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Mechanistic Studies on Metal to Ligand Hydrogen Transfer in the Thermal Reactions of $H(\mu\text{-}H)Os_3(CO)_{10}(CNR)$: Evidence for Proton Barrier Tunneling in a Metal to Ligand Hydrogen Transfer

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The thermal reactions of the series of complexes $X(\mu\text{-}X)Os_3(CO)_{10}(CNR)$ (R = CH_3, C_6H_5, $p\text{-}C_6H_4CH_3$, $o\text{-}C_6H_4CH_3$, 2,6-$C_6H_3(CH_3)_2$; X = H, D, **1a–e**, **1a–e**-d_2) have been studied. In all cases one or more of three products are formed: (μ-H) (μ-η^1-CN(H)R)$Os_3(CO)_{10}$ (**2a,c–e**) resulting from metal to nitrogen hydrogen transfer, (μ-H) (μ-η^2CHNR)$Os_3(CO)_{10}$ (**3b–d**) resulting from metal to carbon hydrogen transfer, and (μ-H)$_2Os_3(CO)_9$(CNR) (**4c–e**) resulting from loss of carbon monoxide. The reaction shows significant steric and electronic components. Thus the metal to nitrogen hydrogen-transfer product is favored with more basic isocyanides (R = CH_3 > $p\text{-}C_6H_4CH_3$ > C_6H_5) while the relative amount of metal to carbon hydrogen transfer decreases with increasing bulkiness of the isocyanide (R = $p\text{-}C_6H_4CH_3$ > $o\text{-}C_6H_4CH_3$ > 2,6-$C_6H_3(CH_3)_2$). Variable-temperature (3–70 °C) kinetics on the methyl derivative **1a**, by ^{1}H NMR spectroscopy in benzene-d_6, showed that metal to nitrogen hydrogen transfer is a first-order process whose rate is very sensitive to even trace amouts of moisture. In the temperature range 32–70 °C, very large isotope effects and a very large difference between calculated $\Delta E_{aH}{}^D$ and $\Delta E_{oH}{}^D$ suggest that metal to nitrogen hydrogen transfer in **1a** proceeds with a significant proton barrier tunneling component. A Bell tunneling model calculation was performed to estimate the barrier width. Addition of base to the reaction quenches the large isotope effects. At 65 °C the phenyl derivative **1b** gives only the metal to carbon hydrogen-transfer product **3b** and shows only a small inverse isotope effect (k_H/k_D = 0.6), suggestive of reversible hydrogen transfer. A comparison of the relative yields obtained from thermolysis of the *p*-tolyl derivative **1c** and its deuteriated analogue at 80 °C in benzene under vacuum and carbon monoxide atmosphere gives further evidence that metal to nitrogen and metal to carbon hydrogen-transfers proceed by distinctly different mechanisms.

Introduction

Metal to ligand hydrogen transfer, and the reverse process, have been under active investigation in recent years, and it is becoming evident that there is more than one mechanism by which the hydrogen transfer can occur.[1–4] These reaction pathways are often very close in energy, and small changes in reaction conditions or in the electronic and steric factors involved can allow a complete shift in reaction mechanism or in product distribution.[3,4] A number of carbon–hydrogen–metal bonding types have been suggested, and in some cases characterized, as intermediates in metal to ligand or ligand to metal hydrogen transfers. Among these are M–H–C agostic interactions[5–9] and C–H σ bond complexation.[2]

In the case of mononuclear complexes, species containing agostic interactions have been isolated and shown to be intermediates in metal to ligand hydrogen transfers. For example, Spencer et al.[6] isolated the agostic species that occurs after protonation of L_2Pt(norbornene), where L_2 can be various bidentate phosphines.

Compounds containing agostic interactions have also been observed in polynuclear metal systems.[5] For example, Shapley et al.[5a] have shown that treatment of the coordinately unsaturated cluster $H_2Os_3(CO)_{10}$ with diazomethane yields a bridging alkyl intermediate, in which a hydrogen of the bridging alkyl is engaged in an agostic interaction with a neighboring osmium atom. Fehlner et al. have shown that deprotonation followed by low-temperature reprotonation of (μ-H)$_3Fe_3(CO)_9$(μ-CH) gives strong ^{1}H NMR and ^{13}C NMR evidence for a C–H–Fe agostic interaction.[5b]

Substantial evidence has recently been gleaned from kinetic studies to support the existence of a σ complex in the thermal elimination of methane from a dicyclopentadienyltungsten alkyl hydride complex.[2]

A possible mechanistic alternative to the agostic interaction or σ complexes, which is well documented in organic chemistry, is proton barrier tunneling.[10–14] In chemical reactions where the ground-state geometry of the reactant closely resembles that of the product, the reaction barrier width can approach the de Broglie wavelength of the proton and the proton can thus have a finite probability of being found on both the reactant and product sides of the barrier. Such reactions are characterized by exceptionally large kinetic deuterium isotope effects (i.e. much larger than the so-called maximum isotope effect calculated from infrared stretching frequencies of the protiated and deuteriated species by using the Bigeleisen equation[15]). The rates of reactions with large tunneling components

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$$k_H/k_D = e^{(hc/2kT)(\nu_H - \nu_D)}$$

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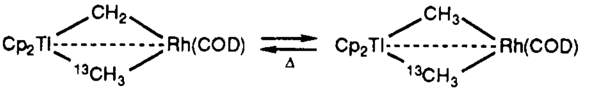
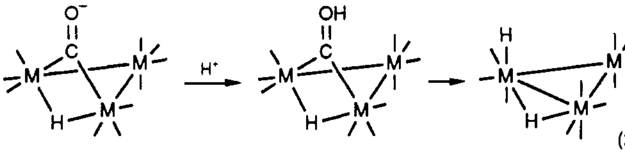
tend to become increasingly temperature independent as the reaction temperature is decreased and also tend to show large negative entropies of activation in the temperature range where the tunneling pathway is dominant. Recently, Grubbs and co-workers have reported an organometallic reaction involving intramolecular transfer of a hydrogen that appears to fit all of the above criteria for tunneling (eq 1).[16] This reaction shows a kinetic deuterium isotope effect (KDIE) of 25 at 45 °C, a dramatic decrease in the slope of the Arrhenius and Eyring plots at temperatures below 45 °C, and a large negative entropy of activation (−65 eu) in this temperature range. This reaction does not involve metal to ligand hydrogen transfer but a carbon to carbon hydrogen transfer in which the reactant and product are chemically equivalent, a case where barrier tunneling might almost be expected.[11-14]



(1)

We have recently observed anomalously large KDIE's ($k_H/k_D \sim 50$) in the intramolecular ligand to metal hydrogen transfer that follows the initial O-protonation of HM$_3$(CO)$_{11}^-$ (M = Ru, Os) at −40 to −80 °C (eq 2).[17] Other workers have also observed large KDIE's in the protonations of polynuclear and binuclear carbonyl complexes that may also arise from similar oxygen to metal proton transfers.[18] Although the O-protonated species (eq 2) has a geometry significantly different from the resulting dihydrido species, the known fluxionality of these clusters may allow the reactant molecule to traverse a geometry closely resembling that of the product dihydride from which proton barrier tunneling could occur. Unfortunately, it was not experimentally feasible to perform the variable-temperature kinetics necessary to demonstrate barrier tunneling in the case of the H(μ-COH)M$_3$(CO)$_{10}$ systems.[17] In order to further investigate the possibility of proton barrier tunneling in metal cluster reactions, we sought a system where the reverse process (i.e. metal to ligand hydrogen transfer) occurs and which has similar structural and fluxional properties to the H(μ-COH)M$_3$(CO)$_{10}$ systems. If the reverse process also exhibits a large isotope effect, the origin of the effect could not be a zero point energy difference effect since light atom (C, O, N) to heavy atom (Ru, Os) hydrogen transfer could not have the same zero point energy difference as a metal to ligand hydrogen transfer due to the much larger difference between X–H and X–D (X = C, O, N) vibrational levels versus M–H and M–D (M = Ru, Os). Such a system is found in the recent work of Adams and Golembeski.[3]



(2)

Adams and Golembeski studied the reaction of H$_2$Os$_3$(CO)$_{10}$ with various isocyanides.[3] The initial product is a 1:1 adduct H(μ-H)Os$_3$(CO)$_{10}$(CNR) (1) with one bridging hydride, one terminal hydride, and the isocyanide ligand taking up an axial coordination site. Thermolysis of this adduct gave different products depending on reaction conditions and on the nature of the isocyanide (Scheme I). When the thermolysis was carried out in poor donor solvents, such as octane, hexanes, or even n-butyl ether, the yellow solution initially turned red to give H$_2$O$_3$(CO)$_9$(CNR) (4), structurally analogous to the starting H$_2$Os$_3$(CO)$_{10}$. Upon further thermolysis, a metal to ligand hydrogen transfer occurred to give H(μ-η^2-HC:NR)Os$_3$(CO)$_{10}$ (3). This transfer of hydrogen from osmium to carbon was shown to occur via an intramolecular pathway. When the thermolysis was done in good donor solvents, such as THF, or in the presence of catalytic amounts of triethylamine, an osmium to nitrogen hydrogen-transfer product (μ-H)(μ-η^1-C:NHR)Os$_3$(CO)$_{10}$ (2) was obtained. An intermolecular process was proposed, in which the proton is pulled off the cluster by the solvent or added base to leave an anionic cluster. This cluster is then reprotonated at the nitrogen. The osmium to nitrogen hydrogen-transfer product 2 does not rearrange to the osmium to carbon hydrogen-transfer product 3 even after prolonged heating.

Scheme I

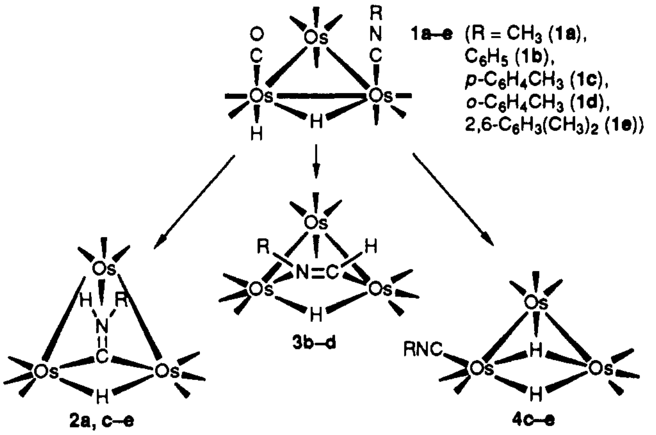


Table I. Rate Constants and Kinetic Deuterium Isotope Effects for the Conversion of 1a to 2a and 1a-d_2 to 2a-d_2

T, °C	10^4k_H, min^{-1}	10^4error	10^4k_D, min^{-1}	10^4error	k_H/k_D
3	0.54	±0.05			
10	1.0	±0.1			
21	1.3	±0.1			
32	8.3	±0.8	0.31	±0.03	27 ± 3
40	34	±3	1.5	±0.16	23 + 2
50	78	±8	4.3	±0.4	18 [illegible] 1
70	310	±30	73	±7	4.2 ± 0.4

Results and Discussion

A. Steric and Electronic Effects. Adams and Golembeski reported that the hydrogen to nitrogen transfer product 2 forms only in the presence of donor solvents or in the presence of base. We have observed slow formation of 2a (R = CH$_3$) quantitatively from its isocyanide precursor, 1a, by ^{1}H NMR spectroscopy in rigorously dried benzene solutions (see Experimental Section). This process follows good first-order kinetics over a range of temperatures (3–70 °C) with reasonable agreement between triplicate runs (±10%, Table I). The presence of trace water does have an effect on the rate of formation of 2a. When benzene-d_6, dried over molecular sieves, is used as the reaction solvent, the rates are faster and less reproducible. Similarly, in methylene-d_2 chloride distilled directly from phosphorus pentoxide, faster but less reproducible rates are observed with variations of ±100%, depending on sample history. The presence of trace water (<1%) relative to 1 can be readily detected in solutions of deuteriated isocyanide adduct, since detectable hydride signals of 2a appear in the ^{1}H NMR spectrum as a result of hydrogen–deuterium exchange. We conclude from these experiments

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Table II. Variation in Product Distribution in the Conversion of 1 to 2–4

R	H(HC=NR)-$Os_3(CO)_{10}$ (3)	H(HN(R)=C)-$Os_3(CO)_{10}$ (2)	$H_2Os_3(CO)_9$-(CNR) (4)
methyl 3–70	>5[a]	>95	<5[a]
phenyl 80	>95	<5[a]	<5[a]
p-tolyl 80	60	30	10

[a] None of this product was detected by ^1H NMR spectroscopy, but according to the signal to noise on the spectra, ~20:1, as much as 5% could be lost in the noise.

Table III. Steric Effects on the Relative Percent Yields for the Thermolysis of H(μ-H)$Os_3(CO)_{10}$(CNR) at 80 °C

R	H(HC=NR)-$Os_3(CO)_{10}$ (3)	H(HN(R)=C)-$Os_3(CO)_{10}$ (2)	$H_2Os_3(CO)_9$-(CNR) (4)
p-tolyl	60	30	10
o-tolyl	39	15	46
2.6-dimethylphenyl	<5	23	75

that with the relatively basic methyl isocyanide, the metal to ligand hydrogen transfer can proceed by an intramolecular pathway but at significantly slower rates than the intermolecular pathway reported by Adams (vide infra).

In dry benzene, heating the phenyl isocyanide complex **1b** at 80 °C yields only the η^2-formimidyl complex **3b** while the *p*-tolyl isocyanide **1c** yields a mixture of **2c**, **3c**, and **4c**, as measured by ^1H NMR spectroscopy (Table II). These results are in accord with the expected intrinsic basicity of the nitrogen atom in the free isocyanides (methyl > *p*-tolyl > phenyl) where increasing basicity yields increasing amounts of the metal to nitrogen hydrogen-transfer product.

The hydrogen to carbon transfer product is an η^2-formimidyl ligand rather than the η^1 amino carbyne of the hydrogen to nitrogen transfer product. With the η^2 geometry, the R group on the isocyanide ligand is brought into much closer proximity to the carbonyls on the neighboring osmium atom. This steric interaction is indicated by the product distribution for the series of compounds given in Table III (all of these data are for an 80 °C thermolysis in dry benzene). In the case of *p*-tolyl the major product is the Os–C hydrogen-transfer product, **3c**, while in the case of *o*-tolyl isocyanide adduct **1d**, there is a reduction in the amount of Os–C hydrogen-transfer product from 60% to 39%. In the case of the 2,6-dimethylphenyl isocyanide adduct **1e**, the metal to carbon hydrogen transfer is essentially blocked. The relative amounts of the osmium to nitrogen hydrogen-transfer products **2c**, **2d**, and **2e** vary considerably less, indicating that this product is less sensitive to the steric bulk of the isocyanide. As might be expected, the relative amounts of the dihydrido species, **4c**, **4d**, and **4e** increase as the hydrogen on carbon transfer products decrease.

B. Kinetic Deuterium Isotope Effects. As mentioned in the previous section, the quantitative conversion of **1a** to **2a** gave good first-order kinetics in the temperature range 3–70 °C. The deuteriated (>98% by ^1H NMR analysis) analogue **1a**-d_2, was examined in the temperature range 32–70 °C and also exhibited good first-order kinetics. Below 32 °C the conversion of **1a**-d_2 to **2a**-d_2 was to slow to observe in a reasonable amount of time. The isotope effects observed between 32 and 70 °C (Table I) are much too large to be accounted for by simple primary isotope effects based only on zero point energy differences. The "maximum" isotope effect for rate-determining cleavage of an Os–H bond in **1a** using the Bigeleisen equation[15] and the observed values of 1932 cm^{-1} for the Os–H stretch and 1386 cm^{-1} for the Os–D stretch is $k_H/k_D = 3.7$ at 32 °C. With the observed values of 1572 cm^{-1} for the Os–H–Os stretch and 1106 cm^{-1} for the Os–D–Os stretch, the "maximum" isotope effect is only $k_H/k_D = 3.1$ at 32 °C.

Table IV. Kinetic Data for Base-Catalyzed Conversion of H(μ-H)$Os_3(CO)_{10}(CNCH_3)$ to (μ-H)$Os_3(CO)_{10}(\mu_3$-η^1-CN(H)CH_3)

base							
$NH_2CH_2CH_2CH_3$				$N(CH_2CH_2CH_3)_3$			
10^3[B]	k_H	k_D	k_H/k_D	10^4[B]	k_H	k_D	k_H/k_D
5.0	0.14	0.11	1.2	4.8	0.073	0.60	1.2
1.2	0.082	0.040	2.1	0.76	0.0055	0.0021	2.6
0.19	0.0083	0.0013	6.3				

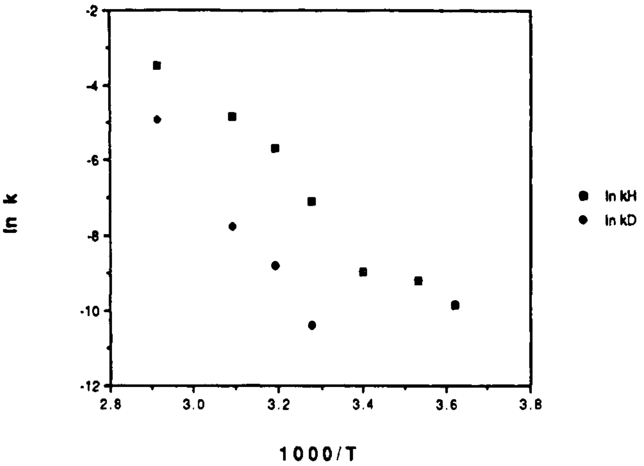


Figure 1. Arrhenius plots for the conversion of **1a** to **2a** and **1a**-d_2 to **2a**-d_2.

The observed k_H/k_D is also too large to result from rate-determining cleavage of an X–H bond (X = O, N), arising from participation of a basic impurity in the reaction mixture. From typical values of nitrogen–hydrogen or oxygen–hydrogen stretching frequencies, isotope effects in the range 6–10 would be expected. Furthermore, we have measured the rate of conversion of **1a** and **1a**-d_2 to **2a** and **2a**-d_2 in the preence of small amounts of tri-*n*-propylamine or *n*-propylamine (Table IV). It can be seen from these data that the isotope effect is progressively quenched with increasing amounts of added base. We also observed the incorporation of protons in the hydride and NH positions of the **2a**-d_2 formed in the presence of *n*-propylamine in the ^1H NMR spectrum. All of these results taken together present strong evidence that base-promoted and intramolecular conversions of **1a** to **2a** proceed by distinctly different mechanisms and that proton barrier tunneling is a plausible explanation for the observed kinetic deuterium isotope effects.

An Arrhenius plot of the variable-temperature kinetics (Table I) is shown in Figure 1. The precision for the kinetic measurements (±10%) does not permit us to clearly see the curvature in the plot expected for a reaction with a large tunneling component.[12,14,16] However, we were able to estimate the activation energies for the protic and deuteriated cases using the data in the 32–70 °C temperature range, which are fairly linear. It was also not possible to obtain reliable values for the preexponential factor in the narrow temperature range investigated given the precision of kinetic measurements. The activation energies (E_a) of the protic and deuteriated reactions are determined from the Arrhenius plots in the temperature range 32–70 °C: $E_{aH} = 22.6$ kcal/mol and $E_{aD} = 30.6$ kcal/mol. The difference in activation energies, $\Delta E_{aH}{}^{D}$, is 8 kcal/mol. The difference in activation energies cal-

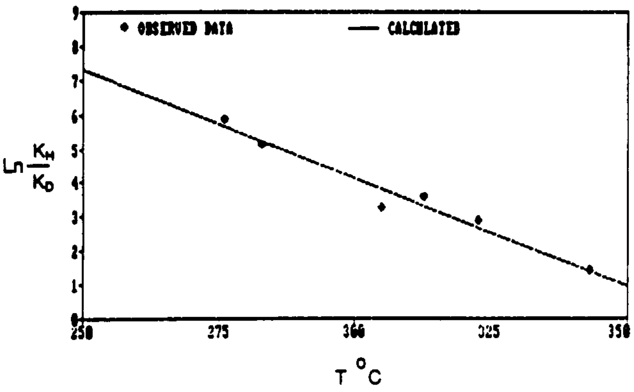


Figure 2. Comparison of observed and calculated kinetic deuterium isotope effect ratios using the Bell tunneling model for the conversion of **1a** to **2a** and **1a**-d_2 to **2a**-d_2.

culated from the Bigeleisen equation[15] and the infrared stretching frequencies (using the terminal hydride stretches) is only $\Delta E_{0H}{}^{D} = 0.78$ kcal/mol. This large difference between $\Delta E_{0H}{}^{D}$ and $\Delta E_{aH}{}^{D}$ is good evidence for barrier tunneling, and the fact that there is a 10-fold difference between $\Delta E_{aH}{}^{D}$ and $\Delta E_{0H}{}^{D}$ shows that there is a very significant tunneling component to this reaction.[12,14]

All the data obtained for the conversion of **1a** to **2a** are suggestive of quantum barrier tunneling. In particular, the fact that $\Delta E_{aH}{}^{D} \gg \Delta E_{0H}{}^{D}$ and the large temperatures dependence of the isotope effect are indicative of quantum barrier tunneling.[10-16] We decided to use the Bell tunneling model[10,19] to estimate the barrier width for this reaction. Details of the calculational method used are available as supplementary materials along with a computer program used to do the calculation.

The Bell tunneling model calculation as we applied it is basically an iterative fit of the observed k_H/k_D ratios to calculated k_H/k_D ratios by varying the barrier width and using the known barrier heights for the protic and deuteriated case. In doing this calculation we needed to make some assumption about the ΔH of the reaction. Even simplified thermodynamic calculations are difficult for metal cluster reactions, as there are very little thermodynamic data available in the literature. We performed the barrier width calculation twice, first assuming the reaction is thermoneutral and then assuming $\Delta H_{rxn} = -30$ kcal/mol. The number for the ΔH_{rxn} was arrived at as follows. There is an abundance of data on metal hydride bonds,[20-23] and they are usually around 60 kcal/mol. We used a value of 90 kcal/mol for the nitrogen–hydrogen bond.[24] We assumed $\Delta H = 0$ on going from the Os—CNR bond to the $Os_2\mu$-C:NH(R) bond. This assumption seems reasonable on the basis of the fact that metal hydrides only vary from about 0 to 5 kcal/mol on going from terminal to bridging bonding modes.[22] For the $\Delta H_{rxn} = 0$ calculation, $E_a = 30.6$ kcal/mol, and the barrier half-width $a = 0.605$ Å. The $\Delta H_{rxn} = -30$ kcal/mol, $E_a = 30.6$ kcal/mol and $a = 0.344$ Å. This is consistent with the fact that as the symmetry of the barrier decreases, tunneling becomes less likely.[14] Thus, for an exothermic (or endothermic) process one needs a narrower barrier to explain the same amount of tunneling as in a thermoneutral reaction. The calculated data are plotted with the observed data in Figure 2 and show a good fit with the observed data.

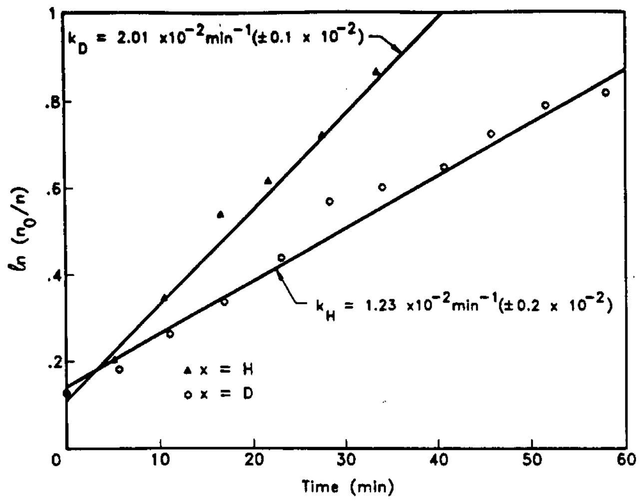
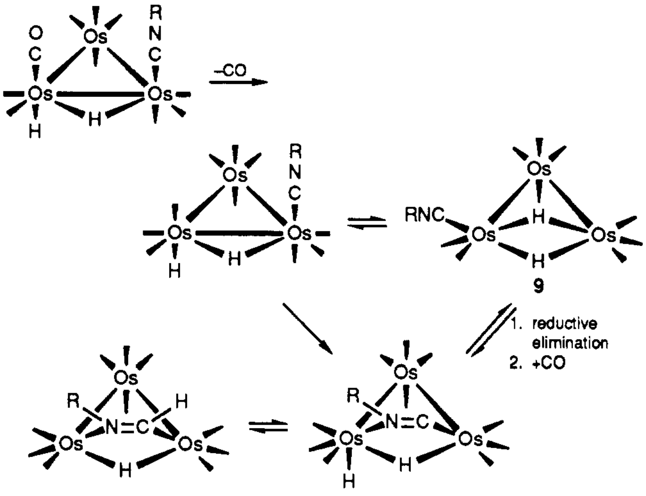


Figure 3. Kinetic data for the first 1.5 half-lives in the conversion of $X(\mu\text{-}X)Os_3(CO)_{10}(CNC_6H_5)$ (X = H (**1b**), X = D (**1b**-d_2) to $(\mu\text{-}X)(\mu\text{-}\eta^2\text{-}XC{=}NC_6H_5)$.

Scheme II



The thermolysis of the phenyl isocyanide adduct of $X_2Os_3(CO)_{10}$, **1b** and **1b**-d_2, was carried out in benzene-d_6 in an NMR tube sealed under vacuum (10^{-2} Torr) at 60 °C. The reaction gave only the product arising from transfer of hydrogen to carbon, **3b** or **3b**-d_2, respectively. The reaction followed first-order kinetics for about 1.5 half-lives, but as the relative concentration of the product increased, the reverse reaction became significant and deviations from first-order kinetics were noted. The kinetic deuterium isotope effect was 0.61 for the first 1.5 half-lives of this process. The plot of ln $\{[R_0]/[R]\}$ vs time (in minutes) for the protic and deuteriated systems, as well as the first-order rate constants for this process, is given in Figure 3.

On the basis of the isotope effect and the dependence of the formation of **3b** on CO[3] (vide infra), we have proposed the mechanism shown in Scheme II. The reaction proceeds via a rate-limiting step that involves the loss of CO. This intermediate can coordinate the terminal hydride into a bridging position to give **4b**. Either **4b** or the initial intermediate from CO dissociation can reductively eliminate a C–H bond and then recapture CO to form **3b**. Alternatively, Adams and Golembeski[3] suggest that the reductive elimination is driven by prior recapture of CO.[3]

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Table V. Product Distributions for the Thermolysis of (μ-X)$Os_3(CO)_{10}$(p-$CNC_6H_4CH_3$) at 80 °C

X	H(HC=NR)-$Os_3(CO)_{10}$ (3)	H(HN(R)=C)-$Os_3(CO)_{10}$ (2)	$H_2Os_3(CO)_9$-(CNR) (4)
H under vacuum	60	30	10
D under vacuum	80	~5	15
H under CO	<5	>95	<5
D under CO	60	35	~5

To account for the inverse isotope effect and the deviation from simple first-order kinetics at high concentrations of product, the metal to ligand hydrogen transfer must be reversible, since the other alternative, a very late transition state that is at least partially rate limiting,[4,25] does not account for the kinetic data in the later phases of the reaction.

The p-tolyl isocyanide adduct, **1c**, gives all three products **2c**, **3c**, and **4c** on thermolysis in benzene at 80 °C. The product distribution for protic and deuteriated samples both under vacuum and under CO are given in Table V. These thermolyses were done in sealed NMR tubes prepared by distilling dry benzene-d_6 into the tubes. Vacuum was $\sim 10^{-2}$ Torr and CO pressure was 1 atm.

The protic sample under vacuum gives the hydrogen to carbon transfer product, **3c**, as the major product, with a substantial amount of the hydrogen to nitrogen transfer product, **2c**. Compound **4c** was observed to initially form and then diminished as the hydrogen to carbon transfer product **3c** formed. Deuterium substitution essentially blocks the hydrogen to nitrogen transfer. On the basis of the large isotope effect observed in the methyl isocyanide case (vide infra), this result is not surprising.

The protic compound, under CO atmosphere, gives only the hydrogen to nitrogen transfer product, **2c**. This suggests that loss of CO is required to form **3c**, but not **2c**. When the deuteriated system was thermolyzed under a CO atmosphere, **3c** is the major product. This can be explained as a manifestation of the inverse isotope effect seen for the phenyl isocyanide system and the tunneling mechanism of the methyl isocyanide case acting in concert. Thus, it is possible to completely invert the product distributions by using CO atmosphere versus deuterium substitution under vacuum.

Conclusions

We have shown that metal to ligand hydrogen transfers can occur via different mechanistic pathways even within the same system. These mechanisms, although different, can lie very close in energy. Small changes in the electronic or steric properties of a system can drastically alter product distributions.

For the metal to ligand hydrogen transfer in the $H_2Os_3(CO)_{10}$ (CNR) systems studied, we have documented a strong dependence on the basicity of the nitrogen as well as the steric bulk of the R group. The more basic the nitrogen, the more likely the hydrogen will be transferred there. This suggests that this intramolecular hydrogen transfer from osmium to nitrogen involves a proton rather than a hydrogen atom or a hydride. The formation of the osmium-to-nitrogen proton-transfer product, **2**, is relatively insensitive to the steric properties of the R group on the isocyanide. The osmium to carbon hydrogen-transfer product, **3**, on the other hand is not formed if the R group is too bulky.

The hydrogen transfer from osmium to nitrogen can occur via a single step, intramolecular transfer that appears to involve a large degree of quantum barrier tunneling. We have documented this through variable-temperature isotope effect studies and we have done a Bell-type calculation that estimates the barrier width to be between 0.34 and 0.60 Å. The apparent tunneling in the metal to ligand hydrogen transfer during the rearrangement of **1a** to **2a** gives support to a tunneling mechanism in the ligand to metal hydrogen transfer in the rearrangement of H(μ-COH)$M_3(CO)_{10}$ to $H_2M_3(CO)_{11}$ (eq 2.)[17] As these two hydrogen transfers are essentially the forward and reverse reactions of the same process; we believe that the high degree of fluxionality present in these systems is what makes the tunneling mechanism possible.[17] At some point during the fluxional process the geometry of the reactant approaches that of the product; this narrows the barrier, and tunneling becomes possible. Studies to further corroborate this hypothesis are under way in our laboratories with related binuclear systems.

Experimental Section

Materials. $H_2Os_3(CO)_{10}$,[26] methyl isocyanide,[27] phenyl isocyanide,[28] p-tolyl isocyanide,[28] o-tolyl isocyanide,[28] and 2,6-dimethylphenyl isocyanide[28] were prepared according to known literature procedures. $Os_3(CO)_{12}$ was either purchased from Strem Chemicals or made from OsO_4 according to known literature procedures.[29] Solvents were ACS reagent grade and were stored over molecular sieves. Deuterated NMR solvents were purchased from Aldrich and stored over molecular sieves unless otherwise indicated. THF was distilled from sodium benzophenone ketyl before use. All reactions were performed under N_2 unless otherwise noted.

Spectra. Nuclear magnetic resonance spectra were obtained on an IBM-NR-80 (^1H NMR 80 MHz) spectrometer operating in the Fourier transform mode. Infrared data were obtained on a Perkin-Elmer 1420 spectrometer operating at a 2.0 wavenumber resolution. All NMR data are given as ppm relative to TMS.

Analysis. Elemental analysis was performed by Schwartzkopf Microanalytical laboratories.

Preparation of $D_2Os_3(CO)_{10}$. Finely ground $Os_3(CO)_{12}$ (500 mg, 0.55 mmol) was refluxed for 2 h in 350 mL of octane in a 500-mL three-neck round-bottom flask while deuterium gas was bubbled through the solution. The yellow solution turned purple and was monitored by analytical TLC (silica) with hexane as the eluent. The solvent was removed on a rotary evaporator, and the resulting purple solid was recrystallized twice from CCl_4 to give 280 mg (60%) of $D_2Os_3(CO)_{10}$ (>98% deuteriated by ^1H NMR analysis).

Preparation of 1a–e and Their Deuteriated Analogues. Neat isocyanide (except the 2,6-dimethylphenyl, which was dissolved in 1.0 mL of pentane) was added via syringe dropwise to a purple solution of 150 mg (0.18 mmol) of $H_2Os_3(CO)_{10}$ in 5 mL of pentane under N_2 at 0 °C until the solution was yellow (approximately three drops). The solution was allowed to stir for 10 min at 0 °C. During this time a yellow precipitate formed. The solvent was removed via syringe and the solid washed with three 5-mL aliquots of cold pentane. The yellow solid was blown dry with N_2 and then put under vacuum overnight giving quantitative yields of product. The deuteriated analogues were made by the same method but starting with $D_2Os_3(CO)_{10}$.

1c. Anal. Calcd (found) for $C_{18}H_9O_{10}Os_3N$: C, 22.29 (22.50); H, 0.94 (1.01); N, 1.44 (1.40). Infrared (hexane) ν(CO): 2094 (w), 2061 (s), 2048 (s), 2032 (m), 2023 (s), 2008 (s), 1995 (m) cm^{-1}. ^1H

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NMR (CD_2Cl_2, -70 °C): δ 6.83 (m, 4 H), 1.77 (s, 3 H), -19.73 (d, 1 H), -10.28 (d, 1 H, J = 3.55 Hz); minor isomer[3] δ -19.16 (d), -9.98 (d, J = 4.1 Hz).

1d. Anal. Calcd (found) for $C_{18}H_9O_{10}Os_3N$: C, 22.29 (22.35); H, 0.94 (1.01); N, 1.44 (1.40). Infrared (hexane) ν(CO): 2094 (w), 2063 (m), 2047 (s), 2031 (m), 2022 (s), 2007 (s), 1995 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, -70 °C): δ 6.60 (m, 4 H), 1.79 (s, 3 H), -19.68 (d, 1 H), -9.9 (d, 1 H, J = 3.50 Hz); minor isomer[3] δ -19.62 (d), -9.70 (d, J = 3.55 Hz).

1e. Anal. Calcd (found) for $C_{19}H_{11}O_{10}Os_3N$: C, 23.19 (23.61); H, 1.13 (1.19); N, 1.42 (1.71). Infrared (hexane) ν(CO): 2102 (w), 2074 (s), 2046 (s), 2036 (m), 2012 (s), 1993 (s), 1956 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, -70 °C): δ 7.19 (m, 3 H), 1.93 (s, 6 H), -19.64 (br, 1 H), -9.9 (d, 1 H); minor isomer δ -19.64 (br), -10.23 (d).

Kinetic Runs for the Conversion of 1a to 2a and 1a-d_2 to 2a-d_2. The rearrangement of **1a** to **2a** and **1a**-d_2 to **2a**-d_2 was followed by ^1H NMR spectroscopy. The samples were prepared as follows. Benzene-d_6 was dried with Na benzophenone ketyl. The dry benzene (0.5 mL) was vacuum-distilled directly into a flame-dried NMR tube fitted with a standard taper 14/35 joint and containing 10 mg (0.011 mmol) of $X_2Os_3(CO)_{10}(CNCH_3)$ via trap-to-trap distillation. The tube was then sealed under vacuum (10^{-4} Torr). The tube was completely immersed in a thermostated water bath (±1 °C) at the appropriate temperature and ^1H NMR spectra were taken periodically with total accumulation times of about 5 min.

The 5-min accumulation time at the probe temperature (32 °C) is the total time out of the constant-temperature bath. According to the rate constant at the probe temperature, the reaction progresses by ~0.4% during each 5-min interval. About 10 kinetic points were taken for each run, and so a systematic error (4% extra conversion at 32 °C) must be acknowledged over the course of the entire experiment for the runs below the probe temperature. This systematic error is small compared with the percent conversion monitored, and it was not practical to keep the NMR spectrometer at low temperature for the entire reaction time (160 h at 3 °C). The time interval between measurements was variable depending on the temperature (5–10 min at 70 °C and ~4 h at 3 °C). The reactions were followed for at least 2.5 half-lives at low temperature and to completion at the higher temperatures. Relative concentrations were obtained by integration of the methyl peak of **1a** at 2.02 ppm and the methyl peak of **2a** at 2.51 ppm. Kinetic plots of $\ln n_0/n$ vs t gave the rate constants shown in Table I with correlation of coefficients >0.99.

Thermolysis of 1b–e. Dry benzene-d_6 (0.5 mL) was delivered into a flame-dried NMR tube containing 10 mg (0.01 mmol) of $X_2Os_3(CO)_{10}(CNR)$ via trap-to-trap distillation. The tubes were sealed under vacuum (10^{-2} Torr). The thermolysis was done in a thermostated water bath at 80 ± 1 °C, and ^1H NMR spectra were taken periodically until reaction was complete. ^1H NMR (C_6D_6, 28 °C), δ: **2c** 6.70 (m, 4 H), 1.98 (s, 3 H), -16.60 (s, 1 H); **2d** 6.59 (m, 4 H), 1.78 (s, 3 H), -16.68 (s, 1 H); **2e** 6.84 (m, 3 H), 1.80 (s, 6 H), -16.90 (s, 1 H); **3b** 10.35 (s, 1 H), 6.29 (m, 5 H), -14.87 (s, 1 H); **3c** 10.31 (s, 1 H) 6.50 (m, 4 H), 19.95 (s, 3 H), -14.93 (s, 1 H); **3d** 9.42 (s, 1 H), -6.77 (m, 4 H), 1.60 (s, 3 H), -11.27 (s, 2 H); **4c** 6.90 (m, 4 H), 1.82 (s, 3 H), -11.27 (s, 2 H); minor isomer[3] -11.29 (s), -12.38 (s); **4d** 6.65 (m, 4 H), 1.97 (s, 3 H), -11.24 (s, 2 H); minor isomer$_3$ -12.41 (s), -12.60 (s); **4e** 6.57 (m, 3 H), 2.03 (s, 6 H), -11.16 (s, 2 H); minor isomer[3] -12.36 (s), -12.40 (s).

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Supplementary Material Available: Textual details of the barrier width calculation (Appendix 1) and the computer program used for the numerical analysis (Appendix 2) (13 pages). Ordering information is given on any current masthead page.