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Relative Rates of $H^{\bullet}$ Transfer from Transition-Metal Hydrides to Trityl Radicals

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Abstract: The tris(*p-tert*-butylphenyl)methyl radical can be made in quantitative yield by treating a toluene solution of the corresponding bromide with copper powder. This radical abstracts $H^{\bullet}$ from all the common transition-metal hydrides but does not stick to the resulting metalloradicals, so that the latter form metal–metal-bonded dimers. The rates of these $H^{\bullet}$ transfer reactions have been measured directly in a stopped-flow apparatus. At 25 °C the $H^{\bullet}$ transfer rate constants vary from <3 $M^{-1}\ s^{-1}$ for $HMn(CO)_4(PEtPh_2)$ to 12000 $M^{-1}\ s^{-1}$ for $HFe(CO)_2Cp$. As a whole these rate constants show that the rates of these $H^{\bullet}$ transfer reactions are substantially influenced by steric factors as well as by bond strengths.

Introduction

Transition-metal hydrides play a pivotal role in organometallic chemistry, functioning as stoichiometric reagents for both organic and organometallic syntheses and appearing as intermediates in catalytic processes such as hydroformylation and hydrogenation.(1) Common to all of these processes is the transfer of the hydride ligand to an organic substrate. The simplest ways in which the transfer can occur are (1) as a proton, (2) as a hydrogen atom, or (3) as a hydride ion.

$$MH + S \rightarrow M^- + SH^+ \quad (1)$$

$$MH + S \rightarrow M^{\bullet} + SH^{\bullet} \quad (2)$$

$$MH + S \rightarrow M^+ + SH^- \quad (3)$$

Enough is known[2] about the thermodynamic acidities of transition-metal hydrides, and the rates at which they transfer protons to various bases (eq 1), to determine the relationship between the two. Thermodynamic driving force has, at least for the common carbonyl hydrides and their monosubstituted derivatives, proven to be the dominant factor determining their rates of proton transfer; structural differences play only a minor role. Thus the relative reactivities of these hydrides are the same in all proton-transfer reactions, and it is easy to identify mechanisms in which proton transfer from these hydrides is rate-determining.

True hydride-transfer reactions of the type shown in eq 3 are rare, as hydride transfer usually occurs *only after previous substrate coordination.*[3] Little information is available on the relative reactivity of various hydrides in reactions like eq 3,[4] and the thermodynamic driving force for such reactions is difficult to evaluate because the coordinatively unsaturated metal remaining after the H^- transfer[4] will rapidly coordinate another ligand.

Hydrogen atom transfer reactions of transition-metal hydrides (eq 2) are common,[5-10] but it is only now becoming possible to investigate the relationship between the rate of such reactions and their thermodynamic driving force. Reliable values of M–H bond dissociation enthalpies, required for the evaluation of ΔH and ΔG for such reactions, are appearing.[11-13] However, appropriate $H^{\bullet}$ transfer rate constants, from transition-metal hydrides of known bond strength to a single acceptor under standard conditions, are needed. Bullock and Samsel have noted that "the relative paucity of absolute rate data for hydrogen atom transfers to carbon-centered radicals contrasts sharply with the data available for other hydrogen atom donors".[14] The lack of such information has made it hard to identify mechanisms in which $H^{\bullet}$ transfer is rate-determining: Jacobsen and Bergman found it "difficult to predict the relative rate of a hydrogen *atom* transfer by $CpMo(CO)_3H$ or $CpMo(CO)_2(PR_3)H$" in the addition of various molybdenum hydrides across the C=C bond of a vinylidene bridge.[15]

While Halpern and co-workers have estimated the rate constant for $H^{\bullet}$ transfer from $HMn(CO)_4P(C_6H_4\text{-}p\text{-}OCH_3)_3$ to $p\text{-}CH_3OC_6H_4CH_2^{\bullet}$ from a complex rate law for a system involving the latter as an intermediate,[16] most known $H^{\bullet}$ transfer rate constants have been determined by radical clock methods.[17] However, radical clock methods cannot give comparable $H^{\bullet}$ transfer rate constants over a series of transition-metal hydrides, for two reasons: (1) radical clock methods require that both rearranged and unrearranged products be seen, which means that

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(3) For a recent review see: Labinger, J. L. Nucleophilic Reactivity of Transition Metal Hydrides. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*, ref 1f.

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only those hydrides for which transfer is competitive with rearrangement can be compared at any one temperature; (2) the radical rearrangement rate constants are generally not known over a range of temperatures and may be unknown at the temperatures where transfer and rearrangement compete.

The construction of a scale of H• transfer ability requires that one be able to measure directly the rates at which many transition-metal hydrides react with a common radical. A suitable radical must be stable, so that H• transfer—and not the formation of the radical—is rate-determining; it must also be thermodynamically capable of abstracting a hydrogen atom from the transition-metal hydrides to be studied, and it is helpful if it can be easily monitored spectroscopically.

An obvious candidate, which has been used to study H• transfer from thiols,[18] is the trityl radical. It has a λ_{max} at 516 nm.[18] As the strength of the Ph_3C–H bond, about 81 kcal/mol,[19-21] exceeds all reliable M–H bond strength estimates,[13,22] we expect $Ph_3C^•$ to abstract H• from transition-metal hydrides, and several reactions in which it does so are known (eqs 4–7).[23]

$$2HW(CO)_2(PPh_3)Cp + 2Ph_3C^• \rightarrow [CpW(CO)_2(PPh_3)]_2 + 2Ph_3CH \quad (4)^{23a}$$

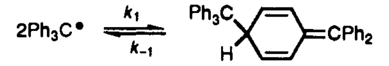
$$2H_2Os(CO)_4 + 2Ph_3C^• \rightarrow H_2Os_2(CO)_8 + 2Ph_3CH \quad (5)^{23b}$$

$$2HCo(CO)_4 + 2Ph_3C^• \rightarrow Co_2(CO)_8 + 2Ph_3CH \quad (6)^{23c}$$

$$HW(CO)_3Cp + Ar_3CCl + L \xrightarrow{Ar_3C^•} ClW(CO)_3Cp + ClW(CO)_2(L)Cp + Ar_3CH \quad (7)^{23d}$$

$$L = PPh_3$$

The kinetics of H• abstraction are complicated by the monomer–dimer equilibrium (eq 8) found for $Ph_3C^•$ itself, because the latter is established at a rate comparable to that of hydrogen atom transfer. It should be possible to obtain k_1, k_{-1}, and the H• transfer rate constant in such a case by detailed analysis of the time dependence of the $Ph_3C^•$ concentration. However, preliminary experiments showed that k_1 and k_{-1} were not accurately determined by this procedure[24]—suggesting that the resulting H• transfer rate constants would be unreliable.



(8)

Bulky substituents in the para position prevent trityl radicals from undergoing the sort of head-to-tail dimerization illustrated for $Ph_3C^•$ in eq 8.[25] The tris(*p-tert*-butylphenyl)methyl radical (**1**), thought to be fully dissociated in solution,[26] has been found by Lewis and co-workers[27] to be a better reagent for studying H• abstraction from thiols than the $Ph_3C^•$ they had previously used.[18]

Table I. Preparation Methods for Tris(*p-tert*-butylphenyl)methyl Radical (**1**) in Toluene

Ar_3CX X =	reductant	time, h	*t*, °C	yield,^{a} %
Cl	Hg	4.5	RT	26
Cl	Hg	16	RT	34
Cl	Hg	22.5	RT	34
Cl	Zn powder^b	1	RT	88–99^c
Cl	mossy Zn^b	2	RT	85^c
Cl	Cu powder^d	1	RT	9
Cl	Cu powder^d	1	70	68
Cl	Cu powder^d	overnight	70	70
Cl	Cu powder^d	4.5	70	60–98
Cl	Ag powder	overnight	RT	60–70
Cl	Ag powder^b	overnight	RT	80–83
Br	Ag powder^b	overnight	RT	95–100
Br	Cu powder^e	4	70	94–100

^{a} Yields were determined from A_{523} of the radical in toluene based on our value of 825 M^{-1} cm^{-1} for its molar absorptivity. ^{b} Small quantity of sand added as abrasive to clean metal surface. ^{c} Presence of strongly absorbing impurity makes this value unreliable. ^{d} Commercial material washed with acid and dried. ^{e} Precipitated from aqueous $CuCl_2$ and Zn.[77]

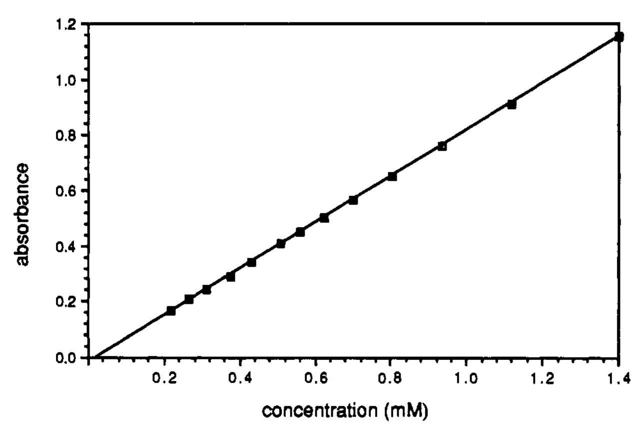


Figure 1. Plot of absorbance in toluene at 523 nm vs concentration of tris(*p-tert*-butylphenyl)methyl radical (**1**) obtained by successive dilution of a sample of **1**. The initial concentration was estimated from our value of the molar absorptivity.

We have improved the synthesis of **1**, confirmed that it is monomeric in solution, and measured the rate at which it abstracts H• from transition-metal hydrides.

Results

Preparation of Tris(*p-tert*-butylphenyl)methyl Radical (1). Although triarylmethyl radicals have been made by the reduction of the appropriate chlorotriarylmethanes with mercury,[18,28] silver or thallium amalgam,[29] zinc,[30] molecular silver,[27,31] and copper,[32] yields have frequently not been reported and in some cases, e.g., mercury,[27,28a] are known to be mediocre. Initially we used the published[27] value of the molar absorptivity at 525 nm[33] of **1** in toluene to determine its concentration and yield. Most of the reducing agents in Table I gave less than quantitative yields of **1** from tris(*p-tert*-butylphenyl)methyl chloride (**2a**). Zinc gave a solution with an absorbance suggesting a good yield of **1**; however, the visible spectrum also contained a previously unseen

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(22) The average BDE of the two Os–H bonds in $H_2Os(CO)_4$ has been estimated at 78 kcal/mol: Calderazzo, F. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 37.

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(24) Our results were compared with the values of k_{-1} in ref 20 and with the equilibrium constants in ref 18.

(25) However, the fact that crystalline head-to-head dimers can be obtained from solutions of tris(2,6-di-*tert*-butyl-4-diphenylyl)methyl radicals (Stein, M.; Winter, W.; Rieker, A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 692) and of tris(3,5-di-*tert*-butylphenyl)methyl radicals (Kahr, B.; Van Engen, D.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 8305) raises the possibility of head-to-head association in solution.

(26) A toluene solution of the radical showed no change in absorbance down to −78 °C: Colle, K. S.; Glaspie, P. S.; Lewis, E. S. *J. Chem. Soc., Chem. Commun.* **1975**, 266.

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(33) The absorption maximum occurred at 523 nm on our spectrophotometer, a minor variation which can be attributed to instrument differences.

Table II. $H^{\bullet}$ Transfer Rate Constants k_H (to Tris(*p-tert*-butylphenyl)methyl Radical (**1**) at 25 °C in Toluene) and Bond Dissociation Enthalpies for Transition-Metal Hydrides

hydride	temp range of rate measurement, °C	wavelength monitored, nm	k_H, $M^{-1}\,s^{-1}$	ΔH^{*}, kcal/mol	ΔS^{*}, eu	BDE,[a] kcal/mol
$HFe(CO)_2Cp$	−35/−5	525	12000 (400)	5.7 (1)	−20.8 (5)	58
$HFe(CO)_2Cp^{*}$	0/45	558	300 (8)	7.3 (3)	−23 (1)	
$HCr(CO)_3Cp$	0/50	523	335 (2)	5.75 (5)	−27.7 (2)	62
$HRu(CO)_2Cp$	25/65	523	1030 (30)	7.1 (2)	−21 (1)	65
$HCo(CO)_4$	−35	525	1600 (900)[b]			67
$HMn(CO)_5$[c]	−40/50	523	741 (8)	7.00 (5)	−22.0 (2)	68
$HMo(CO)_3Cp^{*}$	30/60	540	13.9 (5)	7.7 (3)	−27.4 (8)	69
$HMo(CO)_3Cp$	0/50	542	514 (2)	5.76 (5)	−26.8 (2)	70
$HMn(PEtPh_2)(CO)_4$	50	530	<3			71[d]
$HW(CO)_3Cp$	20/60	500	91 (1)	6.66 (8)	−27.2 (2)	73
$H_2Os(CO)_4$	30/70	530	15.7 (7)	8.7 (3)	−24 (1)	78[e]

[a] From eq 24, using data from ref 12 unless otherwise indicated. [b] Extrapolated from −35 °C data by assuming that ΔS^{*} lies between −21 and −28 eu. [c] Data adjusted in proof according to new data from M. R. Rodkin in our group. [d] From eq 24, using unpublished data from S. S. Kristjãnsdõttir, C. M. Elliott, and J. R. Norton. [e] Average of the two Os–H bonds estimated from a thermochemical cycle (ref 22).

peak at 460 nm that may have arisen from further reduction of the radical.[34]

As residual **2a** interfered in the reaction between radical **1** and some transition-metal hydrides (see below), a procedure that gave complete conversion to **1** was needed. Reduction of bromotris(*p-tert*-butylphenyl)methane (**2b**) with either copper or silver gave **1** in near-quantitative yields—indeed, the yields calculated from the published[27] absorptivity were 107–109%, implying that the published absorptivity was too low. The assumption that the yield of **1** was quantitative in these cases[35] implied that the molar absorptivity of **1** in toluene was really 825 ± 40 $M^{-1}\,cm^{-1}$, and this value was then used in calculating the yields shown in Table I.

A Beer's law plot of absorbance vs concentration of **1** in toluene (Figure 1) was linear from 0.1 to 1.0 absorbance unit, indicating **1** to be monomeric in concentrations below 0.002 M. A careful ESR study of substituted triphenylmethyl radicals published[36] during the course of our work found the ESR signal of a 0.01 M solution of **1** to be invariant over the temperature range −30 to 100 °C, as expected if **1** is monomeric.

Reactions of 1 with Metal Hydrides. The reaction of **1** with each of the hydrides in Table II gave tris(*p-tert*-butylphenyl)methane and the corresponding metal–metal dimer (eq 9). The dimers were the only organometallic products detectable by IR or visible spectroscopy for all L_nMH except $HRe(CO)_5$.

$$2L_nMH + 2Ar_3C^{\bullet} \rightarrow 2Ar_3CH + [L_nM]_2 \qquad (9)$$

The rate of each of these reactions was studied by mixing a toluene solution of **1** and a toluene solution of the hydride in a stopped-flow apparatus under anaerobic conditions. In most cases the reaction was monitored at 523 nm, the position of the absorbance due to the disappearing radical **1**. In some cases (e.g., $HFe(CO)_2Cp$, $HFe(CO)_2Cp^{*}$, $HMo(CO)_3Cp$, and $HMo(CO)_3Cp^{*}$) the product dimer absorbed strongly enough that the absorbance in the visible region increased during the reaction, and the rate was monitored at the wavelength of greatest absorbance change (shown in Table II).

In the presence of a sufficiently large (>10-fold) excess of hydride, *when the solution of **1** was free of unreduced **2a** or **2b***, these reactions obeyed first-order kinetics, with an observed pseudo-first-order rate constant k_{obs}. For each of the hydrides $HMn(CO)_5$, $H_2Os(CO)_4$, and $HMo(CO)_3Cp$, k_{obs} was measured at constant temperature over a 10-fold range in metal hydride concentration. The linearity of the resulting plots of k_{obs} versus $[HML_n]$ (the plot for $HMo(CO)_3Cp$ is shown as Figure 2) showed reaction 9 to be first order in HML_n. We thus established that reaction 9 obeyed the rate law in eq 10 for $HML_n = HMn(CO)_5$, $H_2Os(CO)_4$, and $HMo(CO)_3Cp$. We expected that eq 10 would also hold for the remaining hydrides in Table II and, as a check, determined k_H for each of them at two or more significantly different hydride concentrations; an equivalent result was always obtained.[37]

$$-d[Ar_3C^{\bullet}]/dt = k_H[L_nMH][Ar_3C^{\bullet}] \qquad (10)$$

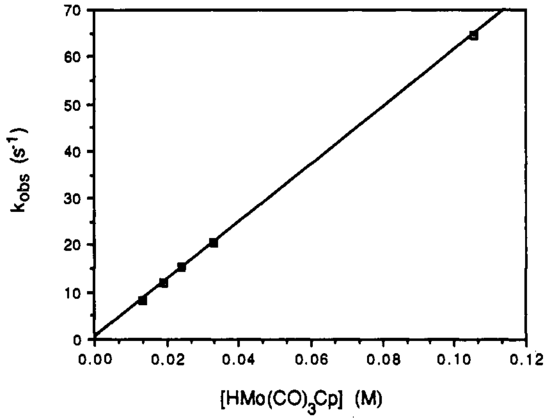

Figure 2. Plot of k_{obs} at 30 °C vs concentration of $HMo(CO)_3Cp$.

The simplest mechanism consistent with this rate law involves rate-determining $H^{\bullet}$ transfer to form metal-centered radicals **3** (eq 11, with rate constant k_H) followed by fast and irreversible dimerization of **3** to form the product **4** (eq 12).

$$L_nMH + Ar_3C^{\bullet} \xrightarrow{k_H} Ar_3CH + \underset{\mathbf{3}}{L_nM^{\bullet}} \qquad (11)$$

$$\underset{\mathbf{3}}{2L_nM^{\bullet}} \xrightarrow{\text{fast}} \underset{\mathbf{4}}{[L_nM]_2} \qquad (12)$$

Known rate constants confirm that the dimerization in eq 12 can be very fast. For example, the dimerization rate constant for $^{\bullet}Mo(CO)_3Cp$ is $3 \times 10^9\ M^{-1}\,s^{-1}$ at 293 K in acetonitrile[38] and that for $^{\bullet}Mn(CO)_5$ is $9.5 \times 10^8\ M^{-1}\,s^{-1}$ at 295 K in *n*-hexane.[39] Substituted metalloradicals dimerize more slowly; the $^{\bullet}Mn(CO)_4PPh_3$ rate constant is $1 \times 10^7\ M^{-1}\,s^{-1}$ at 298 K in *n*-hexane.[40]

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(34) (Triphenylmethyl)lithium in THF has λ_{max} at 502 nm: Gronert, S.; Streitweiser, A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2843.

(35) $H^{\bullet}$ transfer reactions that had previously shown departures from pseudo-first-order behavior caused by residual **2a** (see next section) were repeated with the radical generated from **2b** and no departures from first-order kinetics (in particular, no initial regions where the net rate of radical disappearance was slower than that predicted by first-order kinetics) were observed. This implies a yield of **1** from **2b** of at least 95%.

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(37) This procedure alleviated our concern that some of the more sensitive hydrides such as $HCr(CO)_3Cp$ and $HFe(CO)_2Cp$ might have been decomposing under the reaction conditions; decomposition would have been expected to lead to inconsistent second-order rate constants.

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The speed of reaction 12 is part of the reason why the dimers **4** are the exclusive product of reaction 9. One might also expect the formation of $Ar_3C{-}ML_n$, by analogy to the formation of $Ar_3C{-}SR$ (eq 14) when trityl radicals like **1** are used to study H• abstraction from thiols.[18,27] (Trityl radicals $Ar_3C^\bullet$ react with thiols HSR by the mechanism in eqs 13 and 14, giving the overall reaction shown in eq 15.)

$$Ar_3C^\bullet + PhSH \xrightarrow{k_H} Ar_3CH + PhS^\bullet \qquad (13)$$

$$Ar_3C^\bullet + PhS^\bullet \xrightarrow{\text{fast}} Ar_3C{-}SPh \qquad (14)$$

$$\text{net:}\ 2Ar_3C^\bullet + PhSH \rightarrow Ar_3C{-}SPh + Ar_3CH \qquad (15)$$

However, a single bond between $Ar_3C^\bullet$ (**1**) and a transition metal is unlikely to be stable at the temperatures involved in our $Ar_3C^\bullet$/HM reactions. If we estimate the comparative stability of the $Ph_3C^\bullet$ and $PhCH_2^\bullet$ radicals by the difference (7 kcal/mol) between the $Ph_3C{-}H$ bond strength[19] and the $PhCH_2{-}H$ bond strength[41] and apply that figure to the known[16] benzyl-$Mn(CO)_5$ bond strength (only 25–30 kcal/mol), we predict an $Ar_3C{-}M$ bond strength of 18–23 kcal/mol—and there should be additional steric destabilization (Ar_3C will interact more strongly than $PhCH_2$ with other ligands). $Ar_3C{-}ML_n$ probably forms during our $Ar_3C^\bullet$/HM reactions but immediately dissociates. Only with $HRe(CO)_5$ have we seen a byproduct that may have arisen from interaction between **1** and $L_nM^\bullet$.[42]

$HCo(CO)_4$. The decomposition of $HCo(CO)_4$ to $Co_2(CO)_8$ (reaction 16) is autocatalytic in nonpolar solvents[43] because it is catalyzed by the cobalt metalloradicals $^\bullet Co(CO)_4$ that arise from $Co_2(CO)_8$ (reaction 17). One would thus expect the generation

$$2HCo(CO)_4 \rightarrow H_2 + Co_2(CO)_8 \qquad (16)$$

$$Co_2(CO)_8 \rightleftharpoons 2Co(CO)_4^\bullet \qquad (17)$$

of cobalt metalloradicals $^\bullet Co(CO)_4$ in reaction 11 to exacerbate the normal instability of $HCo(CO)_4$. We were nevertheless able to obtain acceptable first-order decay curves and reasonably accurate k_{obs} measurements for reaction 11 with excess $HCo(CO)_4$ at −35 °C[44] in toluene. These k_{obs} values allowed us to estimate the k_H of $HCo(CO)_4$ at this temperature as $90 \pm 30\ M^{-1}\ s^{-1}$ (with the uncertainty arising from the uncertainty in $[HCo(CO)_4]$ after the solutions had reached the mixing chamber).

$HCr(CO)_3Cp$. Although the decrease in absorbance when the reaction between **1** and $HCr(CO)_3Cp$ in toluene is monitored at 523 nm is approximately exponential, nonexponential behavior is expected because the chromium dimer **4Cr** does not form irreversibly but is rather in equilibrium (eq 18) with the corresponding monomer **3Cr**.[45] The fraction of the chromium product that is in the form of the dimer **4Cr** (eq 19) will vary with the extent of the H• transfer reaction if equilibrium 18 is rapidly maintained. At an initial [**1**] of 6.25×10^{-4} M this fraction can be calculated from the known equilibrium constant[45] as 0.61 at 10% reaction and 0.85 at 100% reaction. The average absorptivity of the product will thus change during the reaction *at any wavelength where there is a significant difference between the absorptivity of the dimer **4Cr** and twice the absorptivity of the monomer **3Cr***. The total absorbance A at this wavelength will *not* be a linear function of [**1**] and the product concentration,[46] and A will not fall to A_∞ exponentially with time.

$$\underset{\mathbf{4Cr}}{[Cr(CO)_3Cp]_2} \overset{K_{eq}}{\rightleftharpoons} \underset{\mathbf{3Cr}}{2{\cdot}Cr(CO)_3Cp} \qquad (18)$$

$$\text{fraction of chromium as dimer } (\mathbf{4Cr}) = \frac{2[\mathbf{4Cr}]}{[\mathbf{3Cr}] + 2[\mathbf{4Cr}]} \qquad (19)$$

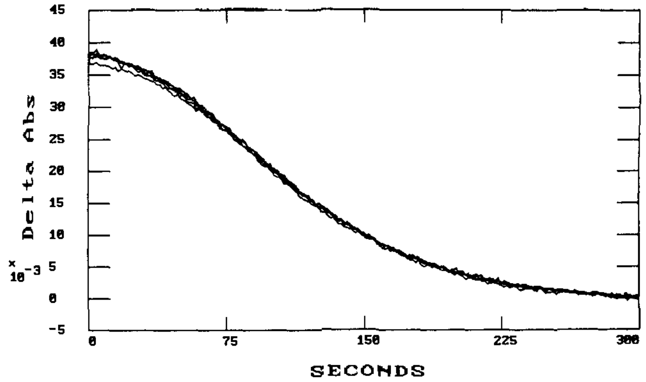

Figure 3. Stopped-flow traces for the reaction in toluene between impure tris(*p-tert*-butylphenyl)methyl radical (**1**) and $HMn(PEtPh_2)(CO)_4$ at 50 °C.

A small departure from exponential behavior was observed for the absorbance at 443 nm (~λ_{max} for the chromium dimer[45]) near the beginning of the reaction between a solution of **1** (6.25×10^{-4} M) and a solution of $HCr(CO)_3Cp$ (7.8×10^{-3} M). *At 523 nm* (λ_{max} of **1**) the correction is smaller. The observations of McLain[47] imply that the 523-nm absorptivity of the chromium monomer **3Cr** is negligible and that of the dimer **4Cr** is about 785 $M^{-1}\ cm^{-1}$.[48] The concentration of **4Cr**, and thus its absorbance can be calculated from K_{eq} and the total product present ([**3Cr**] + 2[**4Cr**]) at any given extent of reaction. The total absorbance due to ***1** and **4Cr*** as a function of time is given by eq 20 (where ϵ_R and ϵ_D are the molar absorptivities of **1** and **4Cr**, respectively, R_0 is the initial concentration of **1**, K_{eq} is the equilibrium constant for eq 18, and k is k_{obs}, the observed first-order rate constant for H• transfer from **1** to excess $HCr(CO)_3Cp$).

$$\text{abs}(t) = (\epsilon_R - \epsilon_D/2)R_0e^{-kt} - (\epsilon_D/16)\{\sqrt{K_{eq}^2 + 8K_{eq}R_0(1 - e^{-kt})} - \sqrt{K_{eq}^2 + 8K_{eq}R_0}\} \qquad (20)$$

Equation 20 was fitted to the 523-nm stopped-flow traces from the reaction of **1** with excess $HCr(CO)_3Cp$. We thus obtained accurate values of k_{obs} at temperatures from 0 to 50 °C. However, the k_{obs} values obtained from eq 20 varied by <4% from those obtained by fitting a simple exponential to the same stopped-flow traces.

Effect of the Presence of Unreduced 2a on the Reaction between 1 and Metal Hydrides. Our first stopped-flow traces for the reaction between **1** and excess $HMn(PEtPh_2)(CO)_4$ showed an induction period (Figure 3) in the decline of the 523-nm absorbance. Similar traces were obtained when reactions between **1** and $HW(CO)_3Cp$ were monitored at 523 nm. This anomalous behavior was traced to the presence of unreduced **2a** in solutions of **1**. $ClMn(PEtPh_2)(CO)_4$ and $ClW(CO)_3Cp$, respectively, were identified as byproducts (eq 21) when the same solutions were

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(40) Walker, H. W.; Herrick, R. S.; Olsen, R. J.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 3748.

(41) McMillen, D. F.; Golden, D. M. Hydrocarbon Bond Dissociation Energies. In *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(42) Under some circumstances the stoichiometric reaction of $HRe(CO)_5$ with **1** gave a small yield of a complex with carbonyl IR bands similar to those of the known $(\eta^3\text{-}Ph_3C)Re(CO)_4$ (see: Crocker, L. S.; Mattson, B. M.; Heinekey, D. M.; Schulte, G. K. *Inorg. Chem.* **1988**, *27*, 3722. Ugo, R.; Cenini, S.; Bonati, F. *Inorg. Chim. Acta* **1967**, *3*, 451).

(43) (a) Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494. (b) Clark, A. C.; Terapane, J. F.; Orchin, M. *J. Org. Chem.* **1974**, *39*, 2405. (c) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1969**, *20*, 205.

(44) This temperature is below the −20 °C reported for decomposition of neat $HCo(CO)_4$ (Clark, R. J.; Whiddon, S. E.; Serfass, R. E. *J. Organomet. Chem.* **1968**, *11*, 637) and well below the solution decomposition temperature of 0 °C (Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *182*, 299).

(45) McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643.

(46) (a) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 22–23. (b) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanisms: A Study of Homogeneous Chemical Reactions*, 3rd ed.; Wiley: New York, 1981; pp 38–40.

(47) McLain, S. J., personal communication of unpublished details of the work in ref 45.

(48) The 523-nm absorbances at 5 and 25 °C of a solution containing a known amount of total chromium in a 1-cm cell[47] were used to calculate the molar absorptivities of **3Cr** and **4Cr**. The concentrations of **3Cr** and **4Cr** in the solution at these temperatures were calculated from the equilibrium constants[45] and the molar absorptivities were obtained by solving two simultaneous equations of the form $[\mathbf{3Cr}]\epsilon(\mathbf{3Cr}) + [\mathbf{4Cr}]\epsilon(\mathbf{4Cr})$ = absorbance.

$$\mathrm{HMn(L)(CO)_4 + Ar_3C^\bullet/Ar_3CCl \rightarrow ClMn(L)(CO)_4 + [Mn(L)(CO)_4]_2 + Ar_3CH} \quad (21)$$

$$\mathrm{L = PEtPh_2}$$

combined outside the stopped-flow spectrophotometer. Normal stopped-flow traces were obtained when these reactions were repeated with **1** generated from **2b**, and neither $BrMn(PEtPh_2)(CO)_4$ nor $BrW(CO)_3Cp$ could be detected as a byproduct.

Apparently the presence of unreduced **2a** adds reaction 22 to reactions 11 and 12. As it will be particularly easy for the Cl$^\bullet$ transfer in reaction 22 to compete when the dimerization of $L_nM^\bullet$

$$\underset{\mathbf{2a}}{\mathrm{Ar_3CCl}} + \underset{\mathbf{3}}{\mathrm{L}_n\mathrm{M}^\bullet} \rightarrow \mathrm{L}_n\mathrm{MCl} + \underset{\mathbf{1}}{\mathrm{Ar_3C}^\bullet} \quad (22)$$

(**3**) in eq 12 is inefficient, it is not surprising that the reactions of $HMn(PEtPh_2)(CO)_4$ are particularly sensitive to the presence of unreduced **2a**. (The dimerization of substituted $^\bullet Mn(CO)_4L$ is, as noted above, relatively slow.[40]) If reaction 22 occurs to the exclusion of reaction 12, all of the **1** consumed by reaction 11 is regenerated and the 523-nm absorbance does not decrease. Thus, if sufficient **2a** is present, reaction 22 initially dominates reaction 12 and the stopped-flow trace is flat; eventually reaction 22 consumes enough **2a** to reduce its own rate below that of eq 12, so that the **1** consumed by eq 11 is not regenerated and the 523-nm absorbance decreases.

Such Cl$^\bullet$ transfer reactions have been reported in other systems where $Ph_3C^\bullet$ abstracts H$^\bullet$ from transition-metal hydrides. Turaki and Huggins[23d] observed Cl$^\bullet$ transfer when they treated $HW(CO)_3Cp$ with $Ph_3C^\bullet$ in the presence of PPh_3 and excess Ph_3CCl (eq 7). Drake and Baird[23a] observed eq 23 along with eq 4 when they treated $HMo(CO)_2(PPh_3)Cp$ with $Ph_3C^\bullet$ that contained unreduced Ph_3CCl.

$$\mathrm{HMn(L)(CO)_4 + Ar_3C^\bullet/Ar_3CCl \rightarrow ClMn(L)(CO)_4 + [Mn(L)(CO)_4]_2 + Ar_3CH} \quad (23)$$

$$\mathrm{L = PPh_3}$$

Temperature Dependence of k_H. Values of k_H were measured over at least a 30 °C temperature range (shown in Table II) for all hydrides other than $HCo(CO)_4$. The activation parameters and the value of k_H at 25 °C were calculated from the measured values of k_H according to the Eyring equation. For all but three of the hydrides, 25 °C was within the temperature range in which measurements were made; the 25 °C k_H value for $HFe(CO)_2Cp$ was extrapolated from lower temperatures, whereas the 25 °C k_H values for $HMo(CO)_3Cp^*$ and $H_2Os(CO)_4$ were extrapolated from higher temperatures.

The range spanned by the above $\Delta S^\ddagger$ values, between −21 and −28 eu, was used to estimate a 25 °C k_H value for $HCo(CO)_4$ from the value measured at −35 °C. The result (between 680 and 2440 $M^{-1}\ s^{-1}$) is given in Table II as 1600 ± 900 $M^{-1}\ s^{-1}$.

Effect of Solvent on k_H. The reaction of **1** with an excess of $HCr(CO)_3Cp$ was observed in THF as well as in toluene. For each run k_{obs} was obtained by fitting an exponential to the decline in absorbance at 523 nm and used to determine the value of k_H. Over a 60 °C temperature range in THF these k_H values gave a $\Delta H^\ddagger$ of 6.30 (7) kcal/mol, a $\Delta S^\ddagger$ of −26.7 (3) eu, and a k_H at 25 °C of 222 (2) $M^{-1}\ s^{-1}$; the corresponding toluene results, determined in the same way over a range of 50 °C, were a $\Delta H^\ddagger$ of 5.75 (5) kcal/mol, a $\Delta S^\ddagger$ of −27.7 (2) eu, and a k_H at 25 °C of 335 (2) $M^{-1}\ s^{-1}$.

Discussion

The similarity between the k_H values and activation parameters measured for $HCr(CO)_3Cp$ in THF and those measured in toluene implies that the transition state for reaction 9 is uncharged. This result is consistent with our belief that the rate-determining step in the mechanism of reaction 9 is the hydrogen atom transfer in reaction 11 rather than a proton or electron transfer. If the transition state were charged a much larger solvent effect would be expected: the reaction between Cp_2ZrMe_2 and $HCr(CO)_3Cp$ involves rate-determining proton transfer and is over two orders of magnitude faster in CH_3CN than in THF.[2b]

Comparison of the rate constants k_H with the thermodynamic driving force for these H$^\bullet$ transfer reactions requires the use of a single set of M–H bond strengths. The values of Tilset and Parker[12] are quoted in Table II, as their method has provided bond strengths for the greatest number of transition-metal hydrides. They have used eq 24 to obtain the M–H bond dissociation enthalpy (BDE) in acetonitrile from the pK_a value of M–H and the reversible potential (relative to the hydrogen electrode) for the oxidation of M$^-$ in the same solvent. The relevant thermodynamic cycle[49–52] is given in Scheme I.

$$\mathrm{BDE} = 1.37\mathrm{p}K_a + 23.06E^\circ_{ox}\,(\mathrm{M}^-) + 58.3 \quad (24)$$

Scheme I. Thermodynamic Cycle for Bond Strength Determination in Solution

$$\mathrm{M{-}H_{(sol)} \rightleftharpoons M^-_{(sol)} + H^+_{(sol)}} \quad \text{(i)}$$

$$\mathrm{M^-_{(sol)} \rightleftharpoons M^\bullet_{(sol)} + e^-} \quad \text{(ii)}$$

$$\mathrm{H^+_{(sol)} + e^- \rightleftharpoons 0.5H_{2(g)}} \quad \text{(iii)}$$

$$\mathrm{0.5H_{2(g)} \rightleftharpoons H^\bullet_{(g)}} \quad \text{(iv)}$$

$$\mathrm{H^\bullet_{(g)} \rightleftharpoons H^\bullet_{(sol)}} \quad \text{(v)}$$

$$\mathrm{M{-}H_{(sol)} \rightleftharpoons M^\bullet_{(sol)} + H^\bullet_{(sol)}}$$

Unfortunately there is some uncertainty about the accuracy of the bond strengths calculated by eq 24.[13] Several values so calculated exceed by ~4 kcal/mol the upper limits[53] imposed by the $\Delta H^\ddagger$ values for H$^\bullet$ transfer from the same hydrides to conjugated olefins.[10] Furthermore, the eq 24 value for $H{-}Mo(CO)_3Cp$ is greater than the calorimetrically determined strength of this bond.[54]

Other results in the literature are more consistent with the exact M–H bond strengths calculated by eq 24. Two recent calorimetric determinations of the $H{-}Cr(CO)_3Cp$ BDE that should be exceptionally accurate[55,56] have given values almost identical with that obtained from eq 24. Furthermore, the observation that H$^\bullet$ is abstracted from Bu_3SnH by $^\bullet Re(CO)_5$[57] is consistent with the exact $H{-}Re(CO)_5$ BDE value given by eq 24 (75 kcal/mol, compared to 73.7 for $Bu_3Sn{-}H$[58]), whereas it would be inconsistent with a lower $H{-}Re(CO)_5$ BDE.

In any case no bond strengths other than those calculated from eq 24 are available for enough transition-metal hydrides to be of use in analyzing the H$^\bullet$ transfer rate constants in Table II. These bond strengths vary over a range of 20 kcal/mol and imply that

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(49) Similar cycles for carbon acids were first written by Breslow[50] and refined by Nicholas and Arnold.[51] They have been used by Bordwell and co-workers[19] to obtain C–H bond strengths in DMSO that agree well with known gas-phase C–H BDE values, although a more recent publication from the same group[52] has suggested that this agreement may have resulted from the fortuitous cancellation of errors.

(50) Breslow, R.; Balasubramanian, K. *J. Am. Chem. Soc.* **1969**, *91*, 5182. Also see subsequent papers in the series.

(51) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

(52) Bordwell, F. G.; Harrelson, J. A., Jr.; Satish, A. V. *J. Org. Chem.* **1989**, *54*, 3101.

(53) These upper limits have been calculated by Tilset and Parker[12] according to a suggestion by Halpern.

(54) Hoff and co-workers have obtained the same result (66 kcal/mol) for the $H{-}Mo(CO)_3Cp$ BDE in three different ways.[11a–c]

(55) Hoff has obtained 61 kcal/mol from the heat of hydrogenation of the chromium dimer, $[CpCr(CO)_3]_2$,[11c,56] and 61.5 kcal/mol from the heat of hydrogenation of $[Cp^*Cr(CO)_3]_2$ combined with the measured ΔH for H$^\bullet$ transfer to $^\bullet Cr(CO)_3Cp$ from $H{-}Cr(CO)_3Cp^*$.[56] Both determinations use Cr–Cr bond strengths derived from *directly measured* monomer/dimer equilibrium constants.[45,56]

(56) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Roper, G. C. *J. Am. Chem. Soc.* **1990**, *112*, 5657.

(57) Hanckel, J. M.; Lee, K. W.; Rushman, P.; Brown, T. L. *Inorg. Chem.* **1986**, *25*, 1852.

(58) Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218.

ΔG for reaction 11 varies over the same range. The range of k_H values in Table II, while over 10^4, is small enough to show that ΔG^* varies much less than ΔG.

These results for $H^\bullet$ transfer to **1** in toluene are to some extent comparable with our previous results for H^+ transfer to aniline in CH_3CN: the range of ΔG^* values for the H^+ transfer reactions is also substantially less than the range of ΔG values.[2b] However, the relationship between individual rate constants and the thermodynamic driving force is quite different for these two types of transfer reaction. The rate constants for H^+ transfer to aniline correlate well with the thermodynamic acidities of the metal hydrides—the rate of H^+ transfer is mainly a function of the thermodynamic driving force. In contrast, the rate constants for $H^\bullet$ transfer to **1** are not *solely* determined by the strength of the M–H bond being broken; the results in Table II show that steric effects are also important. Replacement of a Cp by the bulkier Cp* has a negligible effect (~1 kcal/mol) on the M–H bond strength in $HMo(CO)_3Cp$ but causes an approximately 40-fold decrease in k_H.

An estimate of the influence of thermodynamic driving force on k_H can be obtained by comparing the k_H value for $HMo(CO)_3Cp$ with that for $HW(CO)_3Cp$. The steric difference between these compounds should be negligible since the covalent radii of W and Mo (1.50 and 1.51 Å, respectively) are identical within experimental error.[59] The 3-kcal/mol increase in M–H bond strength from Mo to W produces a decrease in k_H from 514 to 91.9 $M^{-1}\,s^{-1}$. These numbers imply a value of about 0.30 for the Brønsted coefficient α in eq 25. Although α is not well-determined because of the uncertainty in the bond strengths, this value is consistent with the prediction of Marcus theory[60] (the second part of eq 25) that α should be <0.5 for an exothermic reaction.

$$\alpha = \frac{\delta\Delta G^*}{\delta\Delta G^0} \approx \frac{d\Delta G^*}{d\Delta G^0} = \frac{1}{2} + \frac{\Delta G^0}{8\Delta G_0^*} \qquad (25)$$

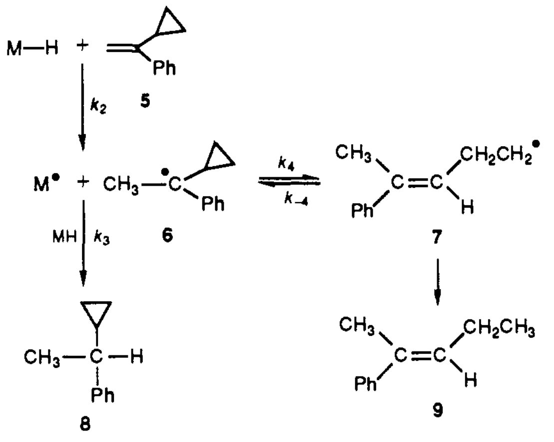
It is noteworthy that k_H for $HCr(CO)_3Cp$ is intermediate between the values for $HMo(CO)_3Cp$ and $HW(CO)_3Cp$ even though the H–Cr bond is considerably weaker than either the H–Mo bond or the H–W bond. The explanation must lie in the length of the H–Cr bond, which must be about 0.2 Å shorter than the H–Mo and H–W bonds.[61] Presumably the steric demands of the trityl radical **1** are so large that the rate of $H^\bullet$ transfer is adversely affected by the shorter H–M bond length.

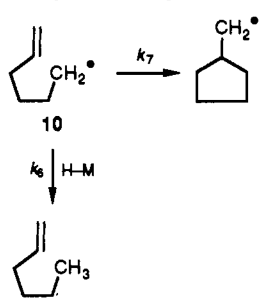
However, the same effect is not observed for iron and ruthenium. $HFe(CO)_2Cp$ reacts with **1** more rapidly than does $HRu(CO)_2Cp$ (Table II), although the H–Fe bond is presumably shorter than the H–Ru bond. The fact that $HFe(CO)_2Cp$ has fewer CO ligands than $HCr(CO)_3Cp$ may make it less sensitive to steric effects.

It is instructive to compare our relative k_H values with the relative $H^\bullet$ transfer rate constants found in two other studies of transition-metal hydrides. Bullock and Samsel[14] have studied the reaction of transition-metal hydrides with α-cyclopropylstyrene and have established the mechanism in Scheme II. The first $H^\bullet$ transfer, to α-cyclopropylstyrene (**5**) to form the methylphenylcyclopropylcarbinyl radical (**6**), is endothermic and rate-determining, and values of the rate constant k_2 have been determined from the overall reaction rate with various hydrides. The second $H^\bullet$ transfer, to the radical **6**, is exothermic and relatively rapid, but values of k_3 relative to k_4 (the rate constant for the rearrangement) have been determined for some hydrides by radical clock techniques.

Franz, Linehan, Alnajjar, and Hicks have measured the $H^\bullet$ transfer rate constants of $CpMo(CO)_3H$ and $Cp^*Mo(CO)_3H$ toward the primary hex-5-enyl radical (**10**).[62] They have generated this radical from two precursors at several temperatures, determined k_6 (eq 26) relative to the rearrangement rate constant k_7 at each temperature, and thus obtained absolute values of k_6 for $CpMo(CO)_3H$ and $Cp^*Mo(CO)_3H$ over a temperature range.

Scheme II





(26)

It is surprising that $HRu(CO)_2Cp$ is unreactive toward α-cyclopropylstyrene (**5**).[14] The k_H value for $HRu(CO)_2Cp$ in Table II is larger than that for any hydride except $HFe(CO)_2Cp$ and $HCo(CO)_4$, and hydrides with relatively low k_H values such as $HMn(CO)_5$, $HMo(CO)_3Cp$, $HW(CO)_3Cp$, $HMo(CO)_3Cp^*$, and $HMn(CO)_4L$ *do* react with **5**.[14]

Because the H–Mo bond strengths in $HMo(CO)_3Cp$ and $HMo(CO)_3Cp^*$ are essentially equal, we would expect them to transfer $H^\bullet$ at similar rates in a reversible process. Thus $\Delta\Delta G^*$ for k_2 between these two hydrides and α-cyclopropylstyrene (**5**) is only 0.2 kcal/mol at 60 °C (the only temperature at which k_2 is known for both hydrides) because the k_2 step in Scheme II occurs by reversible $H^\bullet$ transfer within a radical cage.[14,63] However, the relative reactivity of any *irreversible* $H^\bullet$ acceptor toward $HMo(CO)_3Cp$ and $HMo(CO)_3Cp^*$ measures the *steric* selectivity of that acceptor. For the trityl radical **1**, the methylphenylcyclopropylcarbinyl radical **6**, and the hex-5-enyl radical **10**, $HMo(CO)_3Cp/HMo(CO)_3Cp^*$ $\Delta\Delta G^*$ values can be calculated at 60 °C (the only temperature at which k_3 is known for both hydrides). As we would predict, $\Delta\Delta G^*$ for the crowded **1** (2.2 kcal/mol from the data in Table II) is much more than $\Delta\Delta G^*$ for **10** (0.4 kcal/mol[62]). More surprisingly, $\Delta\Delta G^*$ for **6**, 2.1 kcal/mol,[14] is as large as that for **1**; a possible reason is the perpendicular orientation that the cyclopropyl substituent in **6** will adopt if it stabilizes the radical center.[64]

The relative reactivity of any of these $H^\bullet$ acceptors toward the sterically equivalent $HMo(CO)_3Cp$ and $HW(CO)_3Cp$ measures

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[59] Calculated from the interatomic distances in the $CpM(CO)_3Cl$ complexes: Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197.

[60] Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. Cohen, A. O.; Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 4249. Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475. Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227.

[61] The covalent radius of Cr calculated from $(CpCr(CO)_3)_2SnCl_2$ (Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1975**, 230) is 1.30 Å, which is about 0.20 Å shorter than the corresponding covalent radii of Mo and W.[59]

[62] Franz, J. A.; Linehan, J. C.; Alnajjar, M. S.; Hicks, K. W., submitted for publication; see footnote 29 in: Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 268.

[63] The rate constant k_2 is proportional to the equilibrium constant for the reversible $H^\bullet$ transfer and thus depends only on the strength of the H–M bond being broken.[13]

[64] Because cyclopropyl substituents stabilize carbocations it is reasonable to expect them to stabilize radicals as well; see footnote 52 in ref 13 above. However, Franz, Bushaw, and Alnajjar (ref 62 above) and Newcomb and Glenn (Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275) have argued to the contrary; see also footnote 47 in ref 14 above.

the selectivity of that acceptor toward differences in bond strength. As we would expect, the selectivity of these $\mathrm{H}^\bullet$ transfer reactions decreases as they become more exothermic, and $\Delta\Delta G^\ddagger$ decreases as our $\mathrm{H}^\bullet$ acceptor changes from the olefin **5** to the trityl radical **1** to the benzyl radical **6**.[65] At 100 °C (the only temperature at which k_2 and k_3 are known for both the Mo hydride and the W hydride) the $\mathrm{HMo(CO)_3Cp/HW(CO)_3Cp}$ $\Delta\Delta G^\ddagger$ is 2.8 kcal/mol for **5**,[14] 1.1 kcal/mol for **1** (Table II), and 0.9 kcal/mol for **6**.[14]

The overall pattern of the k_H values in Table II shows that the $\mathrm{H}^\bullet$ transfers in reaction 9 are substantially influenced by both bond strengths and steric factors. Such a pattern is not uncommon for atom transfer reactions, particularly those involving metalloradicals. Howes, Bakac, and Espenson[66] have found that there is only a rough correlation between log k and the C–Br bond strength when $\mathrm{Rh(dmgH)_2PPh_3}$ abstracts $\mathrm{Br}^\bullet$ from various alkyl bromides. Franz, Linehan, Alnajjar, and Hicks[62] have found that the rate of abstraction of $\mathrm{H}^\bullet$ from transition-metal hydrides by **10** is "determined primarily by steric effects".

It may be that the $\mathrm{H}^\bullet$ transfer reactions of transition-metal hydrides are more sensitive to steric effects than the H^+ transfer ones. H^+ transfer reactions are favored by a linear geometry, in contrast to hydride transfer reactions, which (at least from carbon) are known to be facilitated by a triangular transition state.[67] A simple rationalization is offered by the number of electrons involved: an H^+ transfer involves a four-electron, three-center transition state which prefers to be linear, whereas an H^- transfer involves a transition state with an inherently nonlinear two-electron, three-center bond. $\mathrm{H}^\bullet$ transfer transition states then involve three-electron, three-center bonding and thus, even if linear (a geometry that is known to favor $\mathrm{H}^\bullet$ transfer in organic systems[67]), may require closer approach of the donor and acceptor than H^+ transfer.

The data in Table II offer the first comparison of the $\mathrm{H}^\bullet$ transfer ability of the transition-metal hyrides toward a common radical, and thus should be useful in diagnosing $\mathrm{H}^\bullet$ transfer mechanisms in more complex reactions.

Experimental Section

General. The transition-metal hydrides were prepared under an inert ($\mathrm{N_2}$) atmosphere with use of high-vacuum, Schlenk, or inert-atmosphere-box techniques. Solutions of these hydrides and of the trityl radical **1** were introduced into the stopped-flow apparatus under an inert (Ar or $\mathrm{N_2}$) atmosphere. Manipulations involving **1** were carried out in red light.[68] Infrared (IR) spectra were recorded on a Perkin-Elmer 983 spectrometer with a 0.01-cm $\mathrm{CaF_2}$ solution cell. Ultraviolet and visible (UV-vis) spectra were recorded on a Perkin-Elmer Lambda 3B spectrometer with 2 mm or 10 mm cells. ^{1}H NMR spectra were recorded on a Bruker WP-200-SY, IBM WP-270-SY, or WP-300 spectrometer.

Stopped-Flow System. The stopped-flow experiments were performed at constant injection pressure (60 psi) on a Hi-Tech Scientific SF-41 Canterbury stopped flow with an SU-40 spectrophotometer unit. The SF-41 was modified for anaerobic use by isolating the flow circuit from the atmosphere: the foam buffer between the chamber containing the reservoir and drive syringes and the chamber containing the thermostating bath was caulked, along with the leads and wires between the two chambers; helium and a thermal conductivity leak detector were used to check for leaks. The thermostating bath for the flow circuit was filled with trimethylsiloxy-terminated polydimethylsiloxane (PS039 from Petrarch Systems) and the two chambers were purged independently with argon.

The monochromator of the SU-40 was calibrated with a didymium filter by locating the minima of the dark lines at 586 and 573 nm. The thermistor of the constant-temperature bath on the SF-41 was checked by comparison with two Sybron-Taylor calibrated thermometers and found to be accurate to ±0.1 °C. The photomultiplier tube output from the SF-41 was converted to digital form with an Analog Devices A/D converter and analyzed (on either an IBM PC-AT or Compaq 386S Deskpro computer) with software from On-Line Instrument Systems, Inc.

Solvents. Toluene, hexanes, tetrahydrofuran (THF), diethyl ether, and dimethoxyethane were distilled under nitrogen from purple solutions of sodium/benzophenone ketyl. Tetraglyme was distilled from $\mathrm{CaH_2}$ or sodium under high vacuum. Ethyl acetate was purified[69] and distilled under nitrogen from $\mathrm{P_4O_{10}}$.

Materials. The following compounds were prepared by literature methods: tris(*p-tert*-butylphenyl)methyl chloride (**2a**),[27] $\mathrm{HMo(CO)_3Cp^*}$,[70] $\mathrm{HMn(PEtPh_2)(CO)_4}$,[16] $\mathrm{HMn(CO)_5}$ and $\mathrm{HRe(CO)_5}$,[71] $\mathrm{H_2Os(CO)_4}$,[23b] $\mathrm{HFe(CO)_2Cp}$,[72] and $\mathrm{HFe(CO)_2Cp^*}$;[2a,73] $\mathrm{HFe(CO)_2Cp}$ was generated in situ by protonating the anion with HCl in toluene and quantified by adding $\mathrm{CCl_4}$ to the solution and isolating the resulting $\mathrm{CpFe(CO)_2Cl}$. $\mathrm{HM(CO)_3Cp}$ (where M = Cr, Mo, W) was prepared by protonating the corresponding anion[74] with trifluoroacetic acid and purified by sublimation. $\mathrm{HRu(CO)_2Cp}$[14] was generated by reducing $\mathrm{[Ru(CO)_2Cp]_2}$[75] to the anion with potassium containing a catalytic amount of biphenyl and protonating the potassium salt with less than 1 equiv of acetic acid; a toluene solution of the hydride was obtained by extraction and vacuum transfer.

The literature preparation[76] for $\mathrm{HCo(CO)_4}$ was modified by carrying out the disproportionation of $\mathrm{Co_2(CO)_8}$ in a mixture of tetraglyme and pyridine. After the excess pyridine was removed in vacuo the tetraglyme solution was frozen and an approximately 5-fold excess of sulfuric acid added. The solution was melted and the $\mathrm{HCo(CO)_4}$ evolved was condensed into a flask containing toluene. The resulting solution was used for $\mathrm{H}^\cdot$ transfer rate measurements. The concentration of $\mathrm{HCo(CO)_4}$ in it was determined by allowing an aliquot to dimerize and the resulting $\mathrm{Co_2(CO)_8}$ to disproportionate with excess $\mathrm{CH_3CN}$ under $\mathrm{N_2}$. The concentration of $\mathrm{[Co(CO)_4]^-}$ was then determined from its known[2a] IR absorptivity. The yield of $\mathrm{HCo(CO)_4}$ in the toluene solution was typically 40–60% of the theoretical maximum.

Tris(*p-tert*-butylphenyl)methyl bromide (**2b**) was prepared by the method reported[27] for **2a** with acetyl bromide substituted for acetyl chloride; the **2b** was recrystallized from *purified* ethyl acetate.

Tris(*p-tert*-butylphenyl)methyl Radical (1). Typically 30 mg of **2b**, 60 mg of copper powder,[77] and 25 mL of toluene were placed in a high-vacuum bulb and the mixture degassed by 3 freeze–pump–thaw cycles. The bulb was heated to 70 °C for 4 h while being protected from light and then allowed to cool before aliquots of **1** were removed by syringe. The concentration of **1** in the resulting toluene solution (typically corresponding, as shown in Table I, to a yield of 95–100%) was determined by transferring an aliquot of solution to another bulb with a UV cell as a side arm, measuring the absorbance at 523 nm, and assuming ϵ_{523} to be 825 $\mathrm{M^{-1}\,cm^{-1}}$. Substitution of THF for toluene gave a solution that (if the ϵ_{523} of **1** was assumed not to vary between the two solvents) also contained a quantitative yield of **1**.

The use of molecular silver[27] with **2b** in toluene overnight at room temperature also gave quantitative yields of **1** (Table I). The treatment of **2a** with molecular silver according to the method of Lewis,[27] or with any of the other reductants shown in Table I, gave incomplete reduction and yields of **1** appreciably lower than those obtained from **2b**.

Stopped-Flow Experiments. The flow circuit was flushed with 50 mL of dry oxygen-free solvent prior to introducing the reagent solutions. The approximate wavelength of greatest absorbance change for the reaction was found from UV–vis spectra and determined more accurately on the stopped-flow itself. Typically the wavelength used was near 523 nm, the absorption peak for **1**. For all reactions the change in absorbance (ΔA) was in reasonable agreement with that expected from the difference in molar absorptivities between the reactants and the products.

In a typical experiment an approximate 2-mmol sample of **1** was prepared in 25 mL of solvent as described above and the concentration of **1** determined from the absorbance at 523 nm. One reservoir syringe was then filled with this solution and the other with a solution containing at least a 10-fold excess of the metal hydride. The average rate constant

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(65) ΔH for adding $\mathrm{H}^\cdot$ to α-methylstyrene is −46 kcal/mol,[13] to **1** is −81 kcal/mol,[19] and to the benzyl radical is −88 kcal/mol[41] (although ΔH for adding $\mathrm{H}^\cdot$ to the methylphenylcyclopropylcarbinyl radical **6** will be less exothermic than −88 kcal/mol because of the stabilizing effect of the methyl and cyclopropyl[64] substituents).

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at a given temperature was determined by averaging the rate constants from at least nine (typically over fifteen) injections. When the setting of the constant-temperature bath was changed, the system was allowed to equilibrate for 5–10 min before further data were collected.

Curve Fitting and Rate Constant Extrapolation. For all hydrides other than $HCr(CO)_3Cp$ the change in absorbance was a linear function of the extent of reaction and k_{obs} was obtained by a direct exponential fit to the data. However, for $HCr(CO)_3Cp$ the change in absorbance was not a linear function of the extent of reaction (vide supra) and it was necessary to obtain k_{obs} by fitting[78] eq 20 to the data. R_0 and k were the adjustable parameters, while K_{eq}, ϵ_R, and ϵ_D were set as constants. For all hydrides, the second-order rate constant, k_H, was obtained from the relation $k_H = k_{obs}/[MH]$ at each temperature. The activation parameters ΔH^* and ΔS^* were obtained from a linear fit of ΔG^* (calculated from the Eyring equation) versus T; the covariance of ΔH^* and ΔS^* was then equal to the covariance of the intercept and slope of the fitted line. These values of ΔH^* and ΔS^* were used to calculate k_H at 25 °C (Table II). The standard error of k_H at 25 °C was calculated from the standard errors and covariance of ΔH^* and ΔS^*.

Products from Reaction 9. Outside the stopped-flow, solutions of each metal hydride and **1** were mixed and the organometallic products characterized by IR and UV-vis spectroscopy. For all hydrides other than $HCr(CO)_3Cp$ (where an equilibrium mixture of the monomer **3Cr** and the dimer **4Cr**[45] was formed) and $HRe(CO)_5$[42] the corresponding metal–metal dimers were the only organometallic products seen: $Mn_2(CO)_{10}$,[79] $H_2Os_2(CO)_8$,[23b] $Mn_2(CO)_8(PEtPh_2)_2$,[80] $W_2(CO)_6Cp_2$,[81] $Mo_2(CO)_6Cp_2$,[82] $Mo_2(CO)_6Cp^*{}_2$,[83] $Fe_2(CO)_4Cp_2$,[84] $Fe_2(CO)_4Cp^*{}_2$,[84] and $Ru_2(CO)_4Cp_2$.[85] For the reaction between **1** and $HMo(CO)_3Cp$, tris(*p-tert*-butylphenyl)methane[27] and $Mo_2(CO)_6Cp_2$[82] were identified as the only products by ^1H NMR.

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Solvolysis of Allylic Isoprene Phosphorothioate Esters. A Mechanistic Study of the Thiono → Thiolo Rearrangement

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Abstract: The reactions of *O,O*-dimethyl *O*-geranyl phosphorothionate (**1-OPS(OMe)$_2$**), *O,O*-dimethyl *S*-geranyl phosphorothiolate (**1-SPO(OMe)$_2$**), and *O,O*-dimethyl *S*-linalyl phosphorothiolate (**2-SPO(OMe)$_2$**) were studied in 65:35 TFE/water. Solvolysis of **1-OPS(OMe)$_2$** at 20 °C gave substantial amounts of thiolo isomers **1-SPO(OMe)$_2$** and **2-SPO(OMe)$_2$**, along with smaller quantities of solvent addition products. At 40–65 °C, rearrangement of linalyl phosphorothiolate **2-SPO(OMe)** to geranyl phosphorothiolate **1-SPO(OMe)$_2$** and neryl phosphorothiolate **3-SPO(OMe)$_2$** was also accompanied by solvolysis. Phosphorothiolate **1-SPO(OMe)$_2$** reacted at 90–120 °C to give substitution products and **1-SPO$_2$(OMe)$^-$**, formed by hydrolysis of a methyl. The relative reactivities of **1-OPS(OMe)$_2$**, **1-SPO(OMe)$_2$**, and **2-SPO(OMe)$_2$** are $1:(3 \times 10^{-7}):(6 \times 10^{-3})$, respectively. From a combination of kinetic and trapping experiments, we estimate that **1-OPS(OMe)$_2$** is 11 kcal/mol less stable than its thiolo isomer. A dissociative mechanism with ion-paired intermediates is proposed for the thiono → thiolo rearrangements, and the utility of the phosphorothioate moiety as a tool for studying reactions involving ion pairs is discussed.

Phosphate esters and anhydrides fulfill a variety of biological roles in structure, binding, and reactivity that are indispensible. The mono-, di-, and triphosphate units found in numerous intermediary metabolites are excellent leaving groups, imparting the reactivity necessary for enzyme-catalyzed hydrolysis, esterification, nucleophilic displacement, condensation, fragmentation, and elimination reactions of biosynthesis and degradation.[1] At physiological pH, these moieties are negatively charged and, consequently, are relatively benign until sequestered within the catalytic site of an enzyme, where selective neutralization of negative charge can unleash their full reactivity. In contrast, the reactivities of leaving groups commonly encountered in organic chemistry, such as halides and sulfonate esters, cannot be attenuated in a comparable manner.

Substrates for enzyme-catalyzed electrophilic condensation, rearrangement, and cyclization reactions in the central part of the isoprene biosynthetic pathway are simple diphosphate esters.[2] The pathway contains numerous branch points, and at each, different enzymes transform a common substrate into a variety of products. Some prominent examples are the rearrangement of presqualene diphosphate to squalene or botryococcene[3] and the biosynthesis of numerous cyclic mono-,[4] sesqui-,[5] and diterpenes.[6] These reactions are thought to occur within enzyme-bound ion pairs consisting of the isoprene moiety of the substrate and inorganic pyrophosphate. In some cases, for example, the rearrangements of presqualene diphosphate, the precise structure of the ion pair is thought to play a critical role in the regiochemical

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