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Mechanism of Activation of Carbon–Hydrogen Bonds in Tetramethylsilane and Mesitylene and Mechanism of Intramolecular Activation in Trimethylphosphine on Thermolysis of Tetrakis(trimethylphosphine)hydridoneopentylosmium(II)

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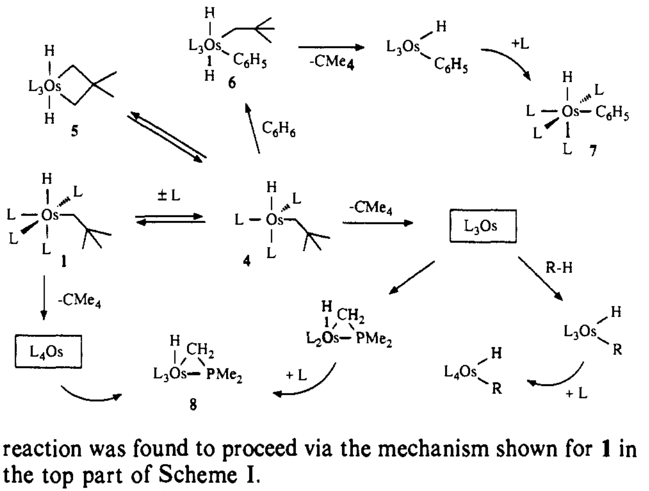
Abstract: Intramolecular and intermolecular activation of carbon–hydrogen bonds has been investigated by the thermolysis of *cis*-$L_4Os(H)$(neopentyl) (**1**, L = PMe_3). Thermolysis of **1** at 80 °C in cycloalkane solvents affords quantitative yields of *fac*-$L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ (**8**). The reaction is inhibited by added L up to a point after which k_{obsd} is independent of L. Thermolysis of **1** in neat $SiMe_4$ at 80 °C results in formation of *cis*-$L_4Os(H)(CH_2SiMe_3)$ (**2**) and **8**. The total rates of reaction (k_{obsd}) are the same in either alkane or $SiMe_4$ solvent at a given concentration of L. Reaction of **1** with a mixture of $Si(CH_3)_4$ and $Si(CD_3)_4$ reveals an isotope effect of 3.6 for the C–H activation step, but no effect on k_{obsd} is found when neat $Si(CD_3)_4$ is used as solvent. Thermolysis of **1** containing a mixture of L and $P(CD_3)_3$ (L′) ligands reveals an isotope effect for the C–H activating step in cyclometalation of 2.2, but only a secondary isotope effect is observed on k_{obsd} upon thermolysis of $(L')_4Os(H)Np$ (**1**-d_3). The secondary k_H/k_D appears to arise essentially from dissociation of L from **1** since the isotope effect for this dissociation for **1**-d_0 vs **1**-d_{36} is 1.3. Thermolysis of **1** in $Si(CD_3)_4$ solvent results in no crossover into the neopentane product. These data are most consistent with a mechanism wherein the L-dependent thermolyses proceed via initial reversible L dissociation followed by reductive elimination of neopentane to form L_3Os^0 and, finally, oxidative addition of C–H bonds intramolecularly in L or intermolecularly in $SiMe_4$. The ratio of **2** to **8** formed from L_3Os is ca. 2.4 and is independent of the concentration of L up to 0.01 M, suggesting that these reactions are much more rapid than uptake of L by L_3Os to form L_4Os. Thermolysis of **1** in mesitylene solvent at 80 °C forms *cis*-$L_4Os(H)[CH_2(3,5\text{-}Me_2C_6H_3)]$ (**12**) and **8** in a ratio of 5/1. Thermolysis of **1**-d_{36} in the presence of excess L′ proceeds via the L-independent path to form **8** with an isotope effect on k_{obsd} of 1.4. The isotope effect on the cyclometalation step itself under these conditions was shown to be 4.7 by thermolysis of **1** in a large excess of 3/1 L′/L. No crossover of deuterium into neopentane product was detected in these experiments. The L-independent path is, therefore, believed to proceed via initial NpH reductive elimination to form L_4Os^0 and then intramolecular L activation to form **8**. Thermolysis of **8** at 178 °C in cycloalkane solvent with 1 M C_6H_6 forms a mixture of **8** and $L_4Os(H)$(phenyl) (**7**) with an equilibrium constant very near to 1. After 7 days in neat $SiMe_4$ at 178 °C, **8** undergoes no conversion to **2**. Thermolysis of **8** at 155 °C in cycloalkane solvent with excess L′ results in incorporation of L′ into all positions at the same rate, including the cyclometalated position.

We have recently described the mild intermolecular activation of the carbon–hydrogen bond in benzene by intermediates generated by the thermolysis of *cis*-$L_4Os(H)R$ (L = $P(CH_3)_3$: R = $CH_2C(CH_3)_3$, **1**; R = $CH_2Si(CH_3)_3$, **2**; R = CH_3, **3**).[1,2] This reaction was found to proceed via the mechanism shown for **1** in the top part of Scheme I.

Scheme I



Initial reversible dissociation of L to form intermediate **4** stereospecifically could be demonstrated by exchange with $P(CD_3)_3$(L′) and by inhibition of the arene activation upon addition of L. Rapid and reversible intramolecular activation of the neopentyl group forming **5** was detected by isotopic labeling. The operation of an Os(II)–Os(IV) rather than an Os(II)–Os(0) formal redox couple was demonstrated by the kinetic dependence of the rate on benzene concentration and by isotopic crossover via intermediate 6.[1]

In this paper we describe the intramolecular activation of C–H bonds of the ligand $P(CH_3)_3$ by two distinct mechanisms to form cyclometalated complex *fac*-$L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ (**8**) and intermolecular reactions of C–H bonds in $SiMe_4$ and in the benzylic

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(1) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 7964–7970.

(2) For references outlining the development of the subject of C–H activation by transition-metal complexes see: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269. (b) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97–143. (c) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843–855. Cf.: Cotton, F. A.; Hunter, D. L.; Frenz, B. A. *Inorg. Chim. Acta* **1975**, *15*, 155–160. (d) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139–144. (e) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080–4089. (f) DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 124–133. (g) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27–35. (h) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994–7001. (i) Cameron, C. J.; Felkin, H.; Fillebeen-Khan, T.; Forrow, N. J.; Guittet, E. *J. Chem. Soc., Chem. Commun.* **1986**, 801–802. (j) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929–3939. (k) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190–7191. (l) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814–4819. (m) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2214–2216. (n) Werner, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 793–794. (o) Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73–93. (p) Gotzig, J.; Werner, R.; Werner, H. *J. Organomet. Chem.* **1985**, *285*, 99–114. (q) Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442–1447. (r) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856–4867. (s) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491–6493. (t) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1987**, *109*, 2825–2826. (u) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203–219. (v) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436–1448. (w) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449–1462. (x) Olah, G. A. *Acc. Chem. Res.* **1987**, *20*, 422–428. (y) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421–428. (z) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731–8733.

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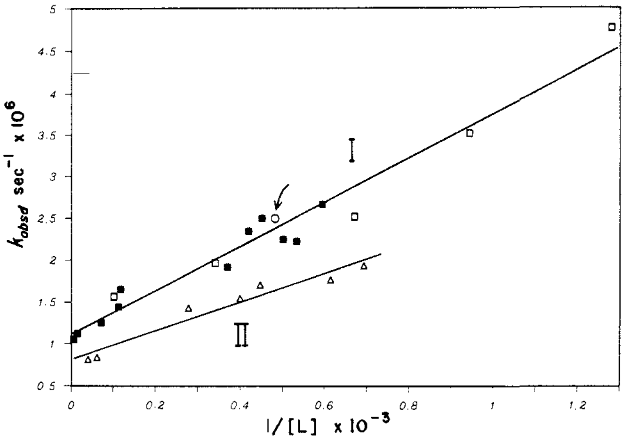
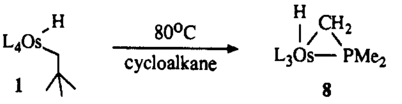


Figure 1. Plot of k_{obsd} for the disappearance of **1** vs 1/[L] for the thermolysis of **1** at 80 °C in the following solvents. Line I: alkane, ■; tetramethylsilane, □; tetramethylsilane-d_{12}, ○ (designated by an arrow). Line II: △, reaction of **1**-d_{36} in alkane solvent. Scatter of the data arises from difficulty in measuring low concentrations of free ligand accurately (i.e., uncertainty in the abscissa).

position in mesitylene. Our data are most consistent with a mechanism involving the intermediates L_3Os^0 and L_4Os^0 from these reactions.[3] Our conclusions are summarized in the lower part of Scheme I. The data and interpretations that lead us to these conclusions are described in detail herein.

Results and Interpretations

Thermolysis Reactions in Cycloalkanes. Thermolysis of **1** at 80 °C in cyclopentane or cyclohexane leads to formation of only **8** (eq 1). No deuterium is incorporated into **8** when C_6D_{12} is used



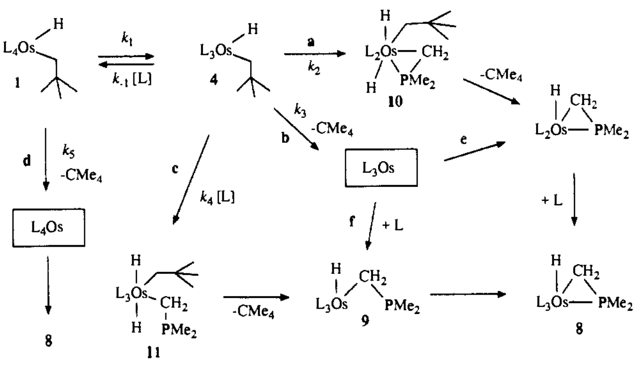
(1)

as solvent. The pyrolysis of **1** is retarded by the addition of free L. It is important to point out at the outset that while pyrolysis of **1** in arenes does not generate any concentration of free L detectable by ^{31}P NMR,[1] pyrolysis in alkanes invariably does generate some L, generally in the range of from 7 × 10^{-4} to 4 × 10^{-3} M, and most usually ca. 2 × 10^{-3} M. Complex **1** is typically employed at concentrations of ca. (3–9) × 10^{-2} M. The free ligand is generated immediately in the reaction, and then its concentration does not change. Since rates are sensitive to [L], it is important to note this concentration when relative rates of reactions are discussed. The source of free L is not known, but other than its inhibitory effect, its generation does not cause any problems that we can detect (see Discussion).

As [L] is increased by the addition of L, the rate does not go to zero but approaches a finite limiting value above ca. 0.1 M L. This relationship is shown in the plot of k_{obsd} vs 1/[L] in line I of Figure 1, for which the intercept is the limiting rate, 1.10 (0.08) × 10^{-6} s^{-1}. Thus, it appears that there are two mechanisms operating, one inhibited by L and the other independent of L.

Phosphine-Independent Path. Several of the most probable mechanisms for formation of **8** are shown in Scheme II. On the basis of data and arguments presented in this section, we have concluded that path d is responsible for the L-independent cyclometalation reaction.

Scheme II



Path d would clearly be independent of L. Any of paths a, b, or c could be L independent in the event that k_1 was rate-determining. The k_1 path can be ruled out as rate-determining, however, since we have previously measured k_1, as mentioned above, from the rate of exchange of **1** with added free L′.[1] The first-order rate constant for this exchange is k_1 = 7.25 × 10^{-4} s^{-1} at 80 °C, about 300 times faster than the formation of **8** with [L] ≈ 2 × 10^{-3} M. Thus, k_{-1}[L] must be larger than k_2, k_3, or k_4[L], and k_1 cannot be rate-limiting. Since k_1 is not rate-limiting, paths a and b would both be inhibited by phosphine but path c would not. The lack of L dependence for path c comes from the fact that k_{-1} and k_4 would both be associated with a first-order dependence on [L]. Thus, the two most reasonable candidates for the mechanism for the L-independent formation of **8** would be paths c and d. We can differentiate between these two paths on the basis of two lines of evidence—isotope effects and isotopic crossover.

Figure 1 includes a plot, line II, of k_{obsd} vs 1/[L′] for thermolysis of $[(CD_3)_3P]_4Os(H)Np$ (**1**-d_{36}) at 80 °C. The intercept for this plot is 8.1 (0.7) × 10^{-7} s^{-1}. This and the intercept for the **1**-d_0 plot, line I, give an isotope effect of 1.36 (0.15) for the L-independent path.

There is evidence that the isotope effect for the C–H oxidative addition step itself is much larger than that seen in k_{obsd} for the L-independent formation of **8**. When one heats **1** at 80 °C in alkane solvent in the presence of a 120-fold molar excess (based on **1**, 30-fold based on L in **1**) of a 3/1 mixture of L′ and L, the four L's coordinated to **1** are completely randomized with the added L′/L mixture very early in the reaction. There is a complication here in that, in addition to the site randomization of L and L′ in **1**, there is scrambling of deuterium between the free ligands L and L′ at a rate that is comparable to that of the conversion of **1** to **8**. This scrambling causes broadening of the ^{31}P resonances since the difference in chemical shift, Δδ, between $OsP(CH_3)_3$ and $OsP(CD_3)_3$ is usually ca. 2 ppm, and so the $OsPC_3D_{9-n}H_n$ resonances fall proportionately between.[4] Nevertheless, it is still possible to carry out the analysis by comparing the intensity of the Os–H resonance to that of the Os–D resonance in **8**. We have accomplished this by preparation of the internal standard $(C_6H_5)_2Si(CH_3)(CD_3)$, a small amount of which can be delivered to the NMR sample in order to give $SiCH_3$ and $SiCD_3$ integrals comparable in intensity to those of Os–H and Os–D, enabling us to determine [OsH]/[OsD] ratios with reasonable accuracy. It is also important to note that the interligand H/D scrambling is not a problem for the interpretation of the experiment. The average H/D ratio in the proposed intermediate L_4Os will be the same for all molecules, independent of how it is distributed within phosphine ligands, and so the isotope effect will be accurately reflected by the OsH/OsD ratio. The product exchanges neither L nor OsH under the reaction conditions, since **8**-d_0 can be heated indefinitely at 80 °C with high concentrations of L′ without any effect. In fact, exchange of **8**-d_0 with L′ only occurs with a significant rate above 150 °C (see below). The

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[3] Parts of this work have been the subject of communications: (a) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1346–1347. The activation of $SiMe_4$ and the phosphine-inhibited intramolecular activation of PMe_3 were suggested in this communication to proceed via Os^{IV} intermediates. For reasons that are clear in the present paper, we now believe that these two reactions proceed via Os^0, not Os^{IV}. (b) Harper, T. G. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915–7916. This communication reports the activation of methane. It alludes to and relies heavily on the mechanistic detail provided in the present paper.

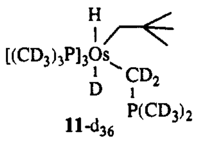
[4] This scrambling does not appear to proceed by catalysis by heterogeneous or colloidal metal and, aside from the analytical complication, causes no obvious problems. See the Discussion.

thermolysis of **1** with L/L′ was conducted two times and yielded $k_H/k_D = 4.7$ (0.2) for the cyclometalation step itself. The second of these measurements was made after the reaction mixture was heated at 80 °C for 2 months, after which analysis of the product OsH/OsD ratio yielded the same answer as the first measurement.

Since, as mentioned above, k_{obsd} for cyclometalation is much slower than the rate of L dissociation, k_1, the full isotope effect of k_4 (4.7) would necessarily be apparent in k_{obsd} for path c. The fact this is so clearly not the case rules out path c.

Parenthetically, the small isotope effect on k_{obsd} for path d (k_5) probably has its origins in steric effects (see Discussion). Reductive elimination of neopentane from **1** must have a strong steric driving force since methyl hydride **3**, which is significantly less crowded than **1**, does not form **8** in an alkane solvent, with or without added L, except above 150 °C.[5a] Thus, the slightly smaller size of deuterium compared to protium[7] could result in reduced crowding that would increase the barrier to reductive elimination of neopentane. If this idea is correct, then since we have shown that initial dissociation of L from **1** is driven by steric crowding, there might be a steric isotope effect on dissociation of L as well. The rate of substitution by free, unlabeled L on **1**-d_{36} was therefore determined by continuous data collection in the probe of the NMR spectrometer at 65 °C, yielding $k_1 = 8.25\ (0.27) \times 10^{-5}\ s^{-1}$. The rate of substitution of L′ (PMe$_3$-d_9) on **1**-d_0 was also determined by the identical procedure at 65 °C and was $1.05\ (0.02) \times 10^{-4}\ s^{-1}$ (both numbers are the average of two determinations). Thus, there is a kinetic isotope effect on the rate of dissociation of L from **1** (k_1) of 1.27 (0.05) at 65 °C. So it seems quite plausible that this size isotope effect could operate on the k_5 step as well.

An additional indication of the absence of path c comes from the fact that an Os(IV) intermediate such as **11** would probably show isotopic crossover under appropriate conditions. Use of **1**-d_{36} as substrate should result in incorporation of some deuterium into the liberated neopentane via **11**-d_{36}. The mass spectrum of the neopentane product revealed no deuterium content above natural abundance. Of course, the absence of crossover is negative evidence, but in the case of benzene-d_6 activation via Os(IV) intermediate **6**, ca. 13% crossover was reproducibly observable,[1] so it is reasonable to assume the likelihood of observing it were such a mechanism to operate here.


11-d$_{36}$

The most reasonable alternative mechanism for the [L]-independent reaction that accommodates the data is path d. Activation parameters were determined for this reaction over the range of 80–110 °C and yielded values of $E_a = 32.9$ (1.5) kcal/mol, $\Delta H^{\ddagger}(80\ °C) = 32.2$ (1.5) kcal/mol, and $\Delta S^{\ddagger}(80\ °C) = 5.0$ (4.4) eu.

Phosphine-Inhibited Path. At concentrations of L below ca. 2×10^{-3} M, most of the **8** from the thermolysis of **1** at 80 °C forms via at path that is sensitive to [L]. The most probable mechanisms for this reaction are paths a and b in Scheme II, either of which would show inhibition by L. The data presented below lead us to conclude that it is mechanism b that operates. These paths can be distinguished by several lines of evidence. Use of kinetic isotope effects to establish the rate-determining step is considered here first.

The slope of each line in Figure 1 is k_1k_n/k_{-1}, where k_n will be either k_2 or k_3 (the kinetic equations are discussed below). Thus, the slope of line I (for **1**) divided by that of line II (for **1**-d_{36}) gives the cumulative isotope effect on these rate constants and is 1.53 (0.18). Dividing this number by the isotope effect on k_1 (1.27,[8a] discussed above) yields the isotope effect on k_n/k_{-1}, which is 1.20 (0.15). Since the isotope effect on k_{-1} should be small,[8b] that of k_n must not be very different from 1.

Table I. Thermolysis of L$_4$Os(H)Np (**1**) at 80 °C in SiMe$_4$ and SiMe$_4$-d_{12} Solvent Showing the Dependence of the L$_3$Os(H)(η^2-CH$_2$PMe$_2$) to L$_4$Os(H)CH$_2$SiMe$_3$ (**8**/**2**) Ratio on [L], on Isotopic Substitution of Solvent, and on the Reaction Path

reactn	(a) $k_{obsd} \times 10^6$	(b) [L] $\times 10^4$	(c) **8**/**2**	(d) % reactn, via k_3	(e) **8**/**2** via k_3 only
1	28.0	1.0^a	0.5	96	0.43
2	4.77	7.8	1.2	77	0.71
3	3.52	11	1.1	68	0.45
4	2.53	15	1.5	56	0.37
5	2.50^b	21	3.4	56	1.43
6	1.97	29	2.2	44	0.42
7	1.57	100	4.0	29	0.45

^{a} Calculated from the best line shown in Figure 1 since it could not be determined by ^{31}P NMR. ^{b} In Si(CD$_3$)$_4$ solvent.

The kinetic isotope effect for the cyclometalation step itself was measured in the following way. Exchange of the ligands of **1** with enough L′ to give a 4/1 exchanged L′/L ratio was carried out at 80 °C for 48 h, sufficient time for the complete randomization of the mixture of ligands throughout **1** rather than just in the mutually trans positions. Exchanged **1** (80% L′) was isolated and submitted to thermolysis at 80 °C in cyclohexane with no added L or L . When phosphine is not added, there is no observable interligand H/D scrambling, so the isotope effect can be calculated directly from the intensities of the two ^{31}P resonances of the unique cyclometalated ligand centered at δ −70.2 (for L) and −72.0 (for L′). This treatment yielded $k_H/k_D = 3.1$ (0.3). This value is a composite of the isotope effect on path d and that of the [L]-dependent path, a or b. Also, the total rate of reaction, k_{obsd}, which is the sum of rates of the two paths (see below), was 1.77 (0.03) $\times 10^{-6}\ s^{-1}$ ([L + L] = 3.8×10^{-3} M). From Figure 1 it can be seen that for thermolysis of a sample of **1** partially labeled with L′ the intercept (k_5 for path d) would fall between those for **1**-d_0 and **1**-d_{36}. It was assumed that the isotope effect on k_5 is linear with regard to isotopic content from **1**-d_0 to **1**-d_{36}, and so for a sample of **1** that was 80% L′, k_5 would be $8.7 \times 10^{-7}\ s^{-1}$. Thus, we can determine that 49% of the reaction proceeds via path d and the other 51% via path a or b. Since it was reported above that k_H/k_D for path d is 4.7, and since the overall isotope effect is 3.1, it can be calculated that k_H/k_D for the phosphine-inhibited path is 2.2 (0.4). An independent determination on a second sample gave the same answer: 2.1 (0.4). The errors are somewhat large because of all the variables in the calculation.

The fact that the isotope effect for k_n/k_{-1} (assuming $k_{-1} \approx 1$) is near 1 and that the isotope effect measured for the cyclometalation step itself is 2.2 is consistent with path b (k_3) being responsible for the formation of **8**, but inconsistent with the operation of path a (k_2).

Having evidence for the operation of path b, we have the remaining question as to whether L$_3$Os reacts intramolecularly to form L$_2$Os(H)(η^2-CH$_2$PMe$_2$) via path e or whether it proceeds intermolecularly with free L via path f to form **9**. This question and some additional evidence that path b is the L-dependent path are discussed below.

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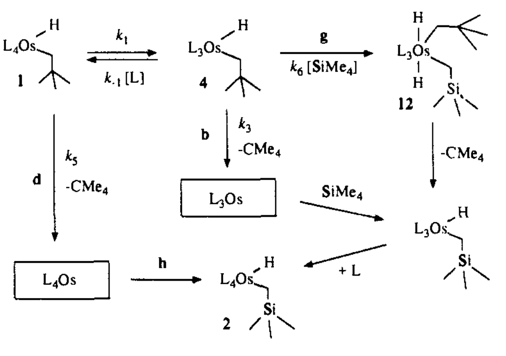
[5] (a) Shinomoto, R. S. Unpublished results. (b) Desrosiers, P. J.; Shinomoto, R. S. Unpublished results. (c) Harper, T. G. P. Unpublished results. (d) Harper, T. G. P.; Shinomoto, R. S.; Deming, M. A. Unpublished results.

[6] Ermer, S. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *Organometallics* **1989**, *8*, 1377–1378.

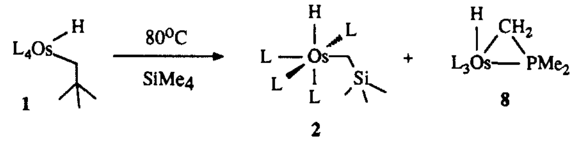
[7] (a) Laurie, V. W.; Herschbak, D. R. *J. Chem. Phys.* **1962**, *37*, 1687–1693. (b) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; John Wiley and Sons: New York, 1984; pp 709–714.

[8] (a) This treatment assumes a negligible change in k_H/k_D for k_1 over a 15 °C range since it was determined at 65 °C, while the data of Figure 1 were all determined at 80 °C. In fact, the change should be 2% or less. (b) According to Hammond's postulate, since the dissociation of L from **1** to form **4** is endothermic, the transition state should be late; i.e., L should be largely dissociated. The activation entropy[1] of 10 eu is in accord with significant L dissociation in the transition state. If the isotope effect on k_1 is indeed steric in origin, then the change in compression should be much less approaching the transition state during L association than the change in compression during L dissociation. Thus, the isotope effect on k_{-1} should be smaller than that on k_1, the latter of which is already a small number.

Scheme III



Thermolysis of 1 in Tetramethylsilane. Thermolysis of 1 in neat $SiMe_4$ at 80 °C results in a very slow and very clean reaction, first-order in 1, leading to formation of 2 but with competitive formation of 8 (eq 2). This reaction is inhibited by added phosphine, and the rate depends on the amount of free phosphine added or spontaneously generated, as shown in Figure 1. At concentrations of L above ca. 0.1 M, the formation of 2 is completely inhibited, but 8 continues to form at the rate of the L-independent path.



(2)

When $Si(CD_3)_4$ is used as solvent, the rate of disappearance of 1 (k_{obsd}) is indistinguishable from that in nondeuterated $Si(CH_3)_4$. There is, however, an effect of changing from $SiMe_4$ to $SiMe_4$-d_{12} solvent on the 8/2 ratio (e.g., Table I, reactions 4 and 5). There is also an effect of phosphine concentration on this ratio (Table I, cf. columns b and c).

Scheme III shows some of the possible mechanisms for formation of 2. This scheme should be superimposed on Scheme II since both 2 and 8 are formed simultaneously. In the remainder of this section, the mechanisms of these two schemes are considered in turn as possible sources of 2 and 8. It is shown that only paths b and d are consistent with the experimental data.

Consider first the possibility that the reaction of eq 2 was to proceed by paths a, d, and g. When the steady-state assumption is applied to the intermediates involved, the corresponding rate expression would be that given in eq 3, where k_5 is the limiting

$$k_{obsd} = k_5 + \frac{k_1(k_2 + k_6[\mathrm{SiMe_4}])}{k_{-1}[\mathrm{L}] + k_2 + k_6[\mathrm{SiMe_4}]} \qquad (3)$$

rate constant in the presence of added L for reaction of 1 in alkanes (path d, 1.1×10^{-6} s^{-1}). Now, if we consider the points in the plot of line I of Figure 1 for only those reactions carried out in alkane solvent, from the slope it can be shown (see below) that k_2 and, since it would be about the same size as k_2, $k_6[SiMe_4]$ must both be negligible compared to $k_{-1}[L]$ for concentrations of L that we observe. Thus, eq 3 reduces to eq 4. The latter

$$k_{obsd} = k_5 + \frac{k_1 k_2}{k_{-1}[\mathrm{L}]} + \frac{k_1 k_6[\mathrm{SiMe_4}]}{k_{-1}[\mathrm{L}]} \qquad (4)$$

is given in such a form as to emphasize the fact that rates of reactions of 1 with its own ligands and with solvents should be additive for the mechanism of paths a and g.

For those reactions in $SiMe_4$, if only the rates of formation of 8 were plotted, then these points should fall on the line in Figure 1. Conversely, if the total rate of disappearance of 1, k_{obsd}, was to be plotted for the $SiMe_4$ reactions, these points should fall on a line with a substantially greater slope than that of the reactions carried out in alkane solvents. In addition, use of $SiMe_4$-d_{12} should effect not only the 2/8 ratio but also the overall rate.

In fact, plotting of the total rate for the $SiMe_4$ reactions gives points falling on line I. As mentioned above, use of $SiMe_4$-d_{12} results in a rate indistinguishable from that in $SiMe_4$. This means that both 2 and 8 come from a common intermediate in reactions after the rate-determining step and is inconsistent with mechanisms proceeding via paths a and g.

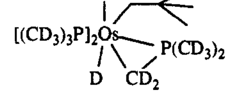
Assuming now that only the mechanisms of paths b and d are operating, the rate expression would be as shown in eq 5. If k_3 is negligible compared to $k_{-1}[L]$ for most [L], then eq 5 reduces to eq 6. As mentioned above, the slope (divided by k_1) and intercept of Figure 1 give $k_5 = 1.10 \times 10^{-6}$ s^{-1} and $k_3/k_{-1} = 3.67$ (0.25) $\times$ 10^{-6} M. For all [L] above ca. 10^{-4} M, k_3 clearly is negligible with respect to $k_{-1}[L]$.

$$k_{obsd} = k_5 + \frac{k_1 k_3}{k_{-1}[\mathrm{L}] + k_3} \qquad (5)$$

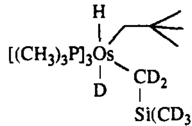
$$k_{obsd} = k_5 + \frac{k_1 k_3}{k_{-1}[\mathrm{L}]} \qquad (6)$$

This expression fully accounts for the data since the total rate of disappearance of 1, k_{obsd}, will be independent of the solvent with which L_3Os reacts. There will also be no isotope effect on k_{obsd} upon use of $SiMe_4$-d_{12} as solvent.

There is an additional check to differentiate path b from paths a and g. An Os(IV) intermediate such as 10 or 12 should show isotopic crossover under appropriate conditions. Use of $(L')_4OsH(Np)$ as substrate should result in incorporation of some deuterium into the liberated neopentane via 10-d_{27}. Use of $SiMe_4$-d_{12} solvent in reaction with unlabeled 1 should also form some neopentane-d_1 via 12-d_{12}.



10-d_{27}



12-d_{12}

We have checked for crossover in the case where $Si(CD_3)_4$ was used as solvent. The mass spectrum of the neopentane product revealed no neopentane-d_1 above natural abundance. As mentioned above, the absence of crossover is negative evidence, but crossover that was observed in the case of benzene-d_6 activation via Os(IV) intermediate 6,[1] analogous to 12, suggests the likelihood of observing it were such a mechanism to operate here.

Knowing the total rate and k_5, one can calculate from k_{obsd} the percentage of each path that contributes to a given reaction. Table I, column d, shows the percent reaction that proceeds via the k_3 path in $SiMe_4$ solvent. Furthermore, since we observe that the k_5 path forms only 8 and not 2 (i.e., path h in Scheme III does not operate), then the 8/2 ratio can be calculated for the k_3 path only. This ratio is shown in Table I, column e. There is some scatter, but it is clear that this ratio is essentially constant at ca. 0.42 and independent of L over this concentration range of L; that is, $SiMe_4$ as neat solvent undergoes C–H activation by L_3Os about 2.4 times as fast as the latter attacks its own ligand.

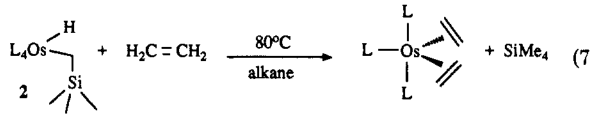
The data in Table I, column e, suggest several things:

First, the constancy of the 8/2 ratio as a function of [L] strongly suggests that L_3Os reacts more rapidly with C–H bonds than it does to take up L to form L_4Os over this range of concentrations of L. Even though L_4Os is undoubtedly crowded, the barrier to coordination of L_3Os by L is probably low, so the barrier to C–H activation must also be quite low.

Second, the constancy of the ratio of 8/2 as a function of L provides good evidence against the formation of 8 via bimolecular C–H activation between L_3Os and free L (path f in Scheme II). This reaction would be second-order overall, first-order in [L]. Were path f to operate, as the concentration of L would be increased by a factor of 100, the ratio of 8/2 should change substantially. Parenthetically, it can be commented that, under conditions where L_3Os is formed, the concentration of L is typically ca. 10^{-3} M while neat $[SiMe_4]$ is ca. 7.3 M. Thus, for reaction between L_3Os and L (path f) to be competitive with reaction between L_3Os and $SiMe_4$, the perhydrogen reactivity of L would have to be ca. 10^4-fold greater than that of $SiMe_4$—quite an unreasonable suggestion.

Third, the **8**/**2** ratio of 1.43 for the reaction run in $SiMe_4$-d_{12} (column e, entry 5) when compared to that of the other reactions implies that there is an isotope effect for the C–H activation of $SiMe_4$ of ca. 3.4.

The magnitude of the isotope effect can be confirmed more directly. Use of a 15/85 molar mixture (determined by mass spectrometry) of $SiMe_4$ and $SiMe_4$-d_{12} as solvent for the pyrolysis of **1** formed a mixture of **2**/**2**-d_{12}. It was not possible to determine the ratio of these two isotopomeric products by integration of the ^1H resonances of the phosphine ligands vs the $SiMe_3$ group because of disparity of the sizes of the integrals and because of the presence of interfering resonances from product **8**. This ratio was determined by conversion of the mixture of isotopomers of **2** into free $SiMe_4$/$SiMe_4$-d_{12} as shown in eq 7, followed by mass spectral analysis, and was found to be 39/61. This corresponds to an isotope effect of 3.6 for C–H activation. The bis(ethylene) complex **13**, which forms quantitatively by NMR, has consistent ^1H and ^{31}P NMR spectra. It has not yielded a good elemental analysis as yet, however, and so cannot be considered fully characterized. Exactly 1 equiv of free L is formed in reaction 7.

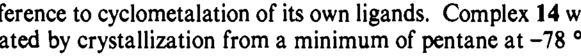


2 **13** (7)

In any event, since the k_H/k_D measured for the C–H activation step itself is 3.6 and that on k_{obsd} when $SiMe_4$-d_{12} is used as solvent is 1, clearly the step of k_6 is not rate-determining. The most reasonable alternative is that the reaction proceeds via L_3Os, the k_3 path.

For comparison to complex **1**, the activation parameters were determined for the dissociation of L from **2** by thermolysis of **2** in the presence of excess L′ over the temperature range 66–99 °C and yielded values of E_a = 34.6 (0.2) kcal/mol, ΔH^{*}(80 °C) = 33.9 (0.2) kcal/mol, and ΔS^{*}(80 °C) = 14.5 (0.6) eu.

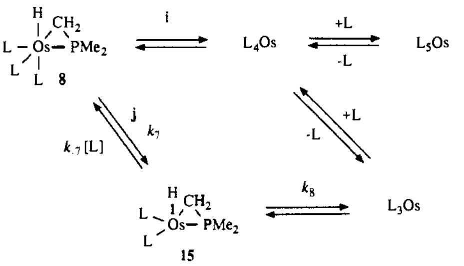
Thermolysis of 1 in Mesitylene. Thermolysis of **1** in neat mesitylene at 80 °C resulted in slow and clean conversion to the product of benzylic C–H activation (**14**) in competition with **8** (eq 8) in an 85/15 ratio. The reaction was again first-order in **1** (k_{obsd} = 3.0 (0.15) × 10^{-6} s^{-1}, [free L generated] = 1.1 × 10^{-3} M). If one assumes that k_5 in mesitylene solvent is close to 5 × 10^{-7} s^{-1} (the value in benzene) rather than 1.1 × 10^{-6} s^{-1} (the alkane value),[9] then the observed rate corresponds to ca. 17% k_5 path and 83% k_3 (L_3Os) path. This is very close to the **8**/**14** ratio and suggests, since we know that the k_5 path forms only **8** (vide infra), that L_3Os activates the benzylic C–H bond in strong preference to cyclometalation of its own ligands. Complex **14** was isolated by crystallization from a minimum of pentane at −78 °C and characterized. A key point is the site of attack by osmium on mesitylene. ^1H and ^{31}P NMR spectra showed evidence of only one isomeric product. The ^1H spectrum revealed two distinct arene resonances at δ 7.57 and 6.70 in a 2/1 ratio, a six-proton singlet for the two arene methyl groups at δ 2.36, and a two-proton, phosphorus-coupled multiplet at δ 2.61 for the $OsCH_2Ar$ group, establishing that the product is that of benzylic attack.

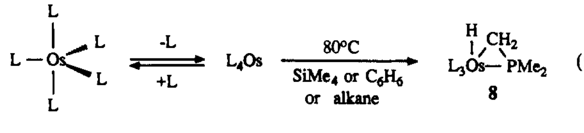


1 **14** **8** (8)

Reaction Path d. We have independent evidence that L_4Os is the intermediate on path d, as postulated, and that it does not activate C–H bonds intermolecularly, that is, for example, that path h (Scheme III) does not operate. We have reported elsewhere our recent preparation of L_5Os and its chemistry,[6] but one interesting feature of its reactivity that is particularly relevant here is that its pyrolysis in benzene or in $SiMe_4$ solvent results in formation of **8** *only*; no phenyl hydride **7** or **2** is formed. The reaction is first-order in L_5Os and is inhibited by added L. We conclude that the reaction of eq 9 takes place, and that L_4Os is not capable of intermolecular C–H activation. In addition, it is clear that L_4Os, while probably rather crowded, is not crowded enough to undergo dissociation of L to form L_3Os during its short lifetime. Were the latter to occur, then in $SiMe_4$ solvent some **2** would form.

Scheme IV





(9)

High-Temperature Reactions. Initially, we had assumed that cyclometalated material **8** was generally thermodynamically preferred over all of the intermolecular C–H activation products. This was eventually shown to be false, at least for benzene, when **8** was heated at 178 °C in benzene. At this temperture, **8** underwent a first-order conversion to phenyl hydride complex **7**. Furthermore, when **7** was heated at 178 °C in hexane, **8** was formed to the extent of 87%. Heating pure **8** in cyclohexane-d_{12} with 1.0 M benzene resulted in ca. a 1/1 ratio of **8**/**7**, (K = 0.98) with no incorporation of deuterium into either material detectable by ^2H NMR.

In contrast to the high-temperature reaction of **8** with benzene, when **8** was heated in neat $SiMe_4$ at 178 °C for 7 days, no change was seen. In light of the benzene result, this is likely to reflect a thermodynamic preference for **8** and not a kinetic problem for the formation of **2**.

In order to determine whether reductive elimination of the C–H bond from **8** to form L_4Os or dissociation of L from **8** is its initial thermal process, **8** was heated in cycloalkane solvent at 155 °C in the presence of a large excess of L′ (ca. 30-fold excess based on Os, ca. 8-fold based on total L). Incorporation of L′ into **8** occurred at all positions at the same rate, including the cyclometalated site, with a half-life of ca. 7 days. Some L/L′ interligand H/D scrambling occurred, but at a rate much slower than that of the ligand exchange, and so caused no problem in interpretation of the ^{31}P NMR spectral data. These exchange data are most consistent with the operation of path i in Scheme IV. We know that at ca. 50 °C L_5Os exchanges with added L′ more rapidly than it converts to **8**.[6] Thus, when **8** would form L_4Os at 155 °C, L_4Os would probably completely exchange with the excess L′ via reversible formation of L_5Os and cyclometalation of the fully exchanged $(L')_4Os$ would yield only **8**-d_{36}. This would give incorporation of L′ into **8** at all four sites at the same rate.

In contrast, if path j in Scheme IV were to operate, intermediate **15** very probably would take up L′ to return to **8** much faster than it would undergo reductive elimination to form L_3Os; i.e., k_{-7}[L] probably would be much larger than k_8. This would mean that **8** would incorporate L′ much more rapidly into the three terminal positions than in the cyclometalated position. In fact, to obtain L′ in the cyclometalated position at all, the L_3Os would need to exchange L/L′ via L_4Os and almost certainly via L_5Os, and then undergo dissociation of L twice to return to L_3Os, and then from there return to **15**, and then to **8**. We know that at 80 °C L_4Os cyclometalates directly to **8** rather than undergo dissociation of

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(9) In benzene solvent at L = 0.65 M, the rate of formation of **8** is 5.3 × 10^{-7} s^{-1}.[5b] Apparently this slower limiting rate compared to that in alkanes is due to a solvent effect on the neopentane reductive elimination. Very similar solvent effects have been reported in the reductive elimination of neopentane[2v] and trifluoroethane[10] from corresponding $(R_3P)_2Pt(H)R$ complexes.

(10) Michilin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831–1834.

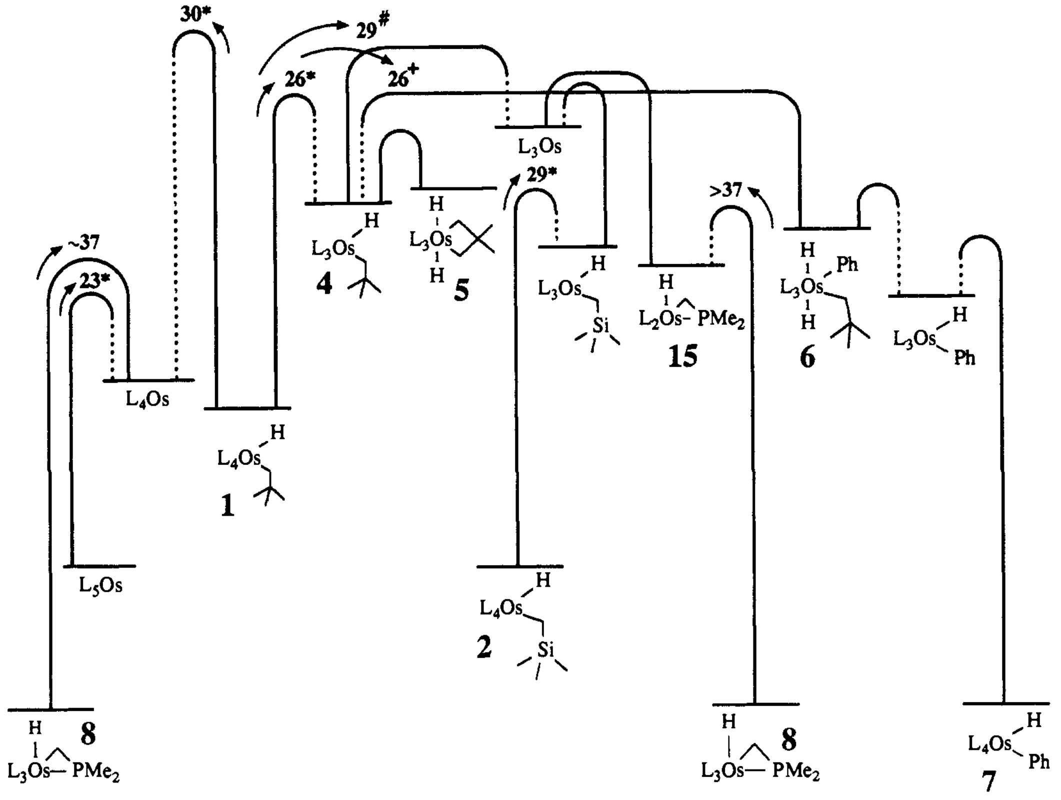

Figure 2. Qualitative free energy diagram for some of the reactions of **1** and related species at 80 °C. Bimolecular steps are represented by dashed lines approaching the transition state. Reactant concentrations are not standard but are those found or estimated under a given set of reaction conditions. Notes for the figure: asterisk, activation parameters have been determined; pound sign, [L] = 7 × 10^{-4} M; plus, [L] = 7.4 × 10^{-5} M, [C_6H_6] = 11.2 M.

L to form L$_3$Os, since heating of L$_5$Os (which produces low concentrations of L$_4$Os) in neat SiMe$_4$ forms only **8** and no **2** and thermolysis of **1** in the same solvent with added L (which proceeds via L$_4$Os) gives no **2**. (Recall, **2** forms only from L$_3$Os in SiMe$_4$.) It seems unlikely that the preference at 80 °C for L$_4$Os to cyclometalate to form **8** rather than dissociate L to form L$_3$Os would be completely reversed at 155 °C, as would be required by L′ incorporation into the cyclometalated site of **8** by path j in Scheme IV.

Discussion

Significant advances in the understanding of C–H "activations" (oxidative addition reactions of C–H bonds or metathetical C–H exchanges) by soluble complexes of the transition metals have been made in recent years,[2] especially in Cp- or Cp*-containing systems (Cp = c-C_5H_5; Cp* = c-$C_5(CH_3)_5$). There has not been as much well-defined mechanistic work on non-Cp- or non-Cp*-containing complexes. The L$_4$Os[11] system described herein has exhibited a rich variety of chemistry including the activation of assorted types of C–H bonds. It is important as an example of a soluble, mononuclear, non-cyclopentadienyl-containing system of metal complexes whose chemistry is clean and unusually diverse. A summary of many of the paths that we have detected in our mechanistic studies so far is given schematically in the qualitative free energy diagram (80 °C) of Figure 2.

Issues of central interest for mechanisms of oxidative addition of C–H bonds include (1) the coordination number and geometry of the reactive intermediate, (2) the orientations, populations, symmetry properties, and energies of the reactive orbitals at the metal, and (3) the competition between intermolecular C–H activation and intramolecular ligand reaction. The first two of these issues are, of course, closely related.

It is generally believed that the essential features of the oxidative addition reaction of a C–H bond to a metal are as shown in Figure 3.[11] The metal is required to possess a vacant, acidic (low-lying) molecular orbital (MO) of σ symmetry and a basic (filled) π-symmetry MO. The initial interaction of the hydrocarbon with the metal center is presumably that of electron density donation from a C–H σ bond to the acidic metal σ MO. As this acid–base coordinate bonding develops and the hydrocarbon comes closer to the metal, the metal π-symmetry basic orbital begins to donate electron density back into the empty C–H antibonding orbital. These two interactions lead to the formation of the two quasi-"symmetric" and quasi-"antisymmetric" σ-bonding combinations of the C–M–H bonds.

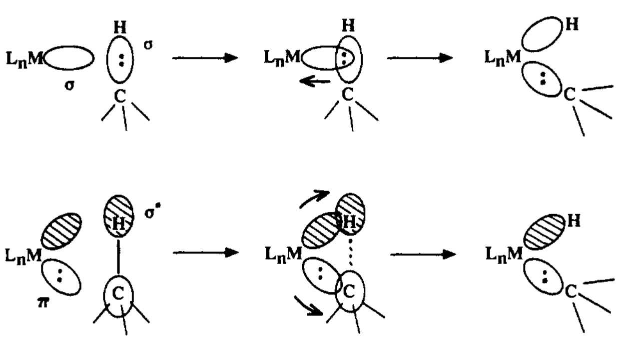

Figure 3. Proposed reaction coordinate for the oxidative addition of C–H bonds to transition-metal centers. The top series of structures traces σ-symmetry changes and the bottom series π-symmetry changes.

In our investigations with this osmium system, we have accumulated evidence for at least three distinct reactive intermediates: **4**, L$_4$Os, and L$_3$Os. We have good evidence[1] that **4** is stereochemically rigid and so probably is square-pyramidal, as would be expected for a five-coordinate, d^6, third-row metal.[12] The orbital at the vacant octahedral site is the LUMO, and there are two filled π-symmetry MOs directed at this site that are essentially the d$_{xz}$ and d$_{yz}$ metal orbitals (Figure 4). Consistent with this picture, intermediate **4** (and the analogue with CH$_2$SiMe$_3$ in place

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

(12) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076.

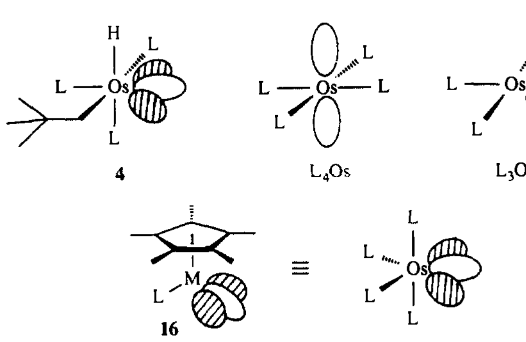

Figure 4. Reactive orbitals of some intermediates relevant to this work. σ-Symmetry lobes are unshaded, while both lobes of π-symmetry orbitals are shaded. Species **4** and L$_3$Os each have a second π-symmetry orbital, orthogonal to the one shown, which has been omitted for clarity. Also, L$_4$Os shows only the empty p$_z$; the filled d$_{z^2}$, collinear with the p$_z$, and the filled π-symmetry d$_{xz}$ and d$_{yz}$ orbitals are not shown.

of Np) has been shown[1] to cyclometalate its own alkyl groups to form **5** (and its silicon analogue) and to attack benzene and other arenes facilely. The intramolecular C–H activation of the neopentyl group in **4** clearly shows that it has no inherent enthalpic problem in the activation of sp^3 C–H bonds. We presume that the absence of any intermolecular reaction of this intermediate with saturated substrates is associated with the substantial bulk of the four PMe$_3$ ligands and the neopentyl group. The alkane simply cannot approach close enough to interact at a competitive rate.

It is interesting to note that while L$_4$Os and L$_3$Os are both reactive enough to attack the C–H bonds of their own phosphine ligands, we have no evidence for the analogous process in **4**; i.e., there is no indication of the formation of **10**. This may suggest that **4** is inherently less reactive than either L$_4$Os or L$_3$Os. Alternatively, it is possible that L$_3$Os(H)Np is predominantly in the cyclometalated form, **5**, and that its lifetime as **4** is too short to allow formation of **10**. This last possibility is less tenable in view of the observation that **4** reacts so readily with benzene[1] and alkenes.[5b]

The fact that **4** does intermolecularly attack the C(sp^2)–H bond in benzene but not C(sp^3)–H bonds is most easily explained by invoking the intermediacy of an arene π complex with **4**, although we have no evidence that bears directly on this issue. Jones et al. have data strongly implicating the intermediacy of η^2-arene complexes in reactions of Cp*Rh(PMe$_3$) with arenes.[21]

Intermediate L$_4$Os would presumably prefer to be square-planar. In a square-planar complex, the two degenerate filled orbitals, essentially d$_{xz}$ and d$_{yz}$, are the reactive π-symmetry orbitals. The essentially p$_z$, which is collinear with the filled d$_{z^2}$ orbital, is the reactive acidic σ orbital. In this case, the acid–base interaction of the empty metal p$_z$ with the C–H σ bond is offset by the repulsive interaction of that σ bond with the filled metal d$_{z^2}$ orbital.[11] Thus, the hydrocarbon cannot get close enough to the metal for back-donation from the metal π-donor orbital to the C–H antibonding orbital to become important, and the oxidative addition does not occur.

Parenthetically, it is generally appreciated that one of the useful features of the Cp or Cp* ligand is that, necessarily occupying three facial coordination sites, it constrains d^8 CpML (16-electron) intermediates to a non-square-planar geometry, as in **16**. Calculations show[13] that the preferred geometry of **16** is the bent one shown in Figure 4. In this geometry, there is a filled orbital of π symmetry with respect to the vacant metal coordination site, and, of course, the acidic σ orbital is the vacant site itself.[13] Thus, the orbital configuration is ideal for C–H activation in this geometry.

In any event, while L$_4$Os, as a four-coordinate d^8 complex, would probably prefer to be square-planar for electronic reasons, it is undoubtedly distorted from this geometry due to the congestion of the four bulky ligands. Substantial puckering is evident in the X-ray crystal structure of [(Me$_3$P)$_4$Rh]$^+$Cl$^-$, which is distorted toward tetrahedral geometry (the two *trans*-P–Rh–P angles are 148° and 151°),[14a] and [(MePh$_2$P)$_4$Ir]$^+$BF$_4^-$ is similarly distorted (both *trans*-P–Ir–P angles are 151°).[14b] In spite of its probable distortion, it appears that L$_4$Os will not undergo intermolecular reactions with alkanes, arenes, or SiMe$_4$, so it may still have the essential orbital features of a square-planar complex that were described above. Alternatively, it may be that the four PMe$_3$ ligands are bulky enough to block access to the metal, even if the complex is rather distorted.[15] Intramolecular C–H oxidative addition of L$_4$Os is discussed below.

Consistent with the above discussion regarding lack of reactivity of square-planar complexes toward intermolecular C–H activations, there is literature precedent that, for oxidative addition of C–H bonds to square-planar, d^8 (16-electron) metal complexes to occur, there must first be dissociation of a ligand to form a three-coordinate, 14-electron intermediate.[16,17] Our data convince us that all of the intermolecular activations of sp^3 C–H bonds proceed via three-coordinate L$_3$Os.

L$_3$Os is probably either T-shaped or Y-shaped.[18] For simplicitly we will assume the former. In this geometry, the vacant site of what would otherwise be a square-planar array is the position of the LUMO, and there are two filled π-symmetry orbitals, essentially d$_{xy}$ and d$_{xz}$.[18] Among the species L$_4$Os, L$_3$Os, and **4**, it is L$_3$Os that is least hindered and on that basis it may be expected to be the most reactive. In addition, since both the σ acidity and π basicity of the metal are important, it is possible that, as an Os(0) complex, L$_3$Os may have significantly greater π basicity and so greater reactivity than **4**.

The importance of understanding the competition between intramolecular ligand activation and intermolecular C–H activation has been generally appreciated.[2a,r,19] In Crabtree's Ir-based alkane activations, the PPh$_3$ ligands, normally so prone to cyclometalation, are innocuous apparently because of the reversibility of their interaction with the metal center.[2h] In the Cp*Ir(PMe$_3$) system of Bergman,[2j] the Cp*Ir(CO) system of Graham,[2k] and the Cp*Rh(PMe$_3$) system of Jones,[2l,19] cyclometalation of the Cp* or PMe$_3$ ligand is not observed. Apparently, the additional energy required to bend the ligand over to allow C–H activation offsets the favorable entropy for intramolecular activation and allows the intermolecular C–H activation to completely dominate the reactivity of these intermediates. This is possible in these cases because of the very low activation energies for the intermolecular reactions. In the case of the unsaturated intermediate Cp*Re(PMe$_3$)$_2$, however, the greater steric congestion about the metal may slow intermolecular reactions with hydrocarbons and also may bend the PMe$_3$ methyl groups a bit closer to the metal. In this case, cyclometalation of the phosphine ligand now takes place competitively with the intermolecular reaction.[2r]

Our data clearly establish that both L$_4$Os and L$_3$Os have a pronounced tendency to cyclometalate. In the case of L$_4$Os, this is to the exclusion of any intermolecular reaction with SiMe$_4$, alkanes, or even benzene or 3,3-dimethylbutene,[6] the last two of

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(13) Hofmann, P.; Padmanabhan, M. *Organometallics* **1983**, *2*, 1273–1284.

(14) (a) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1980**, 511–518. (b) Clark, G. R.; Skelton, B. W.; Waters, T. N. *J. Organomet. Chem.* **1975**, *85*, 375–394.

(15) Werner and Gotzig[20] have observed activation of benzene upon reduction of *all-trans*-(Me$_3$P)$_2$[(*MeO*)$_3$P]$_2$MCl$_2$ (M = Ru, Os) in THF–benzene solvent. This implies that the probable intermediate, (Me$_3$P)$_2$[(MeO)$_3$P]$_2$M (presumably square-planar), does undergo intermolecular C–H activation reactions, at least with arenes.

(16) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725.

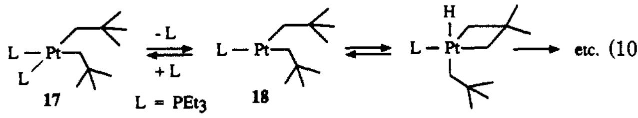
(17) Most information regarding the degree of coordination of metals in reactions with saturated hydrocarbons has come from investigations of reductive eliminations rather than oxidative additions: (a) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227–5228. (b) Basato, M.; Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 3972–3976. (c) Basato, M.; Morandini, F.; Longato, B.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 649–653. (d) Clark, H. C.; Manzer, L. E.; *Inorg. Chem.* **1973**, *12*, 362–368. (e) Brown, M. P.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2457–2465.

(18) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255–7265.

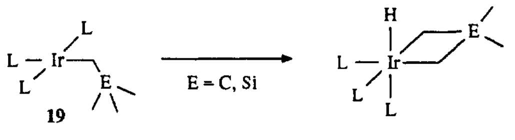
(19) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620–631.

which undergo facile C–H activation with **4**.[1,5b] As mentioned above, L_4Os is probably significantly distorted from planarity. This may in part account for the molecule's facile cyclometalation. Also, the forced propinquity of the C–H bond to the metal would result in the penetration of that bond beyond the zone of net repulsive interaction (between the filled metal d_{z^2} orbital and the C–H bonding electrons) to the point that π backbonding to the C–H antibonding orbital could become important and the oxidative addition could proceed.

It is interesting to note that Whitesides and co-workers have found[2f,16] that **17** does not undergo any intramolecular C–H oxidative addition up to the temperature required for dissociation of phosphine (eq 10). Reaction then proceeds via 14-electron, three-coordinate **18**. Tulip and Thorn reported[20] the cyclometalation reaction of **19** (eq 11), which could be taken to be analogous to that proposed by Whitesides. However, our own investigations[5c] of the Tulip reaction have revealed that the cyclometalation of **19** proceeds directly via the 16-electron complex without phosphine dissociation.



(10)



(11)

Thus, in a very qualitative way, the ease of intramolecular C–H oxidative addition appears to increase across the series of four-coordinate, d^8 metal–phosphine complexes from Pt(II) to Ir(I) to Os(0). This trend parallels the metal basicity, underscoring the importance of the absolute energies of the reactive orbitals to the ease of C–H oxidative addition.

Although we know little quantitatively about the relative energies of the species L_4OsHR, a qualitative free energy picture is given in Figure 2. The reactivity of **1** contrasts sharply with the thermal stability of most of the other L_4OsHR species that we have prepared. It is certain that **1** lies well above **7** and **8** and that **7** and **8** are at about the same energy (at least at 178 °C with 1 M C_6H_6). Steric compression between the neopentyl group and the four phosphines is responsible for **1** being at higher energy. For example, $L_4Os(H)Me$ exhibits a half-life for dissociation of L (measured by exchange with L′)[1] of 4 days at 110 °C and a half-life for conversion to **8** of 1 week at 150 °C.[5d] In comparison, the same two processes for **1** exhibit half-lives of 32 min and 3 days, respectively, both at 80 °C. This higher reactivity of **1** allows observation of relatively clean and mild chemistry of what would otherwise be a highly inert octahedral Os(II) system.

A particularly interesting comparison would be between the activation free energies for the reductive elimination of neopentane from saturated **1** vs unsaturated **4**. Of course we cannot make this comparison quantitatively, because we do not known the rate of uptake of L by **4**, but it is clear that the barrier is significantly lower for elimination from the five-coordinate intermediate. This corroborates a trend seen in reductive elimination chemistry of complexes of Rh, Ir, and Pt[16,17] but is the first example where both process have been clearly observed simultaneously.

We have observed secondary kinetic isotope effects in two reactions of $[(CD_3)_3P]_4Os(H)Np$: the dissociation of L and the reductive elimination of neopentane. The k_H/k_D appears to be about 1.3–1.4 in both cases. Although electronic effects cannot be ruled out, we believe that these isotope effects are most likely to have their origins in steric effects. It is known from microwave spectroscopy that the C–D bond is ca. 0.003 Å shorter than the C–H bond,[7] and both of the reactions involved here are certainly driven by steric crowding. The isotope effect perhydrogen would thus be $(1.4)^{1/36}$ or 1.009. Steric isotope effects larger than this have been reported.[21]

We have measured several deuterium kinetic isotope effects of C–H activation reactions in this system: for oxidative addition of the C–H bond of benzene to the five-coordinate Os(IV) complex **4** (3.3),[1] for activation of $SiMe_4$ and its own phosphine ligand by L_3Os (3.6 and 2.2, respectively), and activation of its own ligand by L_4Os (4.7). These numbers have been very useful in the delineation of mechanistic alternatives, but we believe that speculation as to the significance of their relative magnitudes is premature.

The single-atom H/D exchange in mixtures of L and L′ in the presence of **1** to give L-d_0, -d_1, -d_2, ···, -d_8, and -d_9 is bothersome. It does not appear to arise from random exchange of the system as might be catalyzed by heterogeneous or colloidal metal, however. Conversion of $(L')_nL_{4-n}Os(H)Np$ to **8** at 80 °C without added L/L′ proceeds essentially without any H/D atom interligand exchange. There is no exchange from L′ into nondeuterated solvents or any exchange from cyclohexane-d_{12} or tetramethylsilane-d_{12} solvents into L. Complex **8** must be heated above ca. 150 °C in the presence of L′ before any exchange occurs, and at 155 °C exchange of L′ with coordinated L is far more rapid than interligand H/D atom exchange. We have found that above 90 °C *fac*-$(Me_3P)_3Ir(H)(\eta^2\text{-}CH_2CMe_2CH_2)$ also catalyzes the same intermolecular isotopic exchange in mixtures of L and L′ without any incorporation of deuterium into the hydride or aliphatic ligands of the catalyst.[5c] The nature of this interesting exchange is under investigation. At this point, it does not appear to be a random metal–colloid-catalyzed process.

A question related to the H/D atom exchange is that of the source of free L upon thermolyses of **1** in saturated solvents. As noted above, the amount formed varies over the range of more than a factor of 10 in concentration and typically corresponds to the amount of L present in ca. 1% of the starting material. The observations just cited above regarding the apparent absence of any metal colloid or precipitate strongly suggest that the free L does not come from that source. Whatever the origin of free L, it is quenched by benzene since NMR-detectable quantities of L do not build upon thermolysis of **1** in that solvent. In contrast, mesitylene is attacked only at the saturated C–H site, not at the ring, and detectable L does appear in that reaction. We do not know the source of L, but its generation does not cause any irregularities that we can detect. The rates of thermolysis of **1** are cleanly first-order, and they show a regular inhibitory dependence on [L].

The fact that L_3Os attacks only the benzylic position of mesitylene is to be contrasted to the ability of [bis(dicyclohexylphosphino)ethane]platinum(0) to attack both the ring and the benzylic positions in the same molecule.[2v] In fact, the two Pt(H)(mesityl) structural isomers facilely equilibrate with $K \approx 1$ at 69 °C.[2v]

To date, the goal of using the M–C-bound organic fragment obtained via $C(sp^3)$–H disruption for some useful catalytic reaction remains elusive for soluble late-transition-metal systems. Nevertheless, important insight is being gained into the requirements for C–H reactivity with metal complexes. Activations of methane[3b] and the methyl C–H bonds of linear hydrocarbons by this osmium system have been observed. These results will be presented in detail.[5d] We are currently synthesizing analogues of **1** using other phosphorus ligands with the goal of acquiring information regarding the importance of metal acidity and basicity in C–H oxidative-addition and reductive-elimination reactions.

Experimental Section

General Comments. Chemical shifts of NMR spectra, recorded on 270- or 360-MHz FT spectrometers, are reported in δ downfield from tetramethylsilane for ^1H and ^{13}C and from internal or external PMe_3, which is assigned a value of δ −62.3 with respect to 80% H_3PO_4 for ^{31}P spectra; unless otherwise stated, all coupling constants are apparent, not calculated, with absolute values reported in hertz. All manipulations and reactions involving organometallic compounds were carried out in evac-

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Table II. Rates of Disappearance (k_{obsd}) of $L_4Os(H)Np$ (**1**) and $(L)_4Os(H)Np$ (**1**-d_{36}) on Thermolysis in Various Solvents

reactn	solvent	k_{obsd} ($s^{-1} \times 10^6$)	free [L] ($M \times 10^3$)
		$L_4Os(H)Np$ (**1**)	
1	TMS	4.77	0.78
2	TMS	3.52	1.1
3	TMS	2.53	1.5
4	octane	2.67	1.7
5	TMS-d_{12}	2.50	2.1
6	pentane	2.50	2.2
7	cyclohexane	2.35	2.4
8	pentane	2.25	2.0
9	cyclohexane	2.23	1.9
10	TMS	1.97	2.9
11	cyclohexane-d_{12}	1.92[a]	2.7
12	cyclopentane	1.65	8.5
13	TMS	1.57	10
14	hexane	1.44	8.9
15	hexane	1.25	14
16	hexane	1.12	67
17	hexane	1.05	170
		$(L')_4Os(H)Np$ (**1**-d_{36})	
18	cyclopentane	1.94	1.4
19	cyclopentane	1.78	1.6
20	cyclopentane	1.71	2.2
21	cyclopentane	1.55	2.5
22	cyclohexane-d_{12}	1.43	3.6
23	cyclohexane-d_{12}	0.84	16
24	cyclohexane-d_{12}	0.81	25
		$L_4Os(H)Np$ (**1**)	
25	mesitylene	3.03	1.1

[a] In cyclohexane-d_{12} no D was incorporated into any Os complex.

uated sealed tubes or under an atmosphere of argon or dinitrogen purified over reduced copper catalyst and in flamed-out glassware by standard Schlenk techniques or in a dry nitrogen atmosphere box. THF and Et_2O were distilled from purple solutions of sodium/benzophenone. Pentane, hexane, octane, cyclopentane, and cyclohexane were washed with portions of concentrated H_2SO_4 until the acid remained colorless, washed with aqueous $NaHCO_3$, dried over $MgSO_4$, dried over CaH_2, and distilled from sodium/benzophenone. Literature preparations were used for $L_4Os(H)Np$ (**1**),[1] $L_4Os(H)CH_2SiMe_3$ (**2**),[1] trimethylphosphine-d_9 (a standard procedure, but with CD_3I),[22] and $L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ (**8**).[2p]

Thermolysis Reactions of $L_4Os(H)Np$ (1) in Alkanes or $SiMe_4$. A typical example is as follows. In an inert atmosphere box, a 25–50-mg sample of known weight of **1** 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. The thermolyses were conducted by heating the tubes by total immersion in a constant-temperature oil bath. Products were determined by comparison of their characteristic ^{31}P NMR spectra with those of the known compounds, all of which have quite characteristic and easily distinguished spectral patterns.

Rates were followed by periodic monitoring of the reaction by ^{31}P NMR. In general in these thermolyses, a small amount of free PMe_3 was generated in the first few hours of the reaction; thereafter, the concentration of L was constant. No attempt was made to correct the kinetics calculations for changes in concentration of free L in the vapor space of the NMR (reaction) tubes as a function of temperature, although the reactions were run at 80 °C or above and the ^{31}P NMR spectra were run at ambient temperature. However, after a given sample was cooled to room temperature for the acquisition of a kinetic point, care was taken to always shake the tube to give complete equilibration of the free L between the two phases. Thus, rate constants will be systematically inaccurate by a small constant amount that should have no effect on the interpretations of or conclusions drawn from the data. The results of these reactions are tabulated in Table II, entries 1–17, and are shown in line I of Figure 1. Linear regression analysis of the relationship k_{obsd} vs 1/[L] yielded slope = 2.64 (0.14) × 10^{-9}, intercept = 1.10 (0.08) × 10^{-6}, and R^2 = 0.962. Standard deviations in rate constants were generally less than 5%, sometimes 5–10%; most of the scatter in Figure 1 is from the uncertainty in the concentration of L, with the greatest uncertainty in those samples most dilute in L.

The volatiles from sample 5 run in $SiMe_4$-d_{12}, containing the solvent and the liberated CMe_4, were collected by trap-to-trap distillation, and then a very small portion of these was again trap-to-trap-distilled. GC–mass spectrometric analysis of this sample revealed the m/e = 57 peak of $C_4H_9^+$ and an m + 1 peak of only natural abundance. No CMe_4-d_1 had formed.

Preparation of $[(CD_3)_3P]_4Os(H)Np$. Cyclopentane solvent (2 mL) was distilled onto 970 mg of neopentyl hydride **1** in a 10-mm NMR tube, and ca. 1.5 mL (15 mmol) of L′ was condensed in. After two freeze–evacuate–thaw cycles, the tube was sealed and the sample was heated by total immersion in a bath at 80 °C. After 30 h, the tube was opened, the L and L′ were removed, fresh pure L′ (2 mL) was added, and the tube was sealed as before. Heating was continued for an additional 35 h at 80 °C. The exchanged material was recrystallized twice from a minimum of hexane at −20 °C and dried under vacuum. A ^{31}P NMR spectrum showed that the resonances for **1** at δ −50.7, −58.7, and 63.2 were >96% replaced by L′ resonances at δ −52.6, −60.6, and −65.2.

Thermolysis Reactions of $[(CD_3)_3P]_4Os(H)Np$ (1-d_{36}) in Alkanes; Check for Isotopic Crossover. Seven samples of **1**-d_{36} were prepared in cyclohexane-d_{12} or cyclopentane solvent in sealed NMR tubes as described above for **1**. L′ had been added to two of these; in the other cases traces of free L′ formed as usual after brief heating. The samples were heated by total immersion in a bath at 80 °C, and progress of the reaction was followed by ^{31}P NMR. Rates are recorded in Table I, samples 18–24, and in line II of Figure 1. Linear regression analysis of the relationship k_{obsd} vs 1/[L] yielded slope = 1.73 (0.18) × 10^{-9}, intercept = 8.1 (0.7) × 10^{-7}, and R^2 = 0.949.

Sample 24 was opened, and the volatiles were collected by trap-to-trap distillation. The distillate was washed three times with concentrated HCl in a closed vial to remove the L′, and the organic layer was dried over $MgSO_4$. A very small portion of the volatiles was collected by trap-to-trap distillation, and this was submitted to GC–mass spectrometric analysis. The m/e peak corresponding to the $C_4H_9^+$ ion from neopentane showed no m + 1 peak above natural abundance.

Cyclization Isotope Effect for Thermolysis of $L_4Os(H)Np$ (1) with Excess L. A sample of **1** (35.5 mg, 0.063 mmol) in 0.8 mL of octane was sealed in a 10-mm NMR tube with ca. 13 mmol of a 1/3.3 mixture of L/L′, and the tube was heated by total immersion in a bath at 80 °C. The reaction was monitored by ^{31}P NMR spectroscopy. After 40 h, the L/L′ ligands had completely equilibrated with all the ligand positions in **1**, but no significant conversion to cyclometalation product **8** had occurred. With continued heating, H/D exchange occurred between phosphine ligands at a rate comparable to that of conversion of **1** to **8**, as evidenced by the appearance of peaks in the NMR at one-ninth intervals between L at δ −62.3 and L′ at δ −65.1. Correspondingly, the ^{31}P resonances of **1**, and of **8** as it formed, were increasingly broadened until no information on the state of deuteration of the materials could be obtained from integration. Conversion of **1** to **8** (presumably **8**-d_0–**8**-d_{36}) was essentially complete after 22 days at 80 °C. The isotope effect for the cyclometalation could be determined by comparison of the (^1H integral of the Os–H)/(^2H integral of the Os–D) ratio to the H/D composition of the total ligand pool. The ratio was determined as follows. The volatiles were removed under vacuum, **8** (H/D) was dissolved in C_6F_6, and 1.5 μL of $(C_6H_5)_2Si(CH_3)(CD_3)$ was added. The Os–H ^1H resonance was integrated with respect to $Si(CH_3)$ and the Os–D ^2H resonance with respect to $Si(CD_3)$. This treatment yielded δ(Os–H)/δ(Os–D) = 1.49. Since the L′/L D/H ratio was 3.32, k_H/k_D for the cyclometalation was 4.9.

A second reaction was run in the same fashion as above with 31.5 mg of **1** and a 70-fold excess of a 1/3.26 mixture of L/L′ in 0.8 mL of octane. This time the reaction was heated at 80 °C for 2.5 months to check for the stability of product **8** to H/D exchange under the reaction conditions. Internal standard, $(C_6H_5)_2Si(CH_3)(CD_3)$ (2.0 μL), was added to the cyclometalated product in C_6F_6, and the OsH/OsD ratio was determined. The isotope effect was calculated to be 4.5.

A sample of **8**-d_{36} in cyclohexane-d_{12} was heated in the presence of ca. 100-fold excess of nondeuterated L at 80 °C for 60 days (7 half-lives for the cyclometalation reaction). No appearance of Os–H could be detected in the ^1H spectrum.

Activation Parameters for Thermolysis of $L_4Os(H)Np$ (1) with Excess L. The rate of conversion of **1** to **8** was followed by thermolysis in sealed NMR tubes as above. Samples were all prepared with the same concentration of L at 0.9 M in cyclopentane. Temperatures (°C) and respective rate constants (s^{-1}) were as follows: 80, 1.10 × 10^{-6}; 90.3, 3.90 × 10^{-6}; 99.2, 1.20 × 10^{-5}; 110.0, 3.44 × 10^{-5}. An Arrhenius plot of these data gave E_a = 31.2 (0.9) kcal/mol, ln A = 30.8 (1.2), ΔH^*(80 °C) = 30.3 (0.9) kcal/mol, and ΔS^*(80 °C) = 0.3 (2.4) eu, with R^2 = 0.9985.

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Kinetic Isotope Effect on Dissociation of L from 1. Two samples were prepared in sealed NMR tubes as above. The first contained 18 mg of **1** in 1.2 mL of cyclohexane and 0.67 M L′. The second contained 16 mg of **1**-d_{36} in 1.2 mL of cyclohexane and 0.69 M L. Each of the samples was in turn heated at 65 °C under identical conditions in the probe of a 360-MHz FT NMR spectrometer, after careful temperature calibration of the apparatus. The reaction was followed by ^{31}P NMR. In each sample, the low-field resonances (mutually trans ligands) showed complete exchange equilibration before any exchange of the two high-field resonances (mutually cis ligands) occurred. The low-field resonance for L_2Os appeared at δ −50.7, for $(L')_2Os$ at δ −52.6, and for L′LOs as an AB multiplet at δ −48.8, −51.3, −52.0, and −54.5. Thus, for the reaction of **1** with L′, the rate of the first dissociation of L was determined directly from the dsappearance of the δ −50.7 peak, and for the reaction **1**-d_{36} with L, the rate of the first dissociation of L′ was determined from the disappearance of the δ −52.6 peak. These rate constants were, respectively, $k_{1(H)} = 1.05\ (0.02) \times 10^{-4}$ and $k_{1(D)} = 8.25\ (0.27) \times 10^{-5}$. Thus, $k_H/k_D = 1.27\ (0.05)$.

Cyclization Isotope Effect for Thermolysis of $L_4Os(H)Np$ (1) without Added L. Complex **1** (25.8 mg, 0.0455 mmol) was heated at 80 °C in 1 mL of cyclohexane with 0.7 mmol of L′ for 48 h. The material was recrystallized twice from hexanes, yielding 21 mg (76%) of $L_n(L')_{4-n}Os(H)Np$ (**1**-d_{29}). ^{31}P NMR showed this material to be randomly labeled in an L′/L ratio of 4.0/1. The material was used to prepare two kinetics samples in sealed NMR tubes; 15 mg of **1**-d_{29} in 0.46 mL of cyclohexane was heated at 80 °C, with progress monitored by ^{31}P NMR. The rate was $1.77\ (0.03) \times 10^{-6}\ s^{-1}$ ($[L + L'] = 3.8 \times 10^{-3}$). The composite isotope effect k_H/k_D for the cyclization step via both L_4Os and L_3Os was measured from the ratio of the ^{31}P NMR integrals of the cyclometalated ligands at δ −70.2 (L) vs −72.0 (L′) compared to the L/L′ composition of the ligands in starting **1**-d_{29} and was found to be 3.1 (0.3). Assuming k_H/k_D for the L_4Os path is 4.7 (0.2), the isotope effect for the L_3Os path was calculated as described in the Results to be 2.24 (0.42). The second sample was treated in the same way, except that the NMR tube was prerinsed with neopentyllithium in hexane: 7 mg of **1** in 0.25 mL of cyclohexane; rate = $1.85\ (0.14) \times 10^{-6}\ s^{-1}$ ($[L + L'] = 1.4 \times 10^{-3}$). The composite k_H/k_D was 2.88 (0.32), which led to a calculated value for the isotope effect via L_3Os of 2.14 (0.42).

Thermolysis of $L_4Os(H)Np$ (1) in $SiMe_4$/$SiMe_4$-d_{12}; Isotope Effect on the C–H Activation Step. A mixture of $SiMe_4$ and $SiMe_4$-d_{12} was prepared and its composition was checked by mass spectrometry. The ratio of the peak at $m/e = 73$ for $SiMe_3^+$ to that at $m/e = 82$ for $SiMe_3$-d_9^+ revealed the solvent composition to be 15.1% $SiMe_4$ and 84.9% $SiMe_4$-d_{12}. A sample of 31 mg (0.055 mmol) of **1** in 1.2 mL of this solvent mixture in a sealed NMR tube was heated at 80 °C, and progress of the reaction was followed by ^{31}P NMR. Upon completion of the conversion of **1** to **8** and a mixture of **2** and **2**-D_{12}, the volatiles were removed by trap-to-trap distillation and the residue was dried under vacuum. The residue was taken up in ca. 1 mL of mesitylene in an NMR tube, and the tube was sealed under ca. 2.5 mmol of ethylene. This was heated at 80 °C for 2 days, when NMR showed that the originally formed **8** remained but all of the **2**/**2**-d_{12} had been converted to 1 equiv of free L and a single new phosphorus-containing material. ^{31}P NMR (mesitylene): δ −46.3 (2 P, d, $J_{PH} = 13.2$ Hz), −51.8 (1 P, t). ^{1}H NMR (C_6D_6): δ 0.81 (18 H, vt, $J_{PH} = 5.8$ Hz, *trans*-$Os(PMe_3)_2$), 1.16 (4 H, m =CH_2), 1.40 (9 H, PMe_3), 1.59 (4 H, m, =CH_2). The ^{1}H NMR spectrum contains no OsH resonance. The same material (plus 1 equiv of free L) also forms upon heating of **1** with ethylene at 80 °C. Good elemental analyses are not yet available; tentative assignment is $L_3Os(CH_2{=}CH_2)_2$ (**13**). The volatiles from the reaction of **2**/**2**-d_{12} with ethylene were collected by trap-to-trap distillation and submitted to GC–mass spectrometric analysis. The ratio of the peak for $SiMe_3^+$ to that for $SiMe_3$-d_9^+ showed the composition of the recovered $SiMe_4$ to 38.8% $SiMe_4$ and 61.2% $SiMe_4$-d_{12}. Thus, k_H/k_D for the step involving oxidative addition of the $SiMe_4$ C–H bond was 3.57.

Activation Parameters for Dissociation of L from $L_4Os(H)CH_2SiMe_3$. The rate of incorporation of L′into **2** was determined by heating hexane solutions of **2** in the presence of ca. 1 M L′ in sealed NMR tubes. Each of four samples was heated by total immersion in a heating bath at a different temperature, and the exchange was followed by ^{31}P NMR. The mutually trans phosphines (δ −49.6) exchanged much faster than the two mutually cis phosphines (δ −57.7 and −59.4). Incorporation of L′ into both mutually trans sites moved that resonance to δ −51.8. Incorporation of only the first L′ therefore rendered the two mutually trans L′s nonequivalent and generated an AB multiplet at δ −48.1, −50.5, −51.2, and −53.6, well separated from the original resonance at δ −49.6. Thus, the rate of the first incorporation is exactly the rate of disappearance of the δ −49.6 peak, and this is exactly the rate of the first phosphine dissociation from **2**. Temperature (°C) and the respective first-order rates k (s^{-1}) were as follows: 66.0, 1.48×10^{-6}; 79.3, 1.00×10^{-5}; 90.9, 5.01×10^{-5}; 99.2, 1.42×10^{-4}. An Arrhenius plot of these data gave $E_a = 34.6$ (0.2) kcal/mol, ln $A = 37.9$ (0.3), $\Delta H^\ddagger$ (80 °C) = 33.9 (0.2) kcal/mol, and $\Delta S^\ddagger$(80 °C) = 14.5 (0.6) eu, with $R^2 = 0.9999$.

Thermolysis of $L_4Os(H)Np$ (1) in Mesitylene. Mesitylene was heated at reflux over sodium and distilled. A sample of 100 mg of **1** in 2.0 mL of mesitylene in a sealed NMR tube was heated by total immersion in a bath at 80 °C. Progress of the reaction was monitored by ^{31}P NMR (entry 25 in Table I). The products were (NMR yields) **8** (16%) and $L_4Os(H)[CH_2(3,5\text{-}Me_2C_6H_3)]$ (**12**) (84%). The solvent was removed under vacuum, and the residue was crystallized from pentane at −78 °C and washed with cold pentane. The white solid was collected and vacuum-dried. ^{1}H NMR (C_6D_6): δ −10.11 (1 H, ddt, $J_{PH} = 69.5$, 17.1, 25.7 Hz, OsH), 1.24 (9 H, d, $J_{PH} = 5.9$ Hz, PMe_3), 1.36 (9 H, d, $J_{PH} = 6.2$ Hz, PMe_3), 1.39 (18 H, vt, $J_{PH} = 5.9$ Hz, *trans*-$Os(PMe_3)_2$), 2.36 (6 H, s, $ArCH_3$), 2.61 (2 H, m, Os CH_2Ar), 6.70 (1 H, s, ArH), 7.57 (2 H, s, ArH). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −47.9 (dd, $J_{PP} = 18.6$, 16.2 Hz, *trans*-$Os(PMe_3)_2$), −54.1 (dt,m $J_{PP} = 11.3$, 18.6 Hz, $Os(PMe_3)$ trans to H), −57.4 (dt, $J_{PP} = 11.3$, 16.2 Hz, $Os(PMe_3)$ trans to mesityl). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.0 (dm, $J_{CP} = 45$ Hz, $OsCH_2Ar$), 21.8 (s, $ArCH_3$), 23.1 (dd, $J_{CP} = 20.7$, 2.0 Hz, PMe_3), 24.7 (vt, t, $N_{CP} = 29.5$, $J_{CP} = 3.0$ Hz, *trans*-$Os(PMe_3)_2$), 29.4 (d, $J_{CP} = 24.6$ Hz, PMe_3), 123.8 (s, Ar), 130.7 (d, $J_{CP} = 3.0$ Hz, Ar), 135.5 (s, Ar), 157.2 (d, $J_{CP} = 7.9$ Hz, Ar). Anal. Calcd for $C_{21}H_{48}P_4Os$: C, 41.03; H, 7.87. Found: C, 40.29; H, 7.99.

Equilibration of $L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ (8) with Benzene. A sample of cyclometalated complex **8** and benzene (1.0 M) in cyclohexane solvent in a sealed NMR tube was heated by total immersion in a bath at 178 °C. Progress of the reaction was followed by ^{31}P NMR. The resonances of **8** diminished, and those of phenyl hydride complex **7** grew in at δ −46.0 (2 P), −57.0, and −57.8. The equilibrium constant calculated for the reaction with **7** as reactant and **8** and C_6H_6 as products was K(178 °C) = 0.97. Heating of **8** in neat benzene under the same conditions led to formation of ca. 90% **7**, while heating of **7** in neat hexanes led to ca. 90% of **8**.

Exchange of $L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ (8) with $P(CD_3)_3$. A sealed NMR tube containing 25 mg (0.051 mmol) of cyclometalated material **8** in 1.7 mL of C_6D_{12} and 1.2 mmol of L′ was heated at increasing temperatures until a reasonable rate of reaction was attained at 155 °C. Progress of the reaction was monitored by ^{31}P NMR, and the qualitative rate of incorporation of L′ was found to be the same for all positions of **8** including the cyclometalated position. Incorporation was easily detected because of the isotopic shift on the L resonances [δ L peak position (δ L′ position)]: δ −41.7 (−43.8), −45.7 (−47.7), −51.5 (−53.6), −70.2 (−72.0). Interligand H/D exchange was much slower than L/L′ exchange; only a few percent of the former was evident after several half-lives of the latter.

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