.59 (s, 5 H, C₅H₅).

Ph(CH₃)C=CHCH₂CH₂Br (4). Aqueous HBr (48% solution, 24 mL) was added over a 5-min period to a solution of LiBr⁴⁴ (13.03 g, 0.150 mol) and Ph(CH₃)(c-C₃H₃)COH⁶⁵ (10.4 g, 0.0641 mol) in CH₃CN (10 mL) at -20 °C. After 2.5 h at -20 °C, CH₂Cl₂ (75 mL) was added, and the organic layer was separated, washed with an aqueous saturated NaHCO₃ solution (50 mL), and dried (MgSO₄). The product was isolated by distillation (~0.01 mmHg, 90–100 °C) to give a clear liquid (13.55 g, 0.060 mol, 94%). ¹H NMR (CDCl₃): 7.4–7.2 (m, 5 H, aromatic), 5.75 (tq, *J* = 7.2, 1.4 Hz, 1 H, C=CH), 3.46 (t, *J* = 7.2 Hz, 2 H, BrCH₂), 2.78 (q, *J* = 7.2 Hz, 2 H, BrCH₂CH₂), 2.06 (s, 3 H, CH₃). ¹³C (CDCl₃): 144.6, 138.7 (ipso and PhMeC=C), 129.5, 128.2, 126.9, 125.8 (ortho, meta, para, and C=CH), 33.8, 33.4 (CH₂CH₂ Br), 16.8 (CH₃).

(PBU₃)(dmgH)₂Co-CH₂CH₂CH=C(Ph)CH₃.⁶⁶ An aqueous solution of NaOH (1.8 mL of a 6.25 M solution, 11.3 mmol) was added to (PBU₃)(dmgH)₂CoCl (3.00 g, 5.67 mmol) in CH₃OH (45 mL). NaBH₄ (429 mg, 11.3 mmol) was then added, and the reaction was stirred for 20 min to give a dark blue solution. BrCH₂CH₂CH=C(Ph)CH₃ (1.2 mL, 6.8 mmol) was added, and after 10 min the orange-brown solution was added to H₂O (150 mL). This aqueous solution was extracted with CH₂Cl₂ (3 × 50 mL), dried over Na₂SO₄, and passed through a short alumina (activity III) column. The solvent was evaporated, and the residue was dissolved in hexane (20 mL) and slowly cooled from -35 to -78 °C. The yellow supernatant was decanted from the solid precipitate, but the solid became an oil after being warmed to room temperature. The oil was induced to solidify by stirring it with pentane (5 mL) at 0 °C and slowly pumping off the solvent as the solidification proceeded. Yield: 3.12 g (4.90 mmol, 86%) of orange-yellow solid. ¹H NMR (CDCl₃): δ 18.16 (s, 2 H, OHO bridge), 7.3–7.1 (m, 5 H, aromatic),

(59) For an earlier preparation of HFe(CO)₂(C₅Me₅) by a different route, see: Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1988**, *7*, 1683–1691.

(60) Ellis, J. E.; Fennell, R. W.; Flom, E. A. *Inorg. Chem.* **1976**, *15*, 2031–2036.

(61) For related preparations of HFe(CO)₂(C₅H₅) and leading references to the early literature, see: Reference 6b and references cited therein.

(62) Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284–285.

(63) Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710–1714.

(64) Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* **1987**, *6*, 1141–1145.

(65) Maercker, A.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 1742–1759.

(66) The preparation of this cobalt(III) alkyl complex follows the general procedures reported earlier: (a) Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61–69. (b) Schrauzer, G. N.; Deutsch, E. *J. Am. Chem. Soc.* **1969**, *91*, 3341–3350.

(49) Ketley, A. D.; McClanahan, J. L. *J. Org. Chem.* **1965**, *30*, 942–943.

(50) 2-Cyclopropylpropene may also be prepared by dehydration of dimethylcyclopropylcarbinol: Van Volkenburgh, R.; Greenlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Am. Chem. Soc.* **1949**, *71*, 172–175.

(51) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104–124.

(52) Birdwhistell, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239–241.

(53) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263–268.

(54) Inkrott, K.; Goetze, R.; Shore, S. G. *J. Organomet. Chem.* **1978**, *154*, 337–342.

(55) Warner, K. E.; Norton, J. R. *Organometallics* **1985**, *4*, 2150–2160.

(56) Kalck, P.; Pince, R.; Poiblan, R.; Roussel, J. *J. Organomet. Chem.* **1970**, *24*, 445–452.

(57) Booth, B. L.; Haszeldine, R. N. *J. Chem. Soc. A* **1966**, 157–160.

(58) Asdar, A.; Tudoret, M.-J.; Lapinte, C. *J. Organomet. Chem.* **1988**, *349*, 353–366.

5.78 (t, $J = 7.4$ Hz, vinyl CH), 2.17 (d, $J_{\text{PH}} = 3.4$ Hz, 12 H, CH_3), 1.87 (s, 3 H, $\text{C}=\text{C}(\text{CH}_3)$), 1.71, 1.51 (m, 2 H each, CoCH_2CH_2), 1.4–1.2 (m, 18 H, $\text{PCH}_2\text{CH}_2\text{CH}_2$), 0.89 (t, $J = 7$ Hz, 9 H, $\text{P}(\text{CH}_2)_3\text{CH}_3$). Anal. Calcd for $\text{C}_{31}\text{H}_{54}\text{CoN}_4\text{O}_4\text{P}$: C, 58.48; H, 8.55. Found: C, 58.52; H, 8.54 (Schwarzkopf Microanalytical Lab).

Reactions of Metal Hydrides with α -Cyclopropylstyrene (CPS). The reactions of CPS with metal hydrides were carried out at five different concentrations of metal hydride. In each case the metal hydride was present in excess over the CPS concentration. The general procedure involved preparing a stock solution of metal hydride by weighing out the metal hydride in the drybox, adding it to a 3.0-mL volumetric flask, and diluting to the mark with toluene. Cyclopropylstyrene and dodecane (internal standard) were added to 1.0-mL volumetric flasks. A measured aliquot of the metal hydride solution was added to each of the five flask contents, which were then diluted to the mark. Typical relative concentrations of the metal hydride in each experiment were 1.0, 0.75, 0.50, 0.25, and 0.10. The reactions were carried out in glass vessels equipped with high-vacuum Teflon stopcocks. Aliquots of the reaction were removed periodically in order to monitor the reaction by gas chromatography. The metal hydrides studied by this method are listed below; the first concentration range in parentheses is the range of metal hydride concentrations used, the second number is the range of cyclopropylstyrene concentrations used. All concentrations are molarity. $\text{HMo}(\text{CO})_3\text{Cp}$ at 60 °C (0.98–0.098, 0.05–0.02); $\text{HMo}(\text{CO})_3\text{Cp}$ at 100 °C (0.99–0.099, 0.046–0.02); $\text{HW}(\text{CO})_3\text{Cp}$ at 100 °C (0.69–0.069, 0.033–0.017); $\text{DW}(\text{CO})_3\text{Cp}$ at 100 °C (0.58–0.058, 0.026–0.013); $\text{HFe}(\text{CO})_2(\text{C}_5\text{Me}_5)$ at 60 °C (0.88–0.088, 0.033–0.020); $\text{HMo}(\text{CO})_3(\text{C}_5\text{Me}_5)$ at 60 °C (0.712–0.071, 0.033–0.017); $\text{HMn}(\text{CO})_4\text{PPh}_3$ at 60 °C (0.29–0.029, 0.02–0.007); $\text{HMo}(\text{CO})_2(\text{PMe}_3)\text{Cp}$ at 100 °C (0.57–0.057, 0.033–0.013). Experiments with $\text{HCr}(\text{CO})_3\text{Cp}$ (0.22–0.029 M) and CPS (0.021–0.0027 M) carried out in solutions saturated with the dimer were set up by adding excess $[\text{Cr}(\text{CO})_3\text{Cp}]_2$ to toluene solutions of known $\text{HCr}(\text{CO})_3\text{Cp}$ concentrations. About 20 mg of $[\text{Cr}(\text{CO})_3\text{Cp}]_2/\text{mL}$ of toluene was used in these experiments; this is significantly higher than the solubility limit of $[\text{Cr}(\text{CO})_3\text{Cp}]_2$, and the presence of undissolved dimer ensured that the solution remained saturated throughout the reaction. The $[\text{Cr}(\text{CO})_3\text{Cp}]_2$ used in these experiments had been purified by sublimation and was stored in the drybox. Experiments to determine the $[\text{UN}]/[\text{RE}]$ ratio for $\text{HFe}(\text{CO})_2\text{Cp}$ were carried out similarly, using the $\text{HFe}(\text{CO})_2\text{Cp}$ solution (see preparation above) in toluene as a stock solution. Concentrations of $\text{HFe}(\text{CO})_2\text{Cp}$ ranged from 0.060 to 0.0060 M; CPS concentrations were 0.0053–0.000798 M. The kinetics of hydrogenation of CPS by $\text{HFe}(\text{CO})_2\text{Cp}$ were carried out in separate experiments using excess CPS [initial concentrations 0.13–0.66 M, 10–47 times the initial $\text{HFe}(\text{CO})_2\text{Cp}$ concentration]. The rate of disappearance of the 2015- cm^{-1} band of $\text{HFe}(\text{CO})_2\text{Cp}$ was monitored by IR spectroscopy, and the slope of a plot of the observed pseudo-first-order rate constant vs [CPS] gave the second-order rate constant. The experiments to determine $[\text{UN}]/[\text{RE}]$ for $\text{HMn}(\text{CO})_5$ at 22 °C were prepared by appropriate dilutions of a solution of $\text{HMn}(\text{CO})_5$ (0.054 M in toluene). These experiments encompassed the initial concentration ranges of 0.054–0.0054 M for $\text{HMn}(\text{CO})_5$ and 0.0049–0.00065 M for CPS. Slopes and intercepts of the $[\text{UN}]/[\text{RE}]$ vs [MH] plots are tabulated below.

MH	T, °C	slope	intercept
$\text{HCr}(\text{CO})_3\text{Cp}$	22	66 (2)	1.6 (4)
$\text{HFe}(\text{CO})_2\text{Cp}$	22	464 (7)	10.3 (3)
$\text{HMn}(\text{CO})_5$	22	323 (7)	9.9 (2)
$\text{HFe}(\text{CO})_2(\text{C}_5\text{Me}_5)$	60	8.1 (1)	0.29 (6)
$\text{HMo}(\text{CO})_3(\text{C}_5\text{Me}_5)$	60	0.33 (1)	0.028 (3)
$\text{HMo}(\text{CO})_3\text{Cp}$	60	8.0 (2)	0.3 (1)
$\text{HMn}(\text{CO})_4\text{PPh}_3$	60	0.086 (3)	0.059 (1)
$\text{HMo}(\text{CO})_3\text{Cp}$	100	1.68 (5)	0.21 (3)
$\text{HMo}(\text{CO})_2(\text{PMe}_3)\text{Cp}$	100	0.106 (4)	0.096 (2)
$\text{HW}(\text{CO})_3\text{Cp}$	100	0.54 (1)	0.18 (1)
$\text{DW}(\text{CO})_3\text{Cp}$	100	0.25 (1)	0.15 (1)

A Neslab RTE-9 constant-temperature bath was used for the 60 °C experiments and for $\text{HCr}(\text{CO})_3\text{Cp}$ at 22 °C. A Lauda CS-6D constant-temperature bath was used for the 100 °C experiments. Product ratios for $\text{HFe}(\text{CO})_2\text{Cp}$ and $\text{HMn}(\text{CO})_5$ were determined at room temperature (22 °C) but were not thermostated.

In some cases the metal dimers M_2 precipitated from the reaction solution. In all cases except for $\text{HMo}(\text{CO})_2(\text{PMe}_3)\text{Cp}$, the dimers were the only organometallic product observed; these dimers were identified by comparison of their NMR and IR spectra to authentic compounds. The reaction of $\text{HMo}(\text{CO})_2(\text{PMe}_3)\text{Cp}$ with CPS resulted in a yellow crystalline precipitate identified as $[\text{CpMo}(\text{CO})_3][\text{CpMo}(\text{CO})_2(\text{PMe}_3)_2]^+$. IR (THF): ν_{CO} 1958 m, 1897 s, 1877 s, 1783 s, 1765 sh cm^{-1} . ^1H NMR (CD_3CN): δ 5.40 (t, $J_{\text{PH}} = 1.3$ Hz, 5 H, C_5H_5), 5.06

(s, 5 H, C_5H_5), 1.69 ("filled in doublet"; separation between outer lines of this pattern = $^2J_{\text{PH}} + ^4J_{\text{PH}} = 10.4$ Hz, 18 H, PMe_3). This assignment is supported by the similarity of the IR spectrum to the analogous $[\text{CpMo}(\text{CO})_3][\text{CpMo}(\text{CO})_2\text{L}_2]^+$ ($\text{L} = \text{PEt}_3, \text{PBu}_3, \text{PPh}_3$) compounds previously reported by Haines, Nyholm, and Stiddard.⁶⁷ Spectral data that we observed are very similar to those reported by Alt and Schwärzle⁶⁸ for a compound assigned as $\text{Cp}(\text{CO})(\text{PMe}_3)_2\text{Mo}-\text{Mo}(\text{CO})_3\text{Cp}$. We suggest that the assignment of a metal-metal-bonded species made by Alt and Schwärzle is incorrect and that their product is instead the same ionic species we have obtained.

Determination of k_1 and k_{-1} for the Reaction of $\text{HCr}(\text{CO})_3\text{Cp}$ with CPS. The values of k_1 and k_{-1} were determined by fitting the experimental values of k_{obs} as a function of $[\text{HCr}(\text{CO})_3\text{Cp}]$ to eq 5, using input values for $[\text{Cr}(\text{CO})_3\text{Cp}]$, k_2 and k_3 obtained as described in the text. The resulting values of k_1 and k_{-1} , and the curve shown in Figure 3, were determined with a computer program (GENPLOT, Computer Graphics Service, 221 Asbury Road, Lansing, NY 14882), which incorporates a nonlinear least-squares analysis.¹⁶

Kinetics of the Reaction of $\text{HCr}(\text{CO})_3\text{Cp}$ with 2-Cyclopropylpropene. The chromium hydride (or deuteride) was weighed and added to an NMR tube in the drybox. C_6D_6 solvent was added, and 2-cyclopropylpropene was measured by gas-bulb measurement and added to the NMR tube by vacuum transfer. The solution was freeze-pump-thawed 3 times and flame-sealed. After a $t = 0$ spectrum was recorded, the tube was heated at 68 °C in a Neslab RTE-9 constant-temperature bath. The rate of disappearance of the 2-cyclopropylpropene (and the rate of appearance of the hydrogenated products, isopropylcyclopropane and 2-methyl-2-pentene) was monitored by ^1H NMR vs an internal standard. The isopropylcyclopropane and 2-methyl-2-pentene were further characterized by comparison of their ^1H NMR and GC/MS spectra to those of authentic samples (obtained from Wiley Organics). The reaction is sufficiently slow at room temperature that no appreciable reaction occurred when the tube was removed from the bath for ^1H NMR monitoring. A 30-s delay was used between pulses to ensure accurate integrations.

Acknowledgment. This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. We thank Drs. Carol Creutz, Mark Andrews, Stanley Seltzer, Marshall Newton, Frederick Lemke, and George Gould for many helpful discussions, and Prof. Jack Norton and his group for their comments on an early draft of this paper. We gratefully acknowledge the advice and assistance of Dr. Greg Hall, who carried out the line-fitting (Figure 3) and the Monte Carlo simulation. We also thank Dr. Brian Rappoli for preliminary experiments with $\text{HMn}(\text{CO})_5$, and Elinor Norton for GC/MS analyses.

Appendix

Analysis of the Kinetics of the Mechanism Shown in Scheme I.

$$-\frac{d[\text{CPS}]}{dt} = k_1[\text{MH}][\text{CPS}] - k_{-1}[\text{M}^*][\text{I}] \quad (\text{A1})$$

Neglecting the reversibility of the ring-opening rearrangement and applying the steady-state approximation for [I] gives

$$\frac{d[\text{I}]}{dt} = k_1[\text{CPS}][\text{MH}] - k_{-1}[\text{I}][\text{M}^*] - k_3[\text{MH}][\text{I}] - k_2[\text{I}] \approx 0 \quad (\text{A2})$$

Solving for [I] gives

$$[\text{I}] = \frac{k_1[\text{CPS}][\text{MH}]}{k_{-1}[\text{M}^*] + k_3[\text{MH}] + k_2} \quad (\text{A3})$$

Substituting this value of [I] into eq A1 gives (after algebraic manipulation)

$$-\frac{d[\text{CPS}]}{dt} = k_1[\text{MH}][\text{CPS}] \frac{k_2 + k_3[\text{MH}]}{k_{-1}[\text{M}^*] + k_2 + k_3[\text{MH}]} = k_{\text{obs}}[\text{CPS}] \quad (\text{A4})$$

where

(67) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* 1968, 43–46.

(68) Alt, H. G.; Schwärzle, J. A. *J. Organomet. Chem.* 1978, 162, 45–56.

$$k_{\text{obs}} = k_1[\text{MH}] \frac{k_2 + k_3[\text{MH}]}{k_{-1}[\text{M}^*] + k_2 + k_3[\text{MH}]} \quad (\text{A5})$$

Equation A5 must be used for the reaction of $\text{HCr}(\text{CO})_3\text{Cp}$ with CPS at 22 °C. This rigorous expression for k_{obs} given by eq A5 can be simplified in cases where $[\text{MH}]$ is sufficiently high (and when K_{eq} for the $2\text{M}^* \rightleftharpoons \text{M}_2$ equilibrium is very large). When this is true, then $(k_2 + k_3[\text{MH}]) \gg k_{-1}[\text{M}^*]$ and k_{obs} simplifies to

$$k_{\text{obs}} = k_1[\text{MH}] \quad (\text{A6})$$

In these cases a plot of k_{obs} vs $[\text{MH}]$ has slope = k_1 , and this simplified treatment is appropriate for reactions of all of the metal hydrides other than $\text{HCr}(\text{CO})_3\text{Cp}$.

Relationship between the Product Ratio (UN/RE) and [MH]. This treatment now includes the reversibility of the k_2 step. A steady-state treatment for [2] gives

$$\frac{d[2]}{dt} = k_2[1] - k_{-2}[2] - k_4[\text{MH}][2] \approx 0 \quad (\text{A7})$$

Solving for [1] gives

$$[1] = \frac{(k_{-2} + k_4[\text{MH}])[2]}{k_2} \quad (\text{A8})$$

The rate of appearance of RE is

$$\frac{d[\text{RE}]}{dt} = k_4[\text{MH}][2] \quad (\text{A9})$$

and the rate of appearance of UN is

$$\frac{d[\text{UN}]}{dt} = k_3[\text{MH}][1] \quad (\text{A10})$$

Substituting the value of [1] from eq A8 into eq A10 gives

$$\frac{d[\text{UN}]}{dt} = \frac{k_3[\text{MH}](k_{-2} + k_4[\text{MH}])[2]}{k_2} \quad (\text{A11})$$

From eqs A11 and A9

$$\frac{[\text{UN}]}{[\text{RE}]} = \frac{k_3[\text{MH}](k_{-2} + k_4[\text{MH}])[2]}{k_2k_4[\text{MH}][2]} \quad (\text{A12})$$

This simplifies to

$$\frac{[\text{UN}]}{[\text{RE}]} = \frac{k_3(k_{-2} + k_4[\text{MH}])}{k_2k_4} \quad (\text{A13})$$

$$\frac{[\text{UN}]}{[\text{RE}]} = \frac{k_3k_{-2}}{k_2k_4} + \frac{k_3[\text{MH}]}{k_2} \quad (\text{A14})$$

Equation A14 indicates that a plot of $[\text{UN}]/[\text{RE}]$ vs $[\text{MH}]$ will have a slope of k_3/k_2 and a y intercept of $k_{-2}k_3/k_2k_4$. Therefore the slopes obtained for a series of metal hydrides at a given temperature will provide relative values of k_3 for each of these hydrides. Absolute rate constants for k_3 can be estimated for the three hydrides that react at 22 °C, since k_2 was reported at this temperature. Division of the slope by the y intercept gives k_4/k_{-2} , which gives relative k_4 values for the different hydrides at a given temperature.

Note Added in Proof. The reversibility of ring opening of the tertiary radical **1** deduced from the nonzero y intercept in our plots of $[\text{UN}]/[\text{RE}]$ vs $[\text{MH}]$ is corroborated by a recent communication (Bowry, V. W.; Luszyk, J.; Ingold, K. U. *J. Chem. Soc., Chem. Commun.* **1990**, 923–925), which reports that ring opening of the related secondary α -cyclopropylbenzyl radical is also reversible, with the equilibrium favoring the ring-closed form. This communication also questions the validity of the measurement of the rate constant (k_2) for ring opening of **1** reported in ref 19. It should be recognized that while the absolute rate constants of k_3 estimated in this paper are dependent on the value of k_2 , none of the relative k_3 values reported in Table I are affected. The estimate of $k = 1.3 \times 10^6 \text{ s}^{-1}$ (at 42 °C) made for ring opening of the α -cyclopropylbenzyl radical can be compared to the $k = 2.7 \times 10^5 \text{ s}^{-1}$ (at 22 °C) reported in ref 19. Further studies of the k_2 value for ring opening of **1** are planned.