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Notes

Isotope Effects on Hydrogen Atom Transfer from Transition Metals to Carbon

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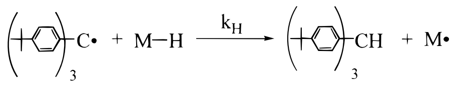
*Summary: The isotope effect for transfer of a hydrogen/deuterium atom from $HMn(CO)_5$/$DMn(CO)_5$ to the monomeric trityl radical $(p\text{-}{}^tBu\text{-}C_6H_4)_3C^\bullet$ (**1**) has been measured from −40 to +60 °C in toluene; the isotope effect for transfer from $H_2Os(CO)_4$/$D_2Os(CO)_4$ has been measured from 30 to 60 °C. Iterative kinetic simulation has been used to correct measured $D^\bullet$ rate constants for the effects of incomplete deuteration. The isotope effect k_H/k_D at 25 °C is 3.18(3) for $HMn(CO)_5$ and 4.3(3) for $H_2Os(CO)_4$. The larger isotope effect in the osmium case may be due to the difference in thermochemistry; the H−Os bond is stronger than the H−Mn one, and $H^\bullet$ transfer from $H_2Os(CO)_4$ to **1** is approximately thermoneutral and in that sense "symmetric".*

Introduction

There are two reasons for examining the isotope effects that accompany the hydrogen-atom-transfer reactions of transition-metal hydride complexes. One is the fact that a knowledge of isotope effects can help *diagnose* $H^\bullet$ transfer reactions;[1] the second is the information about these reactions that isotope effects can provide.

Some years ago we reported[2] the direct observation of $H^\bullet$ transfer from transition-metal hydride complexes to the stable organic radical **1**. Head-to-tail dimerization of **1** is prevented by its *p*-*tert*-butyl substituents,[3] and the disappearance of **1** in reaction 1 is easily monitored by following the disappearance of its band at 523 nm. Most metalloradicals $M^\bullet$ are rapidly consumed by dimerization to M−M.

We have now measured the H/D isotope effects for the $H^\bullet$ transfer reactions of two hydride complexes, one ($HMn(CO)_5$) with a relatively weak H−M bond and one ($H_2Os(CO)_4$) with a relatively strong H−M bond. In the first case the inorganic product is $Mn_2(CO)_{10}$;[4] in the second it is $H_2Os_2(CO)_8$.[2,5]



1 **2** (1)

Results and Discussion

$HMn(CO)_5$/$DMn(CO)_5$. $DMn(CO)_5$ was prepared straightforwardly from $[Mn(CO)_5]^-$ and D_3PO_4. Careful integration of ^1H NMR spectra with hexamethyldisilazane as internal standard showed it to contain 4.6% $HMn(CO)_5$.

The $k_H{}^{Mn}$ values (collected in the Supporting Information, Table S-1) were obtained straightforwardly by monitoring the disappearance of **1** in toluene in the presence of at least a 10-fold excess of $HMn(CO)_5$; they agree well with the values previously reported.[2] The $k_D{}^{Mn}$ values (also in the Supporting Information, Table S-2) were obtained from runs in the presence of at least a 10-fold excess of $DMn(CO)_5$. Under these conditions $[HMn(CO)_5] \approx [\mathbf{1}]$ and $[HMn(CO)_5]$ varied appreciably during a run, so $k_D{}^{Mn}$ was obtained from kinetic simulations; using the known $k_H{}^{Mn}$ and the initial values of $[DMn(CO)_5]$ and $[HMn(CO)_5]$, $k_D{}^{Mn}$ was varied until the calculated time dependence of [**1**] best agreed with that observed.

$$\mathbf{1} + H{-}Mn(CO)_5 \xrightarrow{k_H{}^{Mn}} \mathbf{2} + {}^\bullet Mn(CO)_5 \qquad (2)$$

$$\mathbf{1} + D{-}Mn(CO)_5 \xrightarrow{k_D{}^{Mn}} \mathbf{2}\text{-}d + {}^\bullet Mn(CO)_5 \qquad (3)$$

To improve the precision with which parameters were determined from the temperature dependence of $k_H{}^{Mn}$ and $k_D{}^{Mn}$, these rate constants (as shown in Figure 1) were determined between −40 and +60 °C. The concentrations of $HMn(CO)_5$ and $DMn(CO)_5$ were corrected

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(1) For example, H/D isotope effects have been used to establish atom transfer mechanisms. (a) Cobalt-catalyzed chain transfer: Gridnev, A. A.; Ittel, S. D.; Wayland, B. B.; Fryd, M. *Organometallics* **1996**, *15*, 5116−5126. (b) Binuclear platinum(II) photochemistry: Vlcek, A.; Gray, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 286−287.

(2) Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888−4895.

(3) Colle, K. S.; Glaspie, P. S.; Lewis, E. S. *J. Chem. Soc., Chem. Commun.* **1975**, 266. Dünnebacke, D.; Neumann, W. P.; Penenory, A.; Stewan, U. *Chem. Ber.* **1989**. *122*, 533.

(4) The dimerization of ${}^\bullet Mn(CO)_5$ is almost diffusion-controlled: 9.5×10^8 M^{-1} s^{-1} at 295 K in hexane. Wegman, R. W.; Olsen, R. J.; Gard, D. R.; Faulkner, L. R.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6089.

(5) Edidin, R. T.; Hennessy, K. M.; Moody, A. E.; Okrasinski, S. J.; Norton, J. R. *New J. Chem.* **1988**, *12*, 475.

10.1021/om980917v CCC: $18.00

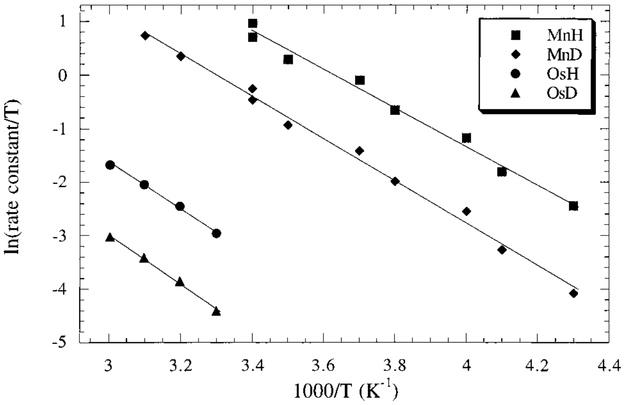

Figure 1. Eyring plots for the $H^\bullet$ ($D^\bullet$) transfer from M−H to **1** in toluene.

Table 1. Isotope Effects and Activation Parameters for Transfer of H and D from Mn to 1 in Toluene

	$HMn(CO)_5$	$DMn(CO)_5$	comparative
k^{Mn}(298 K) (M^{-1} s^{-1})	740(7)[a]	232(4)[b]	$k_H^{Mn}/k_D^{Mn} = 3.18(3)$
E_a (kcal/mol)	7.57(4)	8.43(6)	$\Delta E_a(D) - \Delta E_a(H) = 0.86(7)$
A (M^{-1} s^{-1})	$[2.6(2)] \times 10^8$	$[3.6(5)] \times 10^8$	$A_H/A_D = 0.7(1)$
$\Delta H^\ddagger$ (kcal/mol)	7.02(4)	7.90(7)	$\Delta H^\ddagger(D) - \Delta H^\ddagger(H) = 0.87(9)$
$\Delta S^\ddagger$ (eu)	−21.8(2)	−21.2(3)	$\Delta S^\ddagger(D) - \Delta S^\ddagger(H) = 0.6(3)$

[a] Interpolated rate constant from the activation parameters. [b] Rate constant from kinetic simulation (see Experimental Section).

for the change in density of toluene with temperature.[6] The activation parameters (and the isotope effect k_H^{Mn}/k_D^{Mn} at 25 °C) obtained from the temperature dependence of k_H^{Mn} and k_D^{Mn} are given in Table 1.

The results agree well with those expected for a simple $H^\bullet$ transfer reaction without tunneling.[7−9] In particular, $A_H \approx A_D$. Kwart has stated that "[For] a symmetrical TS of linear H transfer between the reaction centers X and Y...in which the restoring forces on both sides of the hydrogen...are equal or nearly so...the value of A_H/A_D...varies narrowly between the limits of $0.7-2^{1/2}$."[10] Bell has stated that "The ratio of the [semiclassical, i.e., without tunneling] Arrhenius pre-exponential factors...should always lie between 0.7 and 1.2...and will usually be much closer to unity."[11] Furthermore, the activation energy difference in Table 1, $E_a^D - E_a^H = 0.86(7)$ kcal/mol, is statistically indistinguishable from the zero-point energy difference between the H−Mn and D-Mn bonds. The reported[12] ν_{MH} band of $HMn(CO)_5$ appears at 1775 cm^{-1}, and the ν_{MD} band of $DMn(CO)_5$ is at 1285 cm^{-1}, implying a difference in zero-point energies of 0.7 kcal/mol.

$H_2Os(CO)_4$/$D_2Os(CO)_4$. $D_2Os(CO)_4$ was prepared straightforwardly from $Na_2[Os(CO)_4]$ and D_3PO_4. Integration of ^1H NMR spectra with hexamethyldisiloxane as internal standard showed it to have 7.2% residual protons.

The k_H^{Os} values (collected in the Supporting Information, Table S-3) were obtained straightforwardly by monitoring the disappearance of **1** in toluene in the presence of at least a 10-fold excess of $H_2Os(CO)_4$; they agree well with the values previously reported.[2] The k_D^{Os} values at the same temperatures (also in Table S-3 in the Supporting Information) were obtained from runs in the presence of at least a 10-fold excess of $D_2Os(CO)_4$. Under these conditions—as in the $DMn(CO)_5$ measurements described above—the concentration of residual H was ∼[**1**] and varied appreciably during a run. Thus, k_D^{Os} in the osmium case was also obtained from kinetic simulations, although the presence of two equivalent H/D ligand sites on osmium made the situation more complex than in the manganese case: in principle eqs 4−7 should all have different rate constants.

$$\mathbf{1} + \text{H−Os(H)(CO)}_4 \xrightarrow{k_H^{Os}} \mathbf{2} + {}^\bullet\text{Os(H)(CO)}_4 \tag{4}$$

$$\mathbf{1} + \text{H−Os(D)(CO)}_4 \xrightarrow{k_H^{Os}} \mathbf{2} + {}^\bullet\text{Os(D)(CO)}_4 \tag{5}$$

$$\mathbf{1} + \text{D−Os(H)(CO)}_4 \xrightarrow{k_D^{Os}} \mathbf{2}\text{-}d + {}^\bullet\text{Os(H)(CO)}_4 \tag{6}$$

$$\mathbf{1} + \text{D−Os(D)(CO)}_4 \xrightarrow{k_D^{Os}} \mathbf{2}\text{-}d + {}^\bullet\text{Os(D)(CO)}_4 \tag{7}$$

The only way of estimating k_H^{Os} in eq 5 was to neglect secondary isotope effects and to assume that *all H−Os bonds* are *equally reactive*, i.e., that k_H^{Os} for eq 5 will be the same as the k_H^{Os} value determined in the previous experiments for eq 4. Similarly, given the precision of the available data, we could not fit individual rate constants for eqs 6 and 7; we had to assume that *all D−Os bonds* are *equally reactive*, i.e., that k_D^{Os} for eq 7 will be the same as k_D^{Os} for eq 6. Thus, using the known k_H^{Os} and the initial concentrations of $D_2Os(CO)_4$ and residual H, k_D^{Os} could be obtained as the value that gave the best simulation of the observed time dependence of [**1**] from eqs 4−7. Acceptable simulations (and values of k_D^{Os}) were only obtained over a limited temperature range, from 30 to 60 °C.

How valid is the assumption that secondary isotope effects can be neglected? These effects are derived from changes during the reaction in the frequencies of vibrational modes involving the spectator H/D.[13,14] A plausible vibrational model for ${}^\bullet Os(H)(CO)_4$ is $HIr(CO)_4$, for which a complete set of calculated vibrational spectra has just been reported.[15] There is little difference between the Os−H stretching frequencies in $H_2Os(CO)_4$ (experimentally 1971 and 1942 cm^{-1})[6,15] and the Ir−H

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(6) (a) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: New York, 1950; p 152. (b) Hammond, L. W.; Howard, K. S.; McAllister, R. A. *J. Phys. Chem.* **1958**, *62*, 637−639.

(7) Bullock, R. M. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 8.

(8) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 144−147, and earlier sections referenced therein.

(9) Isaacs, N. S. *Physical Organic Chemistry*; Longman/Wiley: New York, 1987; pp 271−272.

(10) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401−408.

(11) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: New York, 1980; p 98.

(12) Braterman, P. S.; Harrill, R. W.; Kaesz, H. D. *J. Am. Chem. Soc.* **1967**, *89*, 2851.

(13) McLennan, D. J. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: New York, 1987; Vol. 7, Chapter 6, pp 393−480.

(14) For the calculation of equilibrium isotope effects (a closely related subject) on the formation of hydride/deuteride complexes from H_2/D_2 see: Abu-Hasanayn, F.; Krogh−Jespersen, K.; Goldman, A. *J. Am. Chem. Soc.* **1993**, *115*, 8019−8023. For the calculation of equilibrium isotope effects on the formation of dihydrogen complexes see: Bender, B. R.; Kubas, G. J.; Jones, L. H.; Swanson, B. I.; Eckert, J.; Capps, K. B.; Hoff, C. D. *J. Am. Chem. Soc.* **1997**, *119*, 9179−9190.

(15) Jonas, V.; Thiel, W. *J. Chem. Phys.* **1996**, *105*, 3636−3648.

Table 2. Isotope Effects and Activation Parameters for Transfer of H and D from Os to 1 in Toluene

	$H_2Os(CO)_4$	$D_2Os(CO)_4$	comparative
k^{Os}(298 K) (M^{-1} s^{-1})	12.5(5)[a]	2.9(1)[b]	$k_H^{Os}/k_D^{Os} = 4.3(3)$
E_a (kcal/mol)	9.3(4)	9.9(4)	$\Delta E_a(D) - \Delta E_a(H) = 0.6(5)$
A (M^{-1} s^{-1})	$[7(3)] \times 10^7$	$[5(3)] \times 10^7$	$A_H/A_D = 1.6(8)$
$\Delta H^\ddagger$ (kcal/mol)	8.6(4)	9.3(4)	$\Delta H^\ddagger(D) - \Delta H^\ddagger(H) = 0.6(5)$
$\Delta S^\ddagger$ (eu)	−24(1)	−25(1)	$\Delta S^\ddagger(D) - \Delta S^\ddagger(H) = 1(2)$

[a] Interpolated rate constant from the activation parameters. [b] Rate constant from kinetic simulation (see experimental).

stretching frequency in $HIr(CO)_4$ (experimentally 1999 cm^{-1});[15,16] there is also little difference between the δ-(C−Os−H) bending frequencies in $H_2Os(CO)_4$ (796, 766, 736, and 694 cm^{-1})[15] and the δ(C−Ir−H) bending frequency in $HIr(CO)_4$ (788 cm^{-1}).[15] Thus, there should be little difference in the spectator H/D vibrational frequencies between $H_2Os(CO)_4$ and $^\bullet Os(H)(CO)_4$ or between $H_2Os(CO)_4$ and the transition state for $H^\bullet/D^\bullet$ transfer to **1**.

An upper limit for the secondary isotope effect in the $H_2Os(CO)_4$ system can be obtained from the secondary isotope effects in organic systems. (It seems reasonable to assume that the vibrational interaction between the two Os−H bonds in $H_2Os(CO)_4$ is less than that between two bonds to hydrogens on the same carbon.) At 25 °C the secondary isotope effect on the chlorination of methane is 1.05 per deuterium.[17] At 37 °C hydroxylation by cytochrome P450 of the methyl groups of *trans*-1-methyl-2-phenylcyclopropane proceeds with a secondary isotope effect of 1.26 per deuterium.[18]

The temperature dependence of k_H^{Os} (the rate constant for H−Os bonds) and of k_D^{Os} (the rate constant for D-Os bonds) is shown in Figure 1. The activation parameters obtained from the data in Figure 1 are given in Table 2. The activation parameter standard deviations given in Table 2 were obtained by normal statistical procedures; they are larger than in the $HMn(CO)_5$ case because of the limited temperature ranges available for $k_{H/D}^{Os}$. The extrapolated isotope effect k_H^{Os}/k_D^{Os} at 25 °C is also given in Table 2, with an uncertainty (±0.3) from the statistical analysis of its temperature dependence which is larger than the uncertainty (±0.2) estimated from the neglected secondary isotope effect.

It seems clear that the primary isotope effect on hydrogen atom abstraction from $H_2Os(CO)_4$ is larger than that from $HMn(CO)_5$. The precision of the activation parameters for $D^\bullet$ transfer from D-Os bonds does not permit the mechanism of atom transfer from H−Os and D−Os to be discussed with any confidence, but there is no evidence that tunneling is important.

The H−Os stretching vibration interacts with the carbonyl vibrations as well as with the other H−Os stretching mode. The stretching frequency of a vibrationally isolated H−Os bond can be estimated as 1951 cm^{-1}, the "H−Os" stretch of $HDOs(CO)_4$.[6] The ν(Os−D) value of a vibrationally isolated Os−D bond can be estimated[19] as 1418 cm^{-1}. The difference in zero-point energies between an H−Os bond and a D−Os one is thus 0.76 kcal/mol.

Comparison of the Mn and Os Isotope Effects. The $HMn(CO)_5/DMn(CO)_5$ zero-point energy difference (0.7 kcal/mol) implies a kinetic isotope effect k_H/k_D of 3.30 at 25 °C if we have a linear symmetric transition state, neglect any change in bending frequencies between the ground and transition states, and can thus apply eq 8.[8,20] Similarly the H−Os/D-Os zero-point energy difference (0.76 kcal/mol) implies a kinetic isotope effect k_H/k_D of 3.96 at 25 °C.

$$\frac{k_H}{k_D} = \exp\left(\frac{\Delta(\mathrm{ZPE})}{k_B T}\right) \tag{8}$$

$$\mathrm{ZPE} = \text{zero point energy}$$

The experimental H−Mn/D-Mn isotope effect in Table 1 is very close to the value just predicted. The (less precise) H−Os/D-Os isotope effect in Table 2 appears higher than the value predicted from eq 8, but it is not *significantly* higher.

It is not clear how much of the increased isotope effect in the osmium system is due to the more symmetric transition state to be expected in that case. The strength of the C−H bond formed as we go from **1** to **2** must be about 81 kcal/mol, the strength of the C−H bond in unsubstituted triphenylmethane.[21] The H−Mn bond in $HMn(CO)_5$ is only 68 kcal/mol,[22] so reaction 2 is *exothermic* by about 13 kcal/mol; in contrast, the H−Os bond in $H_2Os(CO)_4$ is about 78 kcal/mol,[23] so reactions 4 and 5 are approximately thermoneutral. The general expectation for such reactions[24] is that "the hydrogen isotope effect will increase to a maximum at the symmetric transition state".[25]

Thermodynamically comparable to reaction 2 is the transfer of $H^\bullet$ from Bu_3SnH to benzyl radicals (eq 9), which is exothermic by about 14 kcal.[26] Indeed, the

$$PhCH_2^\bullet + Bu_3SnH(D) \xrightarrow{k_{H(D)}} PhCH_2H(D) + Bu_3Sn^\bullet \tag{9}$$

$$Ph^\bullet + Bu_3SnH(D) \xrightarrow{k_{H(D)}} PhH(D) + Bu_3Sn^\bullet \tag{10}$$

kinetic isotope effect (k_H/k_D) values reported for reaction 9 at 25 °C are not too far from the 3.18 we find for eq 2:

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(16) (a) Whyman, R. *J. Chem. Soc., Dalton Trans.* **1972**, 2294. (b) Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1981**, *20*, 249.

(17) Persky, A. *J. Chem. Phys.* **1974**, *60*, 49. As quoted by: Lewis, E. S. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: New York, 1976; Vol. 2, Chapter 4, p 150.

(18) Atkinson, J. K.; Hollenberg, P. F.; Ingold, K. U.; Johnson, C. C.; Le Tadic, M.-H.; Newcomb, M.; Putt, D. A. *Biochemistry* **1994**, *33*, 10630−10637.

(19) The gas-phase IR spectrum of a highly deuterated sample of $Os(CO)_4D_2$ contains a broad peak centered at 1418 cm^{-1} (Okrasinski, S. J.; Bender, B. R., unpublished work).

(20) See pp 24−36 in ref 7 and pp 256−260 in ref 8.

(21) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 1229.

(22) (a) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711. As modified by: (b) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843.

(23) 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.

(24) The relevant theories are summarized in: Smith, K.-T.; Tilset, M.; Kristjánsdottír, S. S.; Norton, J. R. *Inorg. Chem.* **1995**, *34*, 6497−6504.

(25) Reference 7, p 36.

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

a value of 3.24 can be inferred[26] from a tritium study,[27] a product ratio study with Bu_3SnD gave 2.89,[25b] and the most recent result is 2.26.[26] Appreciably more exothermic than reactions 2 or 9 is the transfer of $H^\bullet$ from Bu_3SnH to phenyl radicals (eq 10). Because eq 10 should have an earlier transition state, one would expect it to have a smaller kinetic isotope effect than eq 2 or 9, and a k_H/k_D value of 1.6[28] has been reported.

Experimental Section

Stopped-Flow System. This system and software were described in a previous publication.[2] Solutions of the hydrides and of the trityl radical **1** were introduced into the stopped-flow apparatus under an inert (argon or nitrogen) atmosphere. Manipulations involving **1** were carried out under red light.

Materials. The tris(*p-tert*-butylphenyl)methyl radical **1** was prepared by the method described in a previous publication.[2] Toluene was distilled under nitrogen from purple solutions of sodium/benzophenone ketyl. $HMn(CO)_5$ and $H_2Os(CO)_4$ were prepared on a high-vacuum line as previously reported,[29] from $Na[Mn(CO)_5]$ or $Na_2[Os(CO)_4]$ and H_3PO_4 in tetraglyme. The deuterium analogues of these hydrides were prepared by repeating the same procedures with 98% D_3PO_4.

Typical Kinetic Experiment. A solution of **1** in toluene was prepared and determined (from its A_{523} value)[2] to be 1.45 mM, implying a concentration of 0.73 mM after mixing. Addition of 0.100 g (0.510 mmol) of $HMn(CO)_5$ to 23.6 g (27.2 mL) of toluene gave a solution that was 18.75 mM, implying a concentration of 9.37 mM after mixing.

In an analogous $DMn(CO)_5$ experiment the concentration of **1** was 0.842 mM after mixing, while the total concentration of $DMn(CO)_5$ and $HMn(CO)_5$ was 22.31 mM after mixing; D incorporation of 95.4% implied that $[DMn]_{t=0}$ was 21.29 mM and that $[HMn]_{t=0}$ was 1.02 mM.

Calculation of k_D Values. As in our previous work,[2] the trityl radical absorbance at 523 nm was monitored after solutions such as those described in the previous paragraph were loaded and mixed in the stopped-flow apparatus at the appropriate temperature. The traces of multiple runs were compared, and one (with the apparent k_{obs} value that most closely matched the average of those for all the traces at a particular temperature) was chosen for numerical anslysis. The resulting absorbance vs time data were compared with those calculated by MacKinetics[30] from eqs 2 and 3, the initial concentrations of **1**, $DMn(CO)_5$, and $HMn(CO)_5$, and the known value of k_H (calculated from the parameters in Table 1) for an assumed value of k_D; k_D was then varied iteratively until the best fit was obtained. This procedure gave rate constants that differed only about 3% from those given by a simple first-order treatment. The residuals resulting from the iterative kinetic simulations (which ranged from 0.015 to 0.025) were usually less than those (always >0.020) given by the first-order analysis.

Similarly, absorbance vs time data from osmium runs were compared with those calculated by MacKinetics[30] from eqs 4−7, the initial concentrations of **1**, [D−Os], and [H−Os], and the known value of k_H (measured at that temperature) for an assumed value of k_D; k_D was again varied iteratively.

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Supporting Information Available: Tables of rate constants. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980917V

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[27] (a) Kozuka, S.; Lewis, E. S. *J. Am. Chem. Soc.* **1976**, *98*, 2254. (b) Strong, H. L.; Brownawell, M. L.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 6526.

[28] Garden, S. J.; Avila, D. V.; Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U.; Lusztyk, J. *J. Org. Chem.* **1996**, *61*, 805−809.

[29] (a) Mn: Warner, K. E.; Norton, J. R. *Organometallics* **1985**, *4*, 2150. (b) Os: Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955.

[30] Written by and obtained from: Leipold, W. S., III; Weiher, J. F.; McKinney, R. J. E. I. du Pont de Nemours, Inc.