

# The First Measurements of Activation Volumes for Hydride Fluxionality on Metal Clusters. Intramolecular Exchange of Hydrides on $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$ and $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_9$

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The first volumes of activation for hydride fluxionality on transition-metal clusters have been determined by analysis of  $^1\text{H}$  NMR line shapes recorded at pressures up to 200 MPa. For exchange of the two bridging hydrides of  $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_9$  the value for  $\Delta V^\ddagger$  of  $+4.1 (\pm 0.3) \text{ cm}^3/\text{mol}$  is consistent with an exchange pathway involving migration of one hydride from a doubly bridging coordination mode to a terminal coordination site in the transition state. For exchange of bridging and terminal hydride ligands of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  the value for  $\Delta V^\ddagger$  of  $-0.8 (\pm 0.4) \text{ cm}^3/\text{mol}$  is consistent with a transition state in which both hydrides are bridging.

## Introduction

Hydride mobility is a common feature of metal cluster chemistry, yet the mechanism remains poorly understood.<sup>1</sup> The most common coordination mode for cluster hydrides is bridging two metal atoms ( $\mu\text{-H}$ ), but examples of terminal ( $t\text{-H}$ ), triply bridging ( $\mu_3\text{-H}$ ), or interstitial hydrides are well-known. For clusters of three or more metal atoms hydride migration may occur by either  $\mu\text{-H} \rightarrow t\text{-H} \rightarrow \mu\text{-H}$  or  $\mu\text{-H} \rightarrow \mu_3\text{-H} \rightarrow \mu\text{-H}$  migrations. NMR line-shape analysis can provide rate constants and can identify the exchange pathway for the migration but can provide no information concerning the nature of the transition state for an individual step in the pathway. Kinetic isotope effects and activation parameters as obtained from studies of the temperature dependence of the rate constant cannot unambiguously differentiate between the two possible mechanisms. In two instances it has been estimated that the energy required for hydride migration from an edge-bridging position to a terminal coordination site is ca. 40 kJ/mol, thus accounting for the paucity of clusters containing terminal hydride ligands.<sup>2</sup> However, exceptional clusters containing both bridging and terminal hydride ligands, such as  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{11}$ ,<sup>3,4</sup> serve to remind us that we know very little about the thermodynamics of organometallic systems.

The pressure dependence of the rate constant for a chemical reaction provides information about the volume changes along the reaction coordinate.<sup>5</sup> For a reaction in solution the activation volume,  $\Delta V^\ddagger$ , is defined by eq 1,

$$\Delta V^\ddagger = \bar{V}_\ddagger - \bar{V}_{\text{rs}} \quad (1)$$

where  $\bar{V}_\ddagger$  and  $\bar{V}_{\text{rs}}$  are the partial molar volumes of the activated complex and the reactant state, respectively. If the volume of a proposed transition-state structure may be estimated, then activation volume measurements can provide a more easily interpretable probe of mechanism than can activation enthalpy and entropy measurements. For a fluxional process the net volume change,  $\Delta V^\circ$ , is zero since the reactant state is the same as the product state. Furthermore, the fluxional process is not expected to cause significant differences in charge or dipole moment between the reactant and transition states. Because of these factors distinctions between mechanisms for fluxional processes on the basis of activation volumes should be subject to fewer complications due to solvation effects or changes in  $\Delta V^\circ$  than are frequently encountered for other reaction classes.

The volume change associated with a  $\mu\text{-H} \rightarrow t\text{-H}$  hydrogen migration has been estimated to be as great as  $+7 \text{ cm}^3/\text{mol}$ .<sup>6,10</sup> This estimate was made by comparisons of solid-state molar volumes, determined from the crystal structures, of closely related pairs of cluster hydrides and cluster carbonyls.<sup>25</sup> Thus, activation volume measurements could in principle distinguish between the possible limiting

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(10) In ref 6, estimates of the volume  $\Delta V$  associated with a  $\mu\text{-H} \rightarrow t\text{-H}$  isomerization were made with use of the solid-state molar volumes of two structures having terminal hydride ligands,  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{11}$  ( $+14 \text{ cm}^3/\text{mol}$ ) and  $\text{H}(\mu\text{-H})_3\text{Os}_3(\mu_3\text{-NCH}_2\text{CF}_3)(\text{CO})_9$  ( $+7 \text{ cm}^3/\text{mol}$ ). The mean value of  $+10 \text{ cm}^3/\text{mol}$  was used in the discussion. However, the disorder problem associated with the former structure makes the value based upon this compound an upper limit. In this paper we prefer to use the smaller volume of  $+7 \text{ cm}^3/\text{mol}$ , a value that is still large for an intramolecular process.

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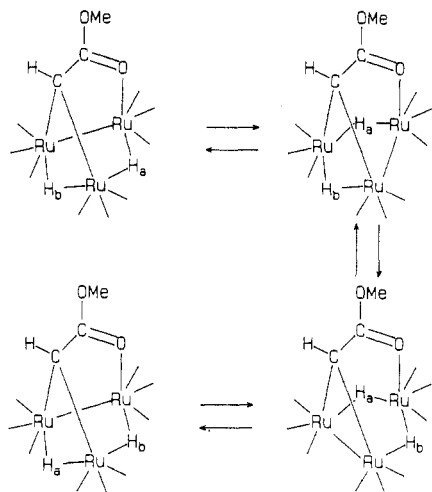
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**Figure 1.** Proposed pathway for exchange of the two hydride ligands of  $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_9$ .

mechanisms for hydride fluxionality.

In this work we have measured for the first time the activation volumes for hydride fluxionality, the intramolecular exchange between bridging and terminal hydride ligands of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  and also between the two bridging hydrides of  $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_9$ . These experiments were undertaken to determine (1) whether nonzero activation volumes could be measured for intramolecular hydride migration and (2) whether these activation volumes might be useful for distinguishing between different mechanisms proposed for fluxionality.

### Experimental Section

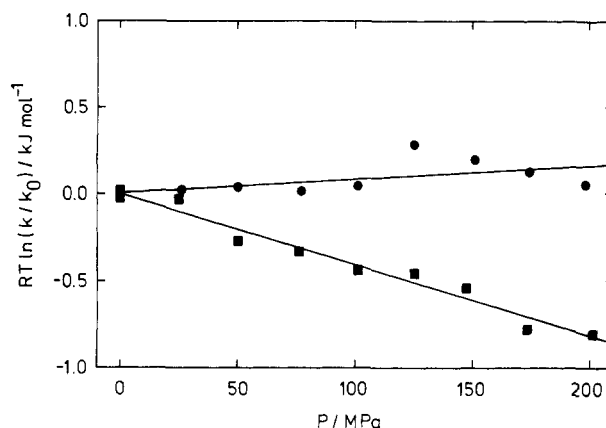
The compounds  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)^8$  and  $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_9^7$  were prepared as described previously. Measurements were conducted on dichloromethane- $d_2$  solutions of the former and toluene- $d_6$  solutions of the latter. Variable-temperature spectra were recorded on a standard Bruker AM-400 spectrometer. Variable-pressure measurements were made with a Bruker AM-400 spectrometer using a special probe designed in Lausanne, Switzerland.<sup>8</sup> Spectra were taken first with rising pressure and then with decreasing pressure. The reversibility of the effect of pressure upon the rate constant was thus confirmed by the lack of hysteresis. Rate constants were determined by line-shape analysis involving simulation of experimental spectra with the program EXCHNG.<sup>9</sup> Activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were determined by linear regression analysis of the Eyring equation  $\ln(k/T) = \ln(k_b/h) + \Delta H^\ddagger/RT - \Delta S^\ddagger/R$ . The activation volumes were determined by linear regression analysis of the equation  $\ln k = \ln k_0 - \Delta V^\ddagger P/RT$ , where  $\Delta V^\ddagger$  is the activation volume,  $k$  is the rate constant at pressure  $P$ , and  $k_0$  is the rate constant at  $P = 0$ . Error limits are reported as 1 standard deviation.

### Results and Discussion

**Activation Volumes for Intramolecular Rearrangements.** A few examples of activation volumes for intramolecular rearrangements of metal complexes have been measured previously.<sup>5</sup> The best known cases are isomerizations of octahedral complexes such as  $[\text{M}(\text{chelate})_3]^{n+}$  and cis-trans isomerizations of  $\text{MCl}_4 \cdot 2(\text{MeO})_3\text{PO}$  adducts ( $\text{M} = \text{Ti},^{20} \text{Zr}^{21}$ ), which are proposed to occur by a trigonal-twist mechanism through a trigonal-prismatic transition state. For reactions of this type  $\Delta V^\ddagger$  varies from  $-2$  to  $+6 \text{ cm}^3/\text{mol}$ , depending upon the metal, the chelating ligands, and the charge on the complex. Carbonyl fluxionality has been investigated for  $\text{Fe}(\text{CO})_2(\text{PPh}_3)(\text{cyclo-octadiene})$  ( $\Delta V^\ddagger = 0 \text{ cm}^3/\text{mol}$ ) and  $\text{Fe}(\text{CO})_2(\text{PPh}_3)(2,3\text{-}\eta\text{:O-}\sigma\text{-7,7-dimethoxybicyclo[2.2.1]hept-2-ene})$  ( $\Delta V^\ddagger = +5 \text{ cm}^3/\text{mol}$ ); in the absence of other comparable data, the

**Table I.** Rate Constants for Hydride Exchange on  $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_9$

$T$ , K	$P$ , MPa	$k$ , $\text{s}^{-1}$	$T$ , K	$P$ , MPa	$k$ , $\text{s}^{-1}$
271	0.1	2.2	309.4	0.1	48.2
284.9	0.1	7.1	309.4	25.	47.3
295.4	0.1	16	309.4	50.	43.1
306.1	0.1	32	309.4	76.	42.1
321.8	0.1	98	309.4	101.	40.4
338.5	0.1	260	309.4	125.	40.1
354.5	0.1	870	309.4	147.	38.8
372.0	0.1	1870	309.4	173.	35.4
			309.4	201.	35.0



**Figure 2.** Plots of  $RT \ln(k/k_0)$  in  $\text{kJ/mol}$  for hydride exchange in  $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_9$  (squares) and  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  (circles) vs pressure in MPa.

positive value for the latter was taken to indicate Fe-O bond cleavage in the transition state.<sup>12</sup> In the absence of solution partial molar volume data for well-defined structures, accurate models are especially important for the interpretation of activation volume measurements.

**Hydride Exchange on  $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_9$ .** Fluxional processes involving the hydride ligands of this cluster were investigated by one of us previously.<sup>13</sup> The proposed pathway (Figure 1) for hydride exchange in  $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_9$  involves migration of hydride  $\text{H}_b$  to the unoccupied Ru-Ru edge, followed by migration of hydride  $\text{H}_a$  to the Ru-Ru edge just vacated by  $\text{H}_b$ . The pathway for exchange of the two hydrides involves two elementary steps, but the transition state most likely involves motion of a single hydride ligand, which may be either terminally coordinated or triply bridging in the transition state. Because of the capping  $\text{CHCO}_2\text{Me}$  ligand, only small changes in the coordination geometries of the non-hydride ligands are expected during the fluxional process. Thus, the primary changes in volume will be due to the changes in volume associated with hydride coordination.

The activation enthalpy and entropy were determined from an Eyring plot with use of rate constants (Table I) at temperatures between 271 and 372 K. The values obtained,  $\Delta H^\ddagger = 54 (\pm 1) \text{ kJ/mol}$  and  $\Delta S^\ddagger = -40 (\pm 3) \text{ J/(K mol)}$ , are in excellent agreement with values obtained previously.<sup>13</sup>

The activation volume,  $\Delta V^\ddagger$ , for exchange of the hydride ligands of  $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_9$  was determined to be  $+4.1 (\pm 0.3) \text{ cm}^3/\text{mol}$ , from the slope of the plot of  $RT \ln(k/k_0)$  vs  $P$  (Figure 2) with use of the rate constants for exchange at pressures between 0.1 and 201 MPa (Table

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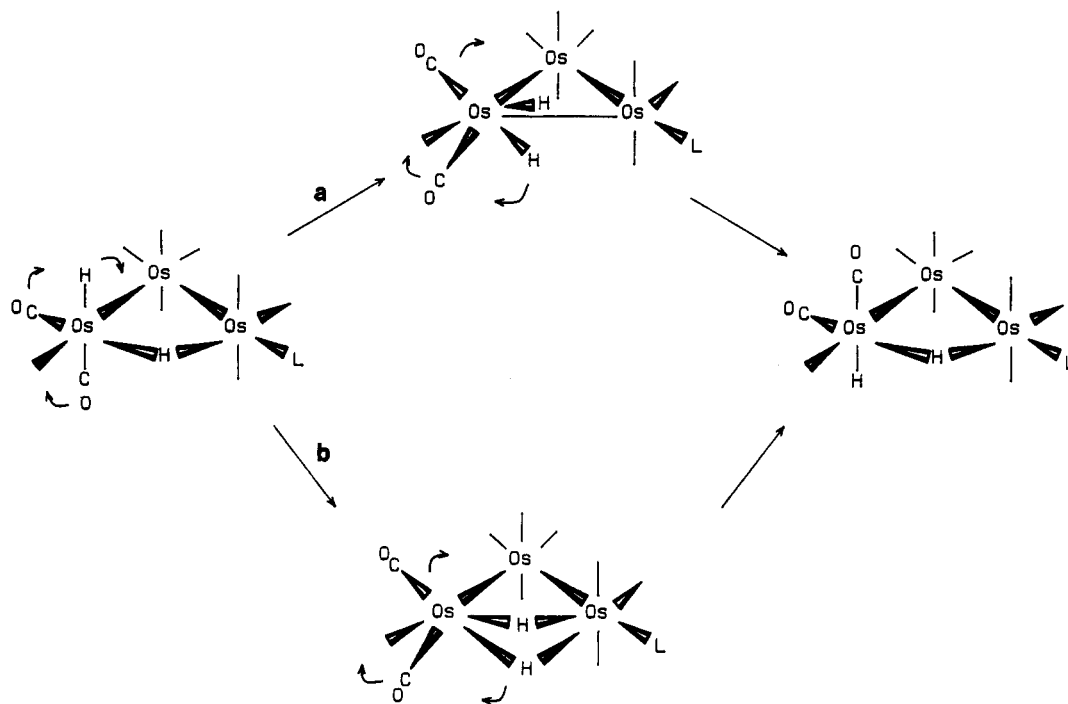


Figure 3. Proposed mechanisms for exchange of the two hydride ligands of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$ .

I). The positive activation volume, relatively large for an intramolecular process, is consistent with a mechanism involving  $\mu\text{-H} \rightarrow \text{t-H}$  migration. The predicted value for such a process, on the basis of crystal structures of model compounds and with consideration of only the change in volume associated with the hydride ligand, was  $+7 \text{ cm}^3/\text{mol}$ ; <sup>10,25</sup> the lower measured value may reflect the relaxation of the other ligands in the coordination sphere to attenuate the change in volume associated with the hydride migration. We estimate that  $\Delta V^\ddagger$  for a  $\mu\text{-H} \rightarrow \mu_3\text{-H}$  mechanism should be  $\leq 0$ , on the basis of the comparison of the solid-state molar volumes<sup>25</sup> of  $(\mu\text{-H})_4\text{Os}_4(\text{CO})_{12}$  ( $296 \text{ cm}^3/\text{mol}$ )<sup>14</sup> and  $(\mu_3\text{-H})_4\text{Re}_4(\text{CO})_{12}$  ( $285 \text{ cm}^3/\text{mol}$ ).<sup>15</sup>

**Fluxionality in  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\text{L}$ .** This system has been studied previously by three research groups, with general agreement on the overall nature of the mechanism.<sup>3</sup> The fluxional process involves a rotational movement of the two hydrides and two carbonyls about an axis defined by one Os-CO bond, the midpoint of the rotation containing a mirror plane coincident with the  $\text{Os}_3$  plane (Figure 3). The kinetic isotope effect for hydride fluxionality of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  was measured to be  $k_{\text{H}}/k_{\text{D}} = 1.5$ .<sup>16</sup> The value of  $\Delta G^\ddagger$  for hydride exchange, which varies from 46 to 57 kJ/mol, increases as the size of L increases and decreases as the polarizability of L increases.<sup>3a</sup>

Table II. Rate Constants for Hydride Exchange on  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$

T, K	P, MPa	k, s <sup>-1</sup>	T, K	P, MPa	k, s <sup>-1</sup>
221.4	0.1	7.6	253.7	0.1	135
237.2	0.1	42	253.7	26	135
246.7	0.1	66	253.7	50	136
255.9	0.1	124	253.7	77	135
265.0	0.1	280	253.7	101	137
278.0	0.1	650	253.7	125	153
286.7	0.1	1240	253.7	151	147
			253.7	174	142
			253.7	198	137

However, the most important question, namely the coordination mode of the hydrides in the transition state, remains unanswered. On the basis of the variation in  $\Delta G^\ddagger$  with the steric and electronic properties of L, Keister and Shapley<sup>3a</sup> proposed that the hydrides were both doubly bridging in the transition state ( $\text{t-H} \rightarrow \mu\text{-H}^\ddagger$ , estimated  $\Delta V^\ddagger = -7 \text{ cm}^3/\text{mol}$ ), but Rosenberg et al.<sup>3b,16</sup> prefer a transition state containing two terminal hydrides ( $\mu\text{-H} \rightarrow \text{t-H}^\ddagger$ , estimated  $\Delta V^\ddagger = +7 \text{ cm}^3/\text{mol}$ ). Thus, this system seemed to be an ideal one for the application of activation volume measurements since the two extreme possibilities should have substantially different activation volumes.

A complete description of the activation parameters for hydride exchange required determinations of both temperature and pressure effects. Previous studies of fluxionality for  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  measured only  $\Delta G^\ddagger$  for hydride exchange over a very limited temperature range. Therefore, we measured the rate constants for exchange at 1 atm and at temperatures between 221 and 287 K (Table II). An Eyring plot allowed the determination of  $\Delta H^\ddagger = 38.0 \pm 1.6 \text{ kJ/mol}$  and  $\Delta S^\ddagger = -54 \pm 6 \text{ J/(K mol)}$ . It is noteworthy that the value of  $\Delta S^\ddagger$  is more negative than the value for hydride fluxionality in  $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-CHCO}_2\text{Me})(\text{CO})_9$ <sup>13</sup> and related clusters in which only  $\mu\text{-H}$  ligands are present in the reactant state and for which a  $\mu\text{-H} \rightarrow \text{t-H}^\ddagger \rightarrow \mu\text{-H}$  mechanism is the preferred one.<sup>23</sup>

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(22)  $V[\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}] = 259 \text{ cm}^3/\text{mol}$ , on the basis of (disordered) crystal structure data.<sup>4</sup>  $V[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}] = 245 \text{ cm}^3/\text{mol}$ .<sup>17</sup>  $V[\text{Os}(\text{CO})_4]$  is estimated as  $0.33V[\text{Os}_3(\text{CO})_{12}] = 36 \text{ cm}^3/\text{mol}$ .<sup>4</sup>  $V[\text{Os}(\text{CO})_3]$  is estimated as  $0.25V[\text{H}_4\text{Os}_4(\text{CO})_{12}] = 74 \text{ cm}^3/\text{mol}$ ,<sup>14</sup> as  $0.25V[\text{Ir}_4(\text{CO})_{12}] = 69 \text{ cm}^3/\text{mol}$ ,<sup>18</sup> or as  $0.25V[\text{Rh}_4(\text{CO})_{12}] = 74 \text{ cm}^3/\text{mol}$ .<sup>19</sup>

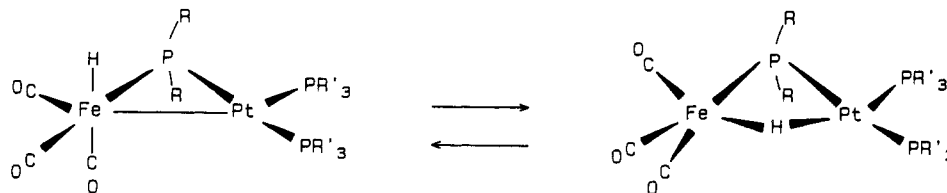


Figure 4. Equilibrium between  $(\text{OC})_3\text{HFe}(\mu\text{-PR}_2)\text{Pt}(\text{PR}'_3)_2$  and  $(\text{OC})_3\text{Fe}(\mu\text{-H})(\mu\text{-PR}_2)\text{Pt}(\text{PR}'_3)_2$ .

The activation volume,  $\Delta V^\ddagger$ , for exchange of the hydride ligands of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  was determined to be  $-0.8 (\pm 0.4) \text{ cm}^3/\text{mol}$  from measurements of the rate constants for exchange at pressures between 0.1 and 198 MPa (Table II). Since the experimental value was so close to zero, intermediate between the values predicted by the first-approximation model for the two possible mechanisms, it was necessary to increase the precision of the model by comparison of appropriate structural analogues in order to take into account changes in volume associated with the other ligands in the coordination sphere. The earlier estimate of the activation volume for  $\mu\text{-H} \rightarrow \text{t-H}$  migration assumed as a first approximation that the only contribution to  $\Delta V^\ddagger$  was due to the differing relative volumes of bridging and terminal hydrides. However, this is not strictly true, since the volume occupied by a given ligand type will depend also upon the packing of the ligands around the metal cluster core. Unlike the case for  $(\mu\text{-H})_2\text{Ru}_3(\mu\text{-CHCO}_2\text{Me})(\text{CO})_9$ , in which the non-hydride ligands are not involved in the fluxional process, the two CO ligands involved in the hydride exchange on  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\text{L}$  undergo large spatial displacements and would be expected to make significant contributions to  $\Delta V^\ddagger$ .

The estimate of  $\Delta V^\ddagger$  for hydride fluxionality requires knowledge of the partial molar volume of the reactant state structure and some method of estimating the relative partial molar volume of the proposed transition state. We will assume that the contribution due to electrostriction is small and will discuss  $\Delta V^\ddagger$  only in terms of the intrinsic volume changes due to changes in bond lengths and angles within the cluster. We will use the volume of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{11}$  and the estimated volume of the hypothetical molecule  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{11}$  as a comparison for  $\Delta V^\ddagger$  for hydride fluxionality in  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  through a transition state containing two bridging hydrides. The geometry of the transition state for the fluxional process described by path b of Figure 3 (two hydride bridges) is similar to the geometry of  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ , except that one  $\text{Os}(\text{CO})_3$  unit is replaced by an  $\text{Os}(\text{CO})_4$  fragment. The activation volume  $\Delta V^\ddagger$  may be estimated by using eq 2, the solid-state molar volumes for  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  and  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{11}$ , and estimates of the volume contribu-

tions of  $\text{Os}(\text{CO})_4$  and  $\text{Os}(\text{CO})_3$  fragments derived from the solid-state molar volumes of  $\text{Os}_3(\text{CO})_{12}$  and  $(\mu\text{-H})_4\text{Os}_4(\text{CO})_{12}$  or  $\text{M}_4(\text{CO})_{12}$  ( $\text{M} = \text{Rh}, \text{Ir}$ ).<sup>22</sup> In this way, the estimated

$$\Delta V^\ddagger = V\{(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}\} - V\{\text{Os}(\text{CO})_3\} + V\{\text{Os}(\text{CO})_4\} - V\{\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{11}\} \quad (2)$$

$\Delta V^\ddagger$  for hydride fluxionality through an intermediate containing two hydrides varies from  $-2$  to  $+3 \text{ cm}^3/\text{mol}$ , depending upon the choice of the volume of the  $\text{Os}(\text{CO})_3$  fragment. In any case, the solution molar volume for  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{11}$  would be slightly smaller than the crystal structure value because of the disorder problem of the latter, making the estimated  $\Delta V^\ddagger$  slightly more positive. The volume contributions due to solvation effects are difficult to predict but would most likely be small and positive, by analogy to bond rotation in organic systems.<sup>5</sup>

The intrinsic activation volume for hydride fluxionality of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  through the doubly bridged transition state should be close to that estimated for  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{11}$ . All of the above arguments can account for the experimentally determined  $\Delta V^\ddagger$  value,  $-0.8 \text{ cm}^3/\text{mol}$ , being less negative than the initial estimate of  $-7 \text{ cm}^3/\text{mol}$  for  $\text{t-H} \rightarrow \mu\text{-H}$  hydride migration, with the best estimate based upon model compounds being ca.  $0 \text{ cm}^3/\text{mol}$ .

On the other hand, a transition state containing two terminal hydrides cannot be smaller in volume than the reactant state. A similar treatment of ligand-packing geometry for a transition state with two terminally coordinated hydrides would lead to a substantially positive  $\Delta V^\ddagger$ . The overall geometry of CO and hydride ligands would be similar to that for the transition state containing two bridging hydrides as described above, so all volume contributions from the change in the arrangement of CO ligands are the same; however, the volume contribution from the two terminal hydrides would be significantly greater than that due to two bridging hydrides because the former are not as geometrically constrained. Therefore, evidence provided by the volume of activation favors a transition state containing two bridging hydrides. This interpretation is also consistent with the more negative value reported here for the activation entropy.

Further support for the presence of two bridging hydrides in the transition state is provided by the close similarity between the kinetic behavior of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\text{L}$  and the thermodynamics of the isomerization between  $(\text{CO})_3\text{HFe}(\mu\text{-PR}_2)\text{Pt}(\text{PR}'_3)_2$  and  $(\text{CO})_3\text{Fe}(\mu\text{-PR}_2)(\mu\text{-H})\text{Pt}(\text{PR}'_3)_2$ . The  $(\text{CO})_3\text{HFe}(\mu\text{-PR}_2)\text{Pt}(\text{PR}'_3)_2/(\text{CO})_3\text{Fe}(\mu\text{-PR}_2)(\mu\text{-H})\text{Pt}(\text{PR}'_3)_2$  system, shown in Figure 4, is a unique one in that isomers having bridging and terminal hydride ligands have almost the same free energies. Crystal structures of an example of each isomer have been reported, and in solution the two isomers are in equilibrium (confounding the generalization that bridging hydrides are more stable than terminal hydrides).<sup>11</sup> The similarities between this equilibrium and fluxionality in  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\text{L}$  include (1) closely related structural changes and (2) a direct relationship between  $\Delta G^\ddagger$  for hydride fluxionality for  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\text{L}$  and  $\Delta G^\circ$  for the rear-

(23) It has been observed that there is a nearly linear correlation between  $\Delta S^\ddagger$  and  $\Delta V^\ddagger$  for isomerization reactions of coordination complexes which proceed via associative or dissociative mechanisms. However, intramolecular isomerizations invariably display more negative values for  $\Delta S^\ddagger$  than would be expected from their small absolute values of  $\Delta V^\ddagger$ . It has been argued that an appreciably negative value for  $\Delta S^\ddagger$  and near-zero value for  $\Delta V^\ddagger$  are characteristic of a trigonal-twist isomerization, in contrast with dissociative and associative mechanisms which display normal  $\Delta S^\ddagger$ - $\Delta V^\ddagger$  relationships.<sup>24</sup> The values of  $\Delta S^\ddagger$  and  $\Delta V^\ddagger$  determined here for hydride fluxionality fall in the same range as those for trigonal-twist isomerizations of monometallic complexes.

(24) Lawrance, G. A.; Suvachittanont, S. *Inorg. Chim. Acta* 1979, 32, L13.

(25) The application of solid-state molar volumes as an indication of solution partial molar volumes must be viewed with caution, since crystal-packing forces and solute-solvent interactions are unlikely to be identical. The values of the volume differences would be best estimated from solution measurements, but solution molar volumes have not been determined for these compounds.

rangement of  $(\text{CO})_3\text{HfFe}(\mu\text{-PR}_2)\text{PtL}_2$  to the isomer containing the bridging hydride. For both systems the isomerization process involves rotational movement of a terminal hydride and two CO ligands about an axis defined by a metal-CO bond to place the hydride in a bridging position; the  $\text{Os}_3$  cluster differs primarily in the presence of a second hydride ligand that remains bridging the metal-metal vector in both the reactant state and the proposed transition state. For both systems the energetics of the dynamic process are influenced by the identities of the phosphine ligands. Thus,  $\Delta G^\circ$  for the equilibrium in Figure 4 and  $\Delta G^\ddagger$  for hydride exchange on  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\text{L}$  both decrease as  $\text{L} = \text{P}(\text{OPh})_3 > \text{PPh}_3 > \text{PEt}_3$ . This trend is most likely due to the stabilization of the bridging hydride, relative to the energy of terminal coordination, by the presence of more basic phosphines on the bridged metal atoms. If the transition state for hydride

exchange in  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\text{L}$  were to involve two terminal hydrides, then the  $\Delta G^\ddagger$  value for exchange would be expected to increase as the basicity of L increases.

**Conclusions.** We have shown here that activation volumes for hydride fluxionality on metal clusters, while small in magnitude, can be measured and that the activation volume may allow a distinction to be made between possible mechanisms for intramolecular processes. The two values measured in this work support the proposal that migration of a bridging hydride to a terminal coordination site is associated with a positive change in volume.

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## Syntheses of [Ethylene-1,2-bis( $\eta^5$ -4,5,6,7-tetrahydro-1-indenyl)]zirconium and -hafnium Hydride Complexes. Improved Syntheses of the Corresponding Dichlorides

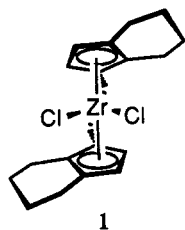
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Treatment of  $(\text{EBTHI})\text{MCl}_2$  [ $\text{M} = \text{Zr}$ , 1;  $\text{M} = \text{Hf}$ , 2; EBTHI = ethylene-1,2-bis( $\eta^5$ -4,5,6,7-tetrahydro-1-indenyl)] with 2 equiv of  $\text{NaEt}_3\text{BH}$  in  $\text{C}_6\text{H}_6$  produces the hydride dimers  $[(\text{EBTHI})\text{MH}(\mu\text{-H})_2]$  ( $\text{M} = \text{Zr}$ , 3;  $\text{M} = \text{Hf}$ , 4). The dimethylhafnium complex  $(\text{EBTHI})\text{HfMe}_2$  (5) is formed when 2 is treated with  $\text{MeLi}$  in  $\text{C}_6\text{H}_6$ . Complexes 3 and 4 can be protonated with the weak acid  $[\text{PhMe}_2\text{NH}][\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$  to give monomeric cationic hydrides  $[(\text{EBTHI})\text{M}(\text{H})(\text{NPhMe}_2)][\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$  ( $\text{M} = \text{Zr}$ , 6;  $\text{M} = \text{Hf}$ , 7), in which the *N,N*-dimethylaniline ligand is very weakly coordinated to the metal. Improved syntheses of the dichloride complexes 1 and 2 are also described.

The synthesis of chiral, enantiomerically pure group 4 metallocene complexes has been an active area of research in the last few years, partly because these complexes show promise in effecting asymmetric synthesis.<sup>1-3</sup> The chiral zirconocene complex,  $(\text{EBTHI})\text{ZrCl}_2$  (1, EBTHI = ethyl-



ene-1,2-bis( $\eta^5$ -4,5,6,7-tetrahydro-1-indenyl)) was first reported by Brintzinger,<sup>4</sup> and a modified synthesis of 1 was later published by Collins.<sup>5</sup> The analogous hafnium

complex,  $(\text{EBTHI})\text{HfCl}_2$  (2), has also been prepared, although in low yield.<sup>6</sup> As part of an ongoing project in which the utility of such compounds in asymmetric synthesis is being examined, we have prepared several derivatives of 1 and 2. Herein we report the syntheses of the bridged hydride dimers  $[(\text{EBTHI})\text{MH}(\mu\text{-H})_2]$  ( $\text{M} = \text{Zr}$ , 3;  $\text{M} = \text{Hf}$ , 4) and the dimethylhafnium compound  $(\text{EBTHI})\text{HfMe}_2$  (5). Protonation of 3 or 4 with the weak acid,  $[\text{PhMe}_2\text{NH}][\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ , gives the corresponding cationic monomeric hydride species  $[(\text{EBTHI})\text{M}(\text{H})(\text{PhNMe}_2)][\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$  ( $\text{M} = \text{Zr}$ , 6;  $\text{M} = \text{Hf}$ , 7); the former, when enantiomerically enriched, catalyzes the asymmetric hydrogenation of  $\alpha$ -ethylstyrene. In addition, improved syntheses for the dichloride complexes 1 and 2 are also described.

### Experimental Section

**General Procedures.** All manipulations were performed by using either a Vacuum Atmospheres drybox under  $\text{N}_2$  or a Schlenk line under Ar, unless stated otherwise. Solvents were purified

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