Activation of Benzene by a Tetrakis(trimethylphosphine)osmium(II) System. The Mechanism of Activation

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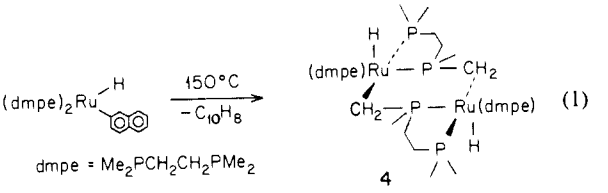
Abstract: The intermolecular activation of the carbon–hydrogen bond in benzene has been investigated by the thermolysis of *cis*-$L_4Os(H)R$ ($L = P(CH_3)_3$; $R = CH_3$, **1**; $R = CH_2C(CH_3)_3$, **2**; $R = CH_2Si(CH_3)_3$, **3**). Thermolysis of **2** at 70 °C in benzene results in activation of the arene C–H bonds to afford $L_4Os(H)(C_6H_5)$, **6**, quantitatively. This reaction is shown to proceed, in the case of **2**, via initial reversible L dissociation to form an unsaturated intermediate, $L_3Os(H)Np$, **9**, which is configurationally stable during its lifetime and which rapidly and reversibly activates the C–H bonds of its own neopentyl ligand. Unsaturated intermediate **9** reacts with benzene by oxidative addition of Ar–H to form an Os(IV) intermediate, $L_3Os(H)_2(Np)(Ar)$, which then undergoes reductive elimination of NpH. The activation step exhibits a kinetic isotope effect, $k_{C_6H_6}/k_{C_6D_6}$, of 3.32 ± 0.30. The thermolyses of **3** in benzene were shown to proceed by the same mechanism of initial dissociation of L, followed by oxidative addition of benzene, reductive elimination of $SiMe_4$, and uptake of L. The unsaturated intermediate in this case, $L_3Os(H)(CH_2SiMe_3)$, **10**, also rapidly and reversibly activates the γ-C–H bond of its own CH_2SiMe_3 ligand. The measured rates of phosphine dissociation for **1**, **2**, and **3** establish a strong steric influence of the alkyl group on the ease of this dissociation.

The mild intermolecular activation of carbon–hydrogen bonds of hydrocarbons by soluble transition-metal complexes is a subject of considerable current interest, and progress in the area has been extensively reviewed.[1] In the context of our work on other aspects of hydrocarbon activation,[2] we became interested in the issue of C–H activation. In particular, we were intrigued by the obvious questions of why molecules containing cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) ligands appear to activate alkanes so much more readily than other complexes, and what factors favor intermolecular over intramolecular activation. This has led us to investigate the reaction chemistry of the system $L_4Os^{II}XY$, where L = PMe_3 and X and Y are various hydrido, alkyl, and aryl ligands.

We have observed the mild activation of carbon–hydrogen bonds, both intramolecularly and intermolecularly by intermediates generated by the thermolysis of *cis*-$L_4Os(H)R$ ($L = P(CH_3)_3$; $R = CH_3$, **1**; $R = CH_2C(CH_3)_3$, **2**; $R = CH_2Si(CH_3)_3$, **3**). In particular, thermolysis of **2** at 80 °C results in C–H bond activation in the coordinated neopentyl (Np) group, in arenes, in tetramethylsilane, and in trimethylphosphine (L), the last proceeding by two distinct mechanisms.[3] The intermolecular activation of alkanes in this system has not yet been observed.

The literature already contains numerous examples of interesting hydrocarbon activation chemistry in iron-group phosphine complexes. Very early, Chatt and Hayter[4] prepared a number of cis and trans, dmpe and diphos hydrido alkyl complexes of Ru and Os, some of which exhibited remarkable stability. Perhaps the earliest structurally well-defined example of an intermolecular C–H activation was the formation of the ruthenium dimer **4** by Chatt and Davidson[5] (eq 1). Later, Tollman and co-workers[6]



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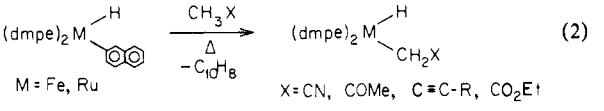
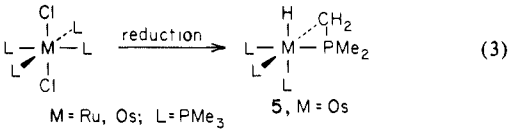
studied the activation of C–H bonds in organic materials by the iron and ruthenium species shown in eq 2. Since all of these activations proceeded at the same rate for a given metal, it was



(2)

concluded that the reductive elimination of naphthalene to form M(0) was the rate-determining step. The corresponding Os complex was found to be extremely stable, and little was done with it.

Some alkyl hydride complexes of ruthenium and osmium, such as $(Me_3P)_4Ru(H)Me$[7] and $(dmpe)_2Os(H)(naphthyl)$,[6] are thermally very stable, and this stability toward reductive elimination may be largely thermodynamic. It is possible that if unsaturated, low valent $Os(PR_3)_n$ fragments could be generated, they would have substantial thermodynamic driving force for the activation of C–H bonds. Some such activations have been reported recently. Werner and co-workers have observed the reduction of eq 3 for



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(1) For extensive references outlining the development of this subject see: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269. (b) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139–144. (c) DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 124–133. (d) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27–35. (e) Crabtree, R. H.; Demoy, P. C.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994–7001. (f) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1235–1236. (g) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929–3939. (h) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190–7191. (i) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491–6493. (j) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620–631. (k) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2214–2216. (l) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550.

(2) (a) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076–6077. (b) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795–1803.

(3) Parts of this work have been the subject of a preliminary communication: Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1346–1347.

(4) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1963**, 6017–6027.

(5) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843–855. The correct structure of this dimer was assigned by: Cotton, F. A.; Hunter, D. L.; Frenz, B. A. *Inorg. Chim. Acta* **1975**, *15*, 155–160.

(6) Tollman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080–4089.

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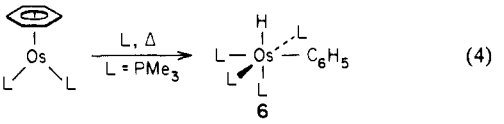
both ruthenium[8a] and osmium[8b] wherein the PMe_3 ligand has been internally metalated. The iron complex analogous to **5** has been known for many years but is substantially less stable than **5**.[9]

Several arene activations have been reported including the intramolecular activation of benzene shown in eq 4, which forms **6**.[10] Reduction of the trimethylphosphite complexes of ruthenium and osmium in benzene as shown in eq 5 affords indirect examples of arene activation.[11]



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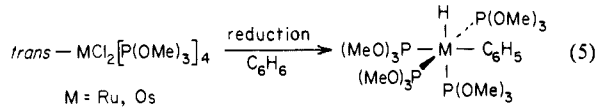
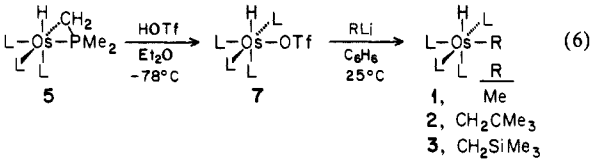


(5)

The present paper describes our investigations on C–H bond activations in arenes. Oxidative additions of nonaromatic C–H bonds will be discussed elsewhere. In view of the numerous examples of arene activation, the contribution of the present work is the cleanness and stability of the system which results in the ability to obtain detailed mechanistic information. Also, in contrast to all of the examples mentioned above in eq 1–5, the C–H activation chemistry reported here has been found to proceed via Os(IV) intermediates and not Os(0). Our results suggest that in a very electron-rich environment, the Os(II)–Os(IV) couple may provide the basis for more tractable catalytic systems than the Os(0)–Os(II) couple.

Results and Interpretations

Preparation of the alkyl hydrido complexes **1–3** begins with compound **5**, which is synthesized by the procedure of Werner and Gotzig (eq 3).[8b] Treatment of complex **5** with trifluoromethanesulfonic acid (triflic acid, HOTf) at −78 °C (eq 6) affords high yields of hydrido triflate complex **7** as an isolable white solid.



(6)

Although the Os–O bond of **7** is probably covalent, reversible ionization of this material in solution is apparently rapid, judging from its ^{31}P NMR spectrum in THF. This spectrum contains a sharp triplet for the two mutually trans phosphines, but the resonances of the two mutually cis phosphines are broadened almost into the base line. At 220 K, the latter resonances are sharp doublets of triplets. Apparently the unsaturated cation L_4OsH^+ is either a trigonal bipyramid or a square pyramid which is fluxional, in effect, only in that the hydride rapidly switches between the two cis sites. On the basis of our observations of the stereochemistry of exchange of L with **2** and **3** (vide infra), we favor the latter explanation. Complex **7** has an extensive and interesting chemistry with ligands and reactants such as H_2, alkenes, phosphines, etc., which will be reported on independently.

Alkylations of **7** with lithium reagents to form **2** and **3** (eq 6) are clean, high-yield reactions. Methyllithium and **7** in near stoichiometric ratios tend to form significant amounts of L_4OsH_2, **8**, in addition to **1**, and to date we have been unsuccessful in separating the two. However, use of a ca. 10-fold molar excess of MeLi yields essentially pure **1**. Reactions of **7** with *n*-butyl- and *n*-pentyllithium do seem to afford the corresponding $L_4Os(R)H$ species, but they are invariably contaminated with large amounts of inseparable dihydride **8** and so have not been completely characterized. ^1H and ^{31}P NMR spectral data for new compounds are given in the Experimental Section.

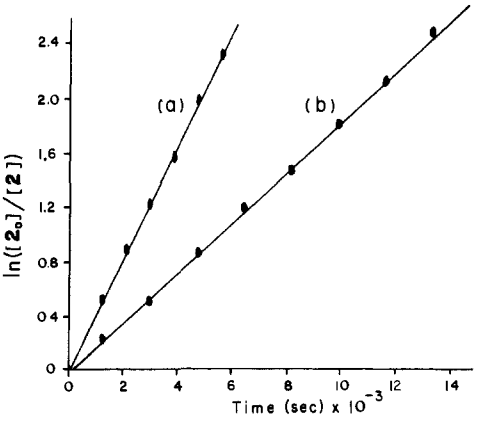


Figure 1. Kinetic plot of thermolysis of **2** in (a) benzene and (b) benzene-d_6 at 80 °C.

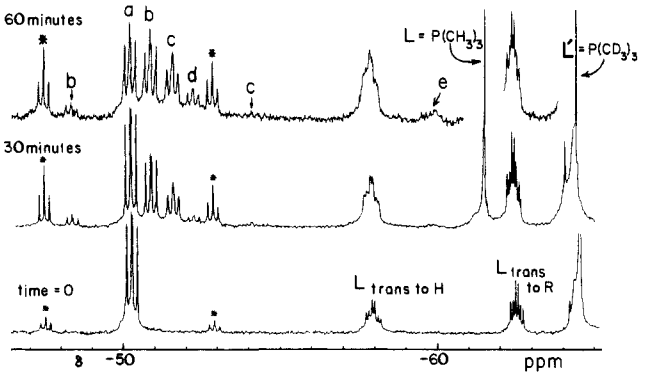
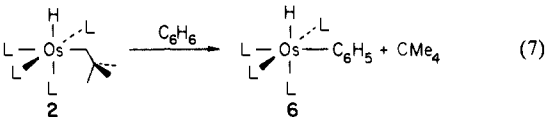


Figure 2. $^{31}P\{^1H\}$ NMR spectra of the exchange between **2** and $P(CD_3)_3$ in C_6H_6 at 70 °C. See the text and eq 8 for assignments. The two triplets designated * are L_4OsH_2, **8**, which integration shows do not increase in intensity relative to the total L_a, L_b, L'_c, and L'_d intensities.

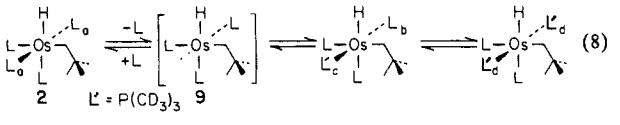
Heating of the neopentyl hydride complex **2** in benzene results in quantitative (by NMR) formation of the known[10] complex $L_4Os(H)(C_6H_5)$, **6** (eq 7). The kinetic plot is cleanly first order



(7)

for several half-lives (Figure 1), with k_{obsd} (80 °C) = 3.61 ± 0.05 × 10^{-4} s^{-1}. Occasionally, after ca. two half-lives, slight curvature might appear, but this is eradicated by the addition of several mole percent of neopentyllithium (NpLi); rates are independent of the NpLi concentration.

The benzene activation by **2** is strongly inhibited by added L. In addition, when **2** is heated at 70 °C in benzene in the presence of a large excess of $P(CD_3)_3$, L′, the labeled ligand was incorporated specifically into the positions of the two mutually trans phosphines (eq 8). Figure 2 shows ^{31}P NMR spectra for this



(8)

transformation. Resonance a corresponds to two mutually trans ligands, L_a (eq 8), resonances b and c comprise an AB pattern for nonequivalent L_b and L'_c trans to one another, and d corresponds to two mutually trans L'_d ligands. Corresponding L′ resonances begin to appear for the two mutually cis ligands (e.g.,

(8) (a) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*, C60–C64. (b) Werner, H.; Gotzig, J. *Organometallics* **1983**, *2*, 547–549.

(9) (a) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Chem. Ber.* **1977**, *110*, 2200–2212. (b) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637–638. (c) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272–3273.

(10) (a) Werner, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 793–794. (b) A related example: Bandy, J. A.; Green, M. L. H.; O'Hare, D.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1402–1404.

(11) Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73–93.

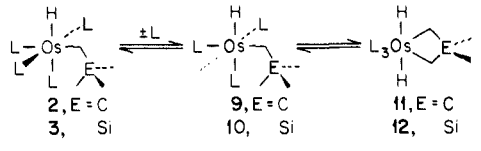
e) only after the trans positions are substantially exchanged, but eventually, all four ligands are fully exchanged. All of these ligand-exchange reactions were followed just as well by ^{1}H NMR. The rate constants at several temperatures for this exchange were k_1 (36 °C) = 2.05 ± 0.04 × 10^{-6}, (56 °C) = 3.65 ± 0.07 × 10^{-5}, and (67 °C) = 1.58 ± 0.02 × 10^{-4} s^{-1}. These yield E_a = 29.2 ± 0.5 kcal/mol and $\Delta S^{\ddagger}$ = 10.0 ± 1.6 eu, which allows calculation of k_1 (80 °C) = 7.25 ± 0.14 × 10^{-4} s^{-1}. It is somewhat surprising that it is the trans ligands which exchange, since conventional wisdom regards hydrides and alkyls as having trans effects somewhat larger than phosphines in octahedral complexes. We conclude from the inhibition and exchange data (1) that arene activation proceeds via ligand dissociation and (2) that the unsaturated intermediate, **9**, has a square-pyramidal structure which is relatively rigid during its lifetime.

Complexes **1** and **3** undergo the same clean first-order reaction as **2** in benzene but at higher temperatures. (Trimethylsilyl)methyl hydride complex **3** reacts at 80 °C with k_{obsd} = 2.64 ± 0.10 × 10^{-6} s^{-1} to form **6**. Addition of excess L′ results in strong inhibition of the reaction and leads to the incorporation of L′ in a way analogous to **2** with k_1 = 9.6 ± 0.5 × 10^{-6} s^{-1}, about 4 times faster than k_{obsd} for the benzene activation. The ligand exchange for **3** is stereospecific in the same way as for **2**, with trans L preferentially dissociating. Methyl hydride complex **1** reacts with benzene solvent to form **6** at 105 °C with k_{obsd} = 1.01 ± 0.02 × 10^{-6} s^{-1}. Again, added L′ strongly inhibits the reaction and leads to the incorporation of L′, except that in this case the incorporation is stereorandom. We cannot tell whether at this temperature the dissociation is stereorandom or if the intermediate is formed stereospecifically but is then fully fluxional during its lifetime. The rate of ligand exchange of **1** is 1.9 ± 0.2 × 10^{-6} s^{-1}, only ca. 2 times faster than k_{obsd} for the benzene reaction. In addition, the thermolysis of **1** in benzene at 105 °C is not sensitive to the presence of NpLi or Na metal.

Overall, it is clear that the thermolyses of **1**, **2**, and **3** in benzene all proceed via initial phosphine dissociation. Furthermore, the substantial differences in the values of k_1 and their corresponding temperatures for these molecules clearly demonstrate that the driving force for this dissociation of L is steric in nature.

The most rapid reaction of the unsaturated intermediate **9** that we have detected is the intramolecular activation of a γ-C–H bond of the Np group. Pyrolysis of $L_4Os(H)[CH_2C(CH_3)(CD_3)_2]$, **2**-$d_6$, in benzene would be expected to yield $C(CH_3)_2(CD_3)_2$, NpH-d_6, which would be unscrambled. In fact, mass spectral analysis of the NpH-d_6 (see Experimental Section) shows it to be nearly random in the location of the six deuteriums throughout the molecule. The randomization can be followed by ^{1}H NMR upon heating **2**-d_6 in C_6D_{12}. The Np methyl resonance at δ 1.02 and the methylene resonance at δ 1.16 diminish, while resonances at 1.00 and 0.98 ppm grow in. The randomization is clearly intramolecular, since the results of the mass spectral analysis of NpH-d_6 are the same whether the reaction is conducted in C_6H_6 or in C_6D_6. Also, mass spectral analysis of the neopentane resulting from pyrolysis of a 1:1 mixture of **2** and **2**-d_6 in C_6H_6 revealed no NpH-d_1 or NpH-d_2 above natural abundance, demonstrating no intermolecular exchange of label.

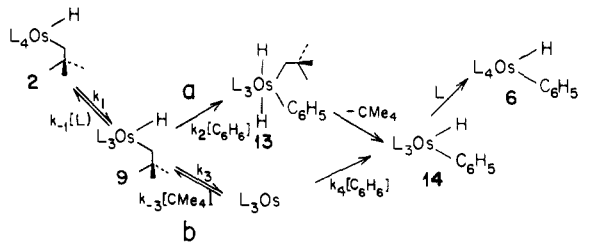
These results are consistent with the reaction sequence of eq 9 proceeding through cyclometalated intermediate **11**. The requirement for this exchange to proceed through the unsaturated intermediate **9** is consistent with the observation that the qualitative



(9)

rate at which the two exchanged peaks appear at δ 1.00 and 0.98 in the ^{1}H NMR spectrum of **2**-d_6 at 70 °C in C_6D_{12} is slightly slower than the rate of phosphine exchange in **2** but faster than the reaction with benzene. A rigorous determination of the rate was made impractical by difficulties in integration of the Np methylene resonances.

Scheme I



To test whether unsaturated intermediate **10** arising from dissociation of L from **3** would also exhibit intramolecular activation of its alkyl ligand, $L_4Os(H)[CH_2Si(CH_3)(CD_3)_2]$, **3**-$d_6$, was prepared. Thermolysis of **3**-d_6 was carried out in benzene, and the liberated $SiMe_4$-d_6 was analyzed by mass spectroscopy (see Experimental Section). This analysis revealed the deuterium label to be nearly randomly located. Thus, **10** is rapidly and reversibly converted to the metallacyclic intermediate **12** in complete analogy with the corresponding intermediates **9** and **11**.

Intermediate **9** most likely would activate benzene in one of the two ways shown in Scheme I. Involvement of Os(IV) intermediate **13** (path a) and not an Os(0) species (path b) is substantiated by kinetic and by isotopic labeling evidence. Use of C_6D_6 as solvent (Figure 1) reveals a kinetic isotope effect (k_{obsd} (80 °C) = 1.64 ± 0.03 × 10^{-4} s^{-1}), k_H/k_D = 2.20 ± 0.07, establishing that benzene is activated in the rate-limiting step. The possibility exists that the benzene activation could be reversible and reductive elimination of neopentane could be rate determining. We believe this is substantially less likely than for k_2 to be rate determining, for reasons given in the Discussion section. The kinetic expressions for mechanisms a and b would be

for mechanism a

$$\frac{-d[\mathbf{2}]}{dt} = \frac{k_1k_2[\mathbf{2}][C_6H_6]}{k_{-1}[L] + k_2[C_6H_6]} \tag{10}$$

leading to the relationship

$$1/k_{obsd} = \frac{k_{-1}[L]}{k_1k_2[C_6H_6]} + \frac{1}{k_1} \tag{11}$$

and for mechanism b

$$\frac{-d[\mathbf{2}]}{dt} = \frac{k_1k_3k_4[\mathbf{2}][C_6H_6]}{k_{-1}k_{-3}[L][NpH] + (k_{-1}[L] + k_3)k_4[C_6H_6]} \tag{12}$$

leading to the relationship

$$1/k_{obsd} = \frac{k_{-1}k_{-3}[L][NpH]}{k_1k_3k_4[C_6H_6]} + \frac{k_{-1}[L]}{k_1k_3} + \frac{1}{k_1} \tag{13}$$

It may be seen from eq 11 and 13 that either mechanism would require that plots of $1/k_{obsd}$ vs. $1/[C_6H_6]$ be linear. This is found to be the case (Figure 3). If oxidative addition of benzene to L_3Os were rate limiting, then either L_3Os must build up in concentration or the formation of L_3Os by reductive elimination must be rapidly reversible. L_3Os concentration does not build up. It is also highly improbable that the NpH reductive elimination could be rapidly reversible because the first term in the denominator of eq 12 must be dominant, since kinetic dependence on benzene concentration is observed, and so there should be increasing inhibition as the concentration of NpH would build up during the course of the reaction. No such nonlinearity is observed. In addition, NpH is not activated by this system under any conditions that we have tried. Thus, the kinetics argue strongly against path b.

Equation 11 also quantitatively describes the phosphine inhibition of benzene activation as a dependence of $1/k_{obsd}$ on [L]. This has also been demonstrated to be the case as shown in Figure 4 for both C_6H_6 and C_6D_6 solvents. From the slopes of these plots, the k_2/k_{-1} ratios are determined to be 6.37 ± 0.64 × 10^{-6} for C_6H_6 and 1.92 ± 0.06 × 10^{-6} for C_6D_6. The isotope effect k_H/k_D for the k_2 step itself is therefore 3.32 ± 0.30. Furthermore, one

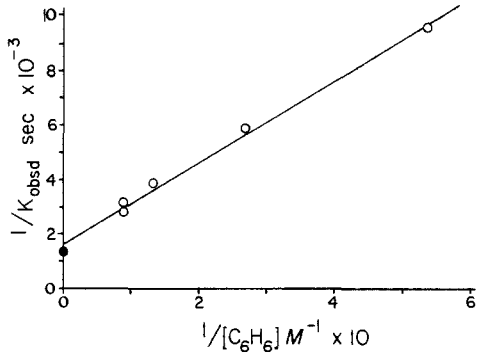


Figure 3. Plot of $1/k_{obsd}$ vs. $1/[C_6D_6]$ for the reaction of eq 1 in neat C_6D_6 or in C_6D_6 diluted in cyclohexane at 80 °C. The *Y*-intercept point is k_1 determined from phosphine-exchange kinetics.

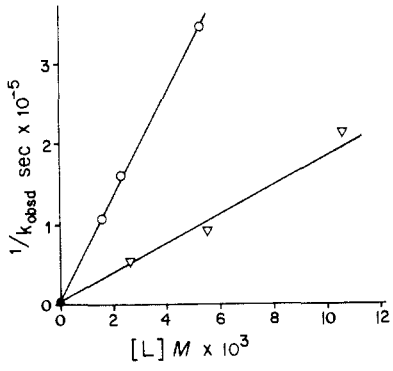
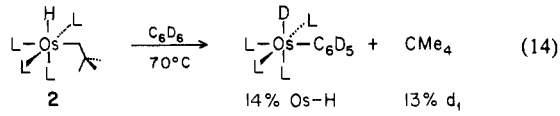


Figure 4. Plot of $1/k_{obsd}$ vs. [L] for the reaction of eq 1 at 80 °C; ▽ = C_6H_6 solvent, ○ = C_6D_6 solvent. The *Y*-intercept point is k_1 determined from phosphine-exchange kinetics.

calculates that the steady-state concentration of L when none is added to the benzene activation reaction is 7.3×10^{-5} M.

Additional corroboration of the isotope effect for the k_2 step comes from a straightforward solvent competition experiment. Thermolysis of **2** in a 1:1 mixture of benzene and benzene-d_6 leads to a competition for unsaturated intermediate **9** by the two solvents, independent of the $k_{-1}[L]/k_2$ ratio, and thus gives a direct measure of $k_{2(H)}/k_{2(D)}$. The ratio of **6** with phenyl-d_0 vs. phenyl-d_5 groups was determined by ^{1}H NMR integration of the phenyl resonance of **6** with respect to its phosphine resonances, and yielded an isotope effect of 3.6 ± 0.3.

The following isotopic labeling experiments corroborate that both C_6H_6 and NpH are present on the metal at the same time at some point, presumably in **13**. When the pyrolysis of **2** is conducted in C_6D_6, the hydride ligand in **6** is 86 ± 4% deuterated as determined by ^{2}H NMR, and the NpH is 13 ± 2% d_1 by mass spectral analysis (eq 14). These numbers are reproducible over



(14)

five different reactions at four different concentrations of C_6D_6 (neat C_6D_6 or in cyclohexane solvent). Starting material **2** shows no large incorporation of deuterium throughout the reaction, and product **6**-d_6 exhibits no H/D exchange with C_6H_6 solvent upon heating for 100 h at 80 °C. It is conceivable that an unsaturated intermediate such as **14** might undergo bimolecular exchange with starting material and/or intermediate **9** might exchange with product. Either of these would give the same crossover result which we observe, and low levels of incorporation of deuterium into the hydride site of **2** might not be detectable in the ^{31}P NMR spectra used to monitor the reaction. To test this, the reaction of **2** with C_6D_6 was run in the presence of a 4-fold molar excess of unlabeled **1**. Since the methyl group is smaller than either Np or Ph, **1** should exchange more readily with **9** and **14** than either **6** or **2**. This should cause depletion of the deuteride in **6**-d_6 well in excess of 14% and should reduce the quantity of NpH-d_1 to much less than 13%. No change in the deuterium distribution of the products was detected in this experiment. Additionally, when a 1:2 molar mixture of **1** and **6**-d_6 was heated in hexanes at 125 °C for several days, no exchange of deuterium was observed.

It is clear that the activation of benzene by **3** proceeds by the same mechanism as does **2**, because of the above-mentioned inhibition of the reaction by added L and incorporation of L′ at a faster rate than k_{obsd}. The presence of an Os(IV) intermediate analogous to **13** is indicated by an isotope effect, k_H/k_D = 1.43 ± 0.08, for the reaction of **3** with C_6H_6 vs. C_6D_6. The measured isotope effect for the reaction of **1** with benzene, k_H/k_D = 1.10 ± 0.05, may be significant, but we are not confident that it is experimentally different from 1.0. Our ability to distinguish between paths a and b for this substrate is tenuous.

Discussion

This L_4Os^{II} system is an unusual example of a system of soluble, mononuclear, non-cyclopentadienyl-containing metal complexes which contains a rich variety of C–H bond activation reactions that are amenable to close mechanistic scrutiny because they are very clean. In regard to the cleanness of this system, in hydrogenolysis reactions of **1** and **5** we have found catalysis by water and by nonhydroxylic protic acids,[12] and so we were concerned initially about possible effects of spurious catalysts in the benzene activation. As mentioned above, in the activation of benzene by **2**, slight curvature of the first-order plots was occasionally found after several half-lives. This curvature was completely eliminated by the addition of several mole percent of NpLi, but the reaction was otherwise insensitive to the concentration of NpLi. In the case of **1** reacting with benzene at 105 °C, addition of ca. 8 mol % of $[L_4OsH_3]OTf$ lead to a rate increase of ca. 50%. In view of these observations, as a general precaution ca. 1–3 mg of NpLi was added to each NMR tube. In this way reliable reproducibility was obtained.

In view of published precedent, we had anticipated that species of type **1**–**3** would be quite stable, and indeed the half-life for reaction of **1** with benzene solvent, for example, is ca. 1 week at 105 °C. It had seemed that the inertness of these molecules to ligand dissociation might at least in part account for this stability, since there is currently significant precedent for a preference, if not a requirement, for coordinative unsaturation in oxidative addition and reductive elimination reactions in square-planar or octahedral complexes of second- and third-row transition metals.[13] The need for unsaturation is established for all three complexes, **1**–**3**, by the inhibition and exchange studies with labeled phosphine. That ligand dissociation is driven by steric crowding seems very likely here, since the reactivity order as shown by the temperature required to obtain comparable magnitudes of k_1 of **2** > **3** > **1** is clearly in line with the size of the alkyl groups. There is no obvious regular electronic change over this series.

The need for phosphine dissociation in the reactions of **1**–**3**, however, is not related to the need for pentacoordination for reductive elimination of R–H to generate Os(0), as we had anticipated. In fact, we have found that while the half-life for phosphine exchange in **2** is ca. 16 min at 80 °C, in non-arene solvent at 80 °C **2** has a half-life of a week or more to afford **5**.[12] We believe, therefore, that the stability of complexes **1**–**3** to reductive elimination whether via five- or six-coordinate intermediates is thermodynamic to a significant degree and speaks of strong M–H and/or M–C bonds.

In all of our investigations of L_4OsXY to date, we have observed only cis geometric isomers. With one exception, we have seen no trace of any molecule to which we can assign a trans geometry.

(12) This work will be described in detail elsewhere: Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C., unpublished results.

(13) (a) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1973**, *12*, 362–368. (b) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725. (c) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227–5228. (d) Basato, M.; Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 3972–3976.

The stereospecific nature of the phosphine exchange reactions of **2** and **3** and the probable square-pyramidal geometry of the cation resulting from ionization of **7** suggest significant barriers to isomerization of unsaturated intermediates. Nevertheless, ligand substitution in **1** is stereorandom, substitution in **2** and **3** eventually is random, and unsaturated intermediates **9** and **10** do rapidly form seven-coordinate Os(IV) intermediates **11** and **12** which probably are relatively stereochemically labile. Thus, there are probably several paths which could lead to formation of trans products in many of the reactions of the L_4OsXY system if such isomers were thermodynamically favorable. We conclude, therefore, that the cis isomers are generally the thermodynamic isomers in this system. The one exception in our experience is the formation of L_4OsCl_2 by reaction of $(Ph_3P)_3OsCl_2$ with L which yields only the trans isomer. We do not understand this exception.

The kinetic data and deuterium crossover in reactions of C_6D_6 with **2** clearly point to an Os(IV) intermediate. This is in stark contrast to all of the related Ru and Os chemistry quoted above in the introduction. Higher oxidation state hydride complexes of the type $OsH_{2n}(phosphine)_{5-n}$ (n = 1–3) are well-known,[14] and even osmium(IV) alkyl phosphine complexes are known,[15] but apparently alkyl hydride complexes of Os(IV) are not stable. We believe this is consonant with a general trend of weaker M–H and M–C bonds in higher oxidation states of M.

In regard to the deuterium crossover of eq 14, the 13% crossover could be interpreted as the relative rate of reductive elimination of NpH vs. NpD from the deuterated analogue of **13**, $L_4OsH(Np)D(C_6D_5)$, which would correspond to k_H/k_D of 6.7. We believe this is much too large an effect for this type of reaction.[13b,c,16] A simple hypothesis to explain this number is to note that in analogy to the five-coordinate intermediate **9**, which is relatively rigid during its lifetime, a seven-coordinate species such as **13** need not be so geometrically mobile as to render the H and D completely equivalent, and the intermediate need not be symmetrical in its spacial disposition of the two isotopes in regard to the neopentyl group. For these reasons it is not possible to infer the size of the isotope effect for this reaction.[17]

The rapid intramolecular deuterium scrambling in **2**-d_6 strongly suggests the intramolecular activation of the neopentyl group as depicted in eq 9. This indicates a substantial kinetic facility of L_3OsHR, **9**, to oxidatively add R′–H to form the Os(IV) complex **11**. Clearly, there is no enthalpic problem (thermodynamic or kinetic) for C–H activation by **9**. This conclusion is reinforced by the observation that the (trimethylsilyl)methyl group in the unsaturate **10** also efficiently cyclometalates to form **12**. The L/L′ exchange reaction of **2** (eq 8) strongly suggests that **9** is square pyramidal, so that **9** would have a vacant σ-symmetry lowest unoccupied molecular orbital (LUMO) and a pair of filled π-symmetry highest occupied molecular orbitals (HOMOs) (d_{xz}, d_{yz}). Complex **9** would then have the "carbene"-like electronic configuration (with the HOMO and LUMO symmetries reversed) which is currently regarded as optimum for C–H oxidative additions.[18] It is difficult to say whether the absolute energies of the HOMO and LUMO and their energy separation are more favorable for the very electron rich **9** than for other pentacoordinate d^6 species, such as $W(CO)_5$ or $Os(CO)_3H(CH_3)$. Structural features of these other types of systems may not be appropriate to detect C–H activation reactions, or experimental conditions may not have been employed that could generate these types of intermediates from corresponding starting materials.

While the sterically congested nature of complexes **1–3** is important in driving phosphine dissociation to form unsaturated intermediates such as **9** in the first place, it will have other effects which will be unfavorable for the intermolecular activation of C–H bonds. Steric crowding in **9** renders access to the metal difficult for an incoming substrate and also causes the bulky phosphines to be bent away from one another and toward the metal. While this bending of L probably causes intramolecular activation to form **5** to compete favorably with intermolecular activation of unreactive substrates such as alkanes,[3] clearly it does not cause it to compete with intramolecular neopentyl group activation. Nor does formation of **5** compete with intermolecular arene activation, unless the arene is present in low concentration. Below concentrations of ca. 1 M benzene in cyclohexane, formation of **5** becomes dominant over formation of **6**. It is likely that this relative order of reactivity is largely geometric in nature and implies that there is a significant barrier to intramolecular activation of L which derives from its need to bend to reach the metal in a favorable orientation to react.[19]

Werner and Werner found that upon treatment of $(\eta\text{-}C_6H_6)OsL_2$ with excess L in C_6D_6, **6** was formed which contained no deuterium.[10a] This strongly suggests that the C–H activation occurs from the π-complexed arene. Jones and Feher[20] have also come to the conclusion that arene activation proceeds via an arene π-complex in their Cp*RhL system. In contrast, Stoutland and Bergman[21] have clearly ruled out Cp*IrL(π-ethylene) as an intermediate on the path to C–H activation of ethylene in that system. We have no evidence bearing on whether an η^2-C_6H_6 complex is an obligatory intermediate or whether such a complex forms at all. A priori, it is not unreasonable that such a species be an intermediate, and it might explain[1b] the apparent higher reactivity of benzene compared to, e.g., $SiMe_4$.[3,12] If such a complex were to lie on the reaction coordinate, the $k_{C_6H_6}/k_{C_6D_6}$ of 2.2 for k_{obsd} in the reaction of **2** would require that π-complexation not be rate determining. Nonetheless, steric compression is an important attribute of this system, and CPK space-filling molecular models clearly indicate the extreme difficulty that must be encountered in trying to coordinate the π-face of benzene to the very crowded vacant site in **9**. For this reason, we believe that a π-complex is unlikely to lie on the activation reaction coordinate.

As mentioned above, it is possible that the k_2 step of Scheme I might be reversible and the next step, i.e., reductive elimination of neopentane from the Os(IV) intermediate **13** to form **14** might be rate determining. In this case, however, there should be only a very small kinetic isotope effect. Whitesides and co-workers[1c] have concluded that the rate-determining step in the pyrolysis of $(Et_3P)_2Pt(Np)_2$ is the reductive elimination of neopentane from a Pt(IV) intermediate and that the kinetic isotope effect for this is ca. 3. Assuming that this same number would obtain in our system and recalling that in C_6D_6 solvent ca. 87% of the reductive elimination involves the elimination of neopentane-d_0 and 13% of neopentane-d_1, then the isotope effect observed here should be ca. 1.3 for the rate-determining step. Conversely, our observed isotope effect of 3.3, which we assign to step k_2, if assigned to the subsequent step, would suggest an isotope effect of 19—clearly an unreasonable number—for the 13% of that reaction involving

(14) Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G.; Koetzle, T. F. *Adv. Chem. Ser.* **1978**, *167*, 73–92.

(15) Alves, A. S.; Moore, D. S.; Andersen, R. A.; Wilkinson, G. *Polyhedron* **1982**, *1*, 83–87.

(16) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916.

(17) A referee has pointed out that more information on the isotope effect of the reductive elimination and the geometric nonrigidity of the intermediate might be obtained by doing the reverse experiment, i.e., thermolysis of $L_4Os(D)$(neopentyl-d_{11}) in C_6H_6. This is true in principle, but if one grants that a seven-coordinate intermediate such as **13** can be at least partially rigid during its lifetime, then the possibility of isomers must be considered. Each isomer may or may not have both the H and D accessible to the leaving neopentyl group. Additionally, even if Np is adjacent to both H and D, the capability of each to reductively eliminate may be affected by asymmetry in the ligand environment, presumably particularly by those ligands which might be nearly "trans" to the H and D. Thus, there is (a) the inherent isotope effect for reductive elimination, (b) the number of isomeric intermediates and their geometries, (c) the isomer distribution of the intermediates and the relative rate of geometric reorganization of each intermediate, and (d) the "trans effects" on reductive elimination in nonsymmetrical isomers of intermediates. In view of the difficulty of preparing the needed starting material and the ambiguity of the result, we have not done the experiment.

(18) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026 and references therein.

(19) This geometric requirement for C–H activation has recently been discussed: Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986–1992.

(20) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663.

(21) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581–4582.

neopentane-d_1 reductive elimination.

In addition, if the reductive elimination were rate determining, then both the k_1 and k_2 steps would be reversible, and incorporation of deuterium into the hydride position of starting complex **2** should be observable. More obviously, a substantial proton resonance of C_6D_5H should be conspicuous in the reaction mixture. No trace of such an exchange between starting material and solvent is detectable.

The isotope effect of 3.3 for the k_2 step is itself quite interesting in its size. There is a paucity of such numbers in the literature for arene or alkane oxidative additions reactions, so it is premature to speculate as to its significance, but two numbers are relevant. Janowicz and Bergman[1g] have reported a kinetic isotope effect of 1.38 for the activation of alkanes by $Cp^*Ir(PMe_3)$, and we[22] have observed k_H/k_D of ca. 4 for the intramolecular cyclization[23] of $(Me_3P)_3Ir$(neopentyl) to $(Me_3P)_3Ir(H)(CH_2CMe_2CH_2)$.

In summary, the activation of benzene by $L_4Os(H)R$ proceeds via dissociation of L which is driven by steric crowding. The resulting unsaturated species exhibits a very high propensity for γ-C–H activation of its own alkyl ligand and oxidatively adds benzene, both reactions proceeding via an osmium(IV) intermediate in preference to reductive elimination of alkane to form L_3Os. The greater facility of the Os(II)–Os(IV) interconversions over the Os(II)–Os(0) couple is a feature of this chemistry which is new compared to transformations of other iron-group phosphine complexes.

It is hoped that additional developments in the chemistry of carbon–hydrogen bond activation in this system in comparison to that of other reported molecules may afford more complete answers to some of the remaining intriguing questions regarding this important reaction type. Additional investigations of the scope and mechanism of C–H bond activation in this system and with analogous Os(II) complexes of other phosphines are in progress.

Experimental Section

General Comments. Chemical shifts of NMR spectra, recorded on a 270-MHz FT spectrometer, are reported in parts per million (ppm, δ) downfield from tetramethylsilane for ^1H spectra and from external 80% H_3PO_4 for ^{31}P spectra; all coupling constants are apparent, not calculated, with absolute values reported in hertz. Melting points are taken in sealed, evacuated capillaries and are uncorrected. All reactions involving organometallic compounds, unless otherwise noted, were carried out under an atmosphere of dinitrogen purified over reduced copper catalyst and in flamed-out glassware, using standard Schlenk techniques, or in a dinitrogen atmosphere box. THF and Et_2O were distilled from purple solutions of sodium/benzophenone. Hexane was distilled from sodium/potassium/benzophenone. $(Me_3P)_3Os(\eta^2\text{-}CH_2PMe_2)(H)$, **5**, was prepared according to the literature.[8b]

Deuterium-Labeled Ligands and Reagents. 1-Lithio-2,2-dimethyl-d_3-propane was synthesized by first preparing $(CD_3)_2(CH_3)COH$ in 80% yield from acetone-d_6 and MeMgI in ether in the usual way. This alcohol was converted to $(CD_3)_2(CH_3)CCl$ in 90% yield by shaking with concentrated HCl, and this was in turn converted to the Grignard reagent in ether. Formaldehyde monomer was generated over the vigorously stirred Grignard solution by gently pyrolysis of paraformaldehyde in a solids addition funnel. Normal workup yielded 55% $(CD_3)_2(CH_3)CCH_2OH$, which was converted to the chloride by PPh_3Cl_2 in THF. Spinning band distillation of the chloride afforded pure material in 15% yield overall from acetone-d_6. This was converted to the lithium reagent in hexanes, the solution was filtered, and the solvent was removed. The lithium reagent was stored as a powder in an inert atmosphere box. (Lithiomethyl)methyldimethyl-d_3-silane was prepared by a simple Grignard reaction of commercially available $(ClCH_2)Si(CH_3)Cl_2$ and CD_3MgI, followed by the usual conversion to the lithium reagent. Trimethylphosphine-d_9 was similarly prepared by the standard preparation[24] using CD_3MgI ($^{31}P\{^1H\}$ NMR (C_6D_6) δ −64.9).

Hydrido(trifluoromethanesulfonato)tetrakis(trimethylphosphine)osmium(II), 7. A solution of triflic acid in ether (4 mmol in 35 mL) was added dropwise over 1 h to **5** (2.0 g, 4.0 mmol) in Et_2O (20 mL) at −78 °C. The white precipitate was allowed to settle, and the solvent was removed by forced siphon (cannula). After washing with cold Et_2O (3 × 50 mL), the solid was vacuum dried overnight, yielding 1.86 g (72%) of **7** as an off-white solid: mp 155–160 °C (darkening at 150 °C); ^1H NMR (260 K, THF-d_8) δ −7.0 (dq, J_{PH} = 73.8, 21.0, OsH), 1.42 (d, J_{PH} = 6.2, PMe_3), 1.49 (d, J_{PH} = 9.3, PMe_3), 1.63 (vt, J_{PH} = 6.2, *trans*-$Os(PMe_3)_2$), at ambient temperature the resonances for the cis PMe_3 ligands were a broad doublet, and the hydride resonance was very broad; $^{31}P\{^1H\}$ NMR (200 K, THF) δ −36 (t, J_{PP} = 18.2, *trans*-$Os(PMe_3)_2$), −37 (dt, J_{PP} = 4.5, 18.3, PMe_3 trans to OsH), −46 (dt, J = 4.5, 18.2, PMe_3 cis to OsH). Anal. ($C_{13}H_{37}F_3O_3OsP_4S$) C, H.

Hydrido(methyl)tetrakis(trimethylphosphine)osmium(II), 1. Complex **7** (0.39 g, 0.61 mmol), solid methyllithium (0.13 g, 5.9 mmol), and benzene (20 mL) were combined and stirred at room temperature for 24 h. Solvent removal gave a waxy yellow solid which was extracted with hexanes (10 mL), and this solution was filtered. Removal of solvent and vacuum drying overnight gave 0.18 g (58%) of analytically pure **1**. Additional purification could be effected by sublimation (0.1 torr, 100 °C), giving a white solid: mp 187–189 °C (without darkening); ^1H NMR (C_6D_6) δ −10.5 (m, OsH), 0.11 (m, OsMe), 1.24 (d, J_{PH} = 5.8, PMe_3), 1.42 (d, J_{PH} = 6.2, PMe_3), 1.43 (vt, J_{PH} = 5.1, *trans*-$Os(PMe_3)_2$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −46.7 (dd, J_{PP} = 18.2, 15.7, *trans*-$Os(PMe_3)_2$), −55.6 (m, two mutually cis PMe_3). Anal. ($C_{13}H_{40}OsP_4$) C, H.

Hydrido(neopentyl)tetrakis(trimethylphosphine)osmium(II), 2. Complex **7** (1.0 g, 1.6 mmol), solid neopentyllithium (0.12 g, 1.6 mmol), and benzene (35 mL) were combined and stirred at room temperature for 2 h. Filtration and solvent removal gave an off-white solid which was extracted with pentane (2 × 20 mL), and the solution was filtered through decolorizing charcoal. Removal of solvent and vacuum drying overnight gave 0.60 g (66%) of analytically pure **2**, but it can be recrystallized from pentane: darkened at 122–126 °C without melting; ^1H NMR (C_6D_6) δ −10.4 (dq, J_{PH} = 70.4, 20.5, OsH), 1.11 (d, J_{PH} = 5.8, PMe_3), 1.36 (d, J_{PH} = 6.0, PMe_3), 1.41 (m, CH_2), 1.45 (s, CMe_3), 1.50 (vt, J_{PH} = 5.2, *trans*-$Os(PMe_3)_2$), there is a strong solvent effect on the chemical shifts of **2**; ^1H NMR (C_6D_{12}) δ −10.5 (dq, OsH), 1.02 (s, CMe_3), 1.16 (m, CH_2; with $[(CD_3)_3P]_4Os(Np)(H)$, this resonance is visible as a dq, J_{PH} = 11.0, 5.6), 1.21 (d, PMe_3), 1.44 (d, PMe_3), 1.53 (vt, *trans*-$Os(PMe_3)_2$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −50.7 (dd, J_{PP} = 20.7, 16.9, *trans*-$Os(PMe_3)_2$), −58.7 (dt, J_{PP} = 9.2, 20.7, PMe_3 trans to OsH), −63.2 (dt, J_{PP} = 9.2, 16.9, PMe_3 cis to OsH). Anal. ($C_{17}H_{48}OsP_4$) C, H.

Hydridotetrakis(trimethylphosphine)[(trimethylsilyl)methyl]osmium(II), 3. Complex **7** (100 mg, 0.16 mmol), solid (trimethylsilyl)methyllithium (18 mg, 0.18 mmol), and benzene (10 mL) were combined and stirred at room temperature for 2 h. Filtration and solvent removal gave an off-white solid which, after further vacuum drying, proved to be analytically pure: 75 mg (80%); mp 120–122 °C (without darkening); ^1H NMR (C_6D_6) δ −10.43 (ddt, J_{PH} = 75.7, 24.3, 17.3, OsH), −0.41 (ddt, J_{PH} = 11.8, 7.1, 6.2, CH_2), 0.48 (s, $SiMe_3$), 1.16 (d, J_{PH} = 5.8, PMe_3), 1.36 (d, J_{PH} = 6.4, PMe_3), 1.42 (vt, J_{PH} = 5.1, *trans*-$Os(PMe_3)_2$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −49.8 (dd, J_{PP} = 19.0, 17.6, *trans*-$Os(PMe_3)_2$), −57.4 (dt, J_{PP} = 9.7, 19.0, PMe_3 trans to OsH), −59.3 (dt, J_{PP} = 9.7, 17.6, PMe_3 cis to OsH). Anal. ($C_{16}H_{48}OsP_4Si$) C, H.

Thermolysis Reactions. A typical example is as follows. In an inert atmosphere box, a 25–50-mg sample of known weight of $L_4Os(H)(R)$ was loaded into an NMR tube equipped with a ground-glass joint. The appropriate solvent was distilled into the tube on a vacuum line, any additional reactant, such as excess L, was admitted or distilled in, the sample was submitted to at least three freeze–evacuate–thaw cycles, and the tube was sealed under vacuum. Concentrations of the osmium starting material ranged from 0.02 to 0.09 M in all experiments.

Thermolyses were conducted by heating the tubes either in a constant-temperature oil bath or in the heated probe of a 270-MHz NMR spectrometer. Recent temperature recalibration of the probe of the 270-MHz NMR spectrometer used revealed that the temperatures previously reported[3] for the corresponding experiments were ca. 9 deg too low. Thus, those rate constants are different from those reported here for experiments which were repeated by heating in an oil bath.

As mentioned above, **6** and **6**-d_6 are known compounds.[10a] They were invariably formed in quantitative yield as determined by ^{31}P NMR and possessed spectral parameters identical with the literature values.

Thermolysis of 2-d_6. $L_4Os(H)[CH_2C(CH_3)(CD_3)_2]$, **2**-$d_6$, was heated in C_6H_6 at 80 °C overnight. The volatiles were separated on a vacuum line, and the neopentane was submitted to GC/mass spectral analysis.[25] The relative intensities of the *tert*-butyl cation fragments which would arise from nonrandomized and from completely randomized NpH-d_6 are shown in Table I, along with the observed intensities for NpH from this

(22) Desrosiers, P. J.; Harper, T. G. P.; Flood, T. C.; Tulip, T. H.; Thorn, D. L., unpublished results.
(23) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448–2450.
(24) Wolfsberger, W.; Schmidbaur, H. *Synth. Inorg. Met.—Org. Chem.* **1974**, *4*, 149–156.
(25) For a complete discussion of the mass spectral analysis of deuterated neopentanes, see; Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725 and references therein.

Table I. Expected and Observed Intensities of *tert*-Butyl Fragments from Neopentane-d_6

mass	nonrandom (calcd)	obsd $C(CH_3)_2(CD_3)_2$	random (calcd)	obsd
57		1.17		0.00
58		1.25		1.31
59		2.89		1.71
60	45.51	38.44	7.21	10.88
61	1.91	2.92	37.03	31.12
62	0.07	2.20	43.89	37.76
63	53.96	48.76	11.37	12.12
64	2.48	2.25	0.50	4.74
65	0.08	0.10	0.01	0.22
66		0.00		0.14

experiment and observed intensities of $C(CH_3)_2(CD_3)_2$ from hydrolysis of the lithium reagent. Calculated intensities include natural abundance isotopes and appropriate isotope effects for fragmentation, but intensities of the M-1 and M-2 peaks are not included. It is apparent that extensive but not complete scrambling of the isotopes has occurred.

Thermolysis of 3-d_6. $L_4Os(H)[CH_2Si(CH_3)(CD_3)_2]$, **3**-$d_6$, was heated in C_6H_6 at 80 °C for ca. a week. The volatiles were separated on a vacuum line, and the $SiMe_4$-d_6 was submitted to GC/mass spectral analysis. The scrambling information was determined from the base peak, $[SiMe_3]^+$, by a procedure completely analogous to that described above for neopentane-d_6. The ion mass patterns were extremely similar to those given for $[CMe_3]^+$ in Table I and so are not given here. As in the neopentyl case above, it is clear that extensive but not complete scrambling of the isotopes has occurred.

Thermolysis of 2 in C_6D_6. Crossover Analysis. Samples of unlabeled **2** were heated at 70 or 80 °C in NMR tubes in neat C_6D_6 and in mixtures of C_6D_6 at 7.5, 3.7, and 1.8 M in C_6D_{12}. In each reaction, integration of the ^2H NMR signal for Os–D with respect to the C_6D_5 resonance in product **6**-d_6 allowed the calculation of a OsH/OsD ratio of ca. 0.16, corresponding to ca. 14% OsH. Because of the nature of the integration, this number is inherently rather imprecise but was reasonably reproducible from sample to sample and fell in the range 10–18%. The ^1H NMR spectrum of **6**-d_6 clearly showed the hydride resonance of a small amount of $L_4Os(H)(C_6D_5)$, but quantitation was not practical by this technique. The neopentane was submitted to mass spectral analysis and was found in all cases to be 13 ± 2% d_1. These results were independent of the composition of the solvent.

A sample containing a 1:4 ratio of **2**:**1** in C_6D_6 was heated at 80 °C to complete conversion of **2** to **6**. Analysis of **6** and NpH as above revealed no change in the labeling of the products.

Thermolysis of 2. Dependence on C_6H_6. Samples of **2** in neat C_6H_6 and in mixtures of C_6H_6 in cyclopentane corresponding to data points in Figure 3 in sealed NMR tubes were heated at 80 °C in an oil bath. No free phosphine was added. Rates of conversion to **6** were followed by ^{31}P NMR and were all cleanly first order. The inverse of the rate constants are recorded in Figure 3.

Thermolysis of 2. Dependence on [L] in C_6D_6 and in C_6H_6. Two sets of three samples of **2** were sealed in NMR tubes, one set in C_6D_6, and one in C_6H_6, each set with three different concentrations of added PMe_3. The samples were heated at 80 °C in an oil bath. The rates of conversion to **6**-d_6 and **6**, respectively, were followed by ^{31}P NMR and were cleanly first order. In the case of the highest L concentration in C_6D_6, the rate was slow enough that ca. 15% of cyclometalated complex **5** was formed. Compound **5** is known[12] to form under these conditions by a phosphine-independent first-order path and so could simply be subtracted from the overall rate of disappearance of **2** to give the correct rate of formation of **6**-d_6. The inverse of the observed first-order rate constants and the phosphine concentrations are given in Figure 4.

Exchange of 1, 2, and 3, with $P(CD_3)_3$. Samples were prepared in sealed NMR tubes in pentane solvent in the presence of excess L′ ($P(CD_3)_3$). All samples were heated in an oil bath at the temperature indicated in the Results section and were followed by ^{31}P NMR, yielding the rate constants given in the Results section: **1**, 0.10 and 2.0 M L′; **3**, 0.10 and 2.0 M L′; **2**, three samples all at 0.035 and 3.5 M L′ at three temperatures. A fourth sample of **2**, 0.05 and 0.1 M L′, was heated at 80 °C in the probe of the NMR spectrometer. The qualitative results are shown in Figure 2, but the rate was too rapid for reliable quantitation.

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Registry No. **1**, 100909-34-0; **2**, 100909-35-1; **3**, 100909-36-2; **5**, 84108-58-7; **6**, 78856-95-8; **7**, 100909-37-3; **9**, 104977-28-8; **10**, 104977-29-9; $(CD_3)_2C(CH_3)OH$, 53853-65-9; $(CD_3)_2C(CH_3)Cl$, 26216-07-9; $(CD_3)_2C(CH_3)CH_2OH$, 104977-23-3; $(CD_3)_2C(CH_3)CH_2Cl$, 104977-24-4; $(CD_3)_2C(CH_3)CH_2Li$, 104977-25-5; $(CD_3)_2Si(CH_3)CH_2Li$, 104977-26-6; $Cl_2Si(CH_3)CH_2Cl$, 1558-33-4; $(CD_3)_2Si(CH_3)CH_2Cl$, 104977-27-7; $(CD_3)_3P$, 22529-57-3; D_2, 7782-39-0; H_2, 1333-74-0; acetone-d_6, 666-52-4; formaldehyde, 50-00-0; paraformaldehyde, 30525-89-4; neopentyllithium, 7412-67-1; (trimethylsilyl)methyllithium, 1822-00-0.