Inter- and Intramolecular C-H Bond Forming and Cleavage Reactivity of Two Different Types of Poly(trimethylphosphine)ruthenium Intermediates

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Abstract: The products and mechanisms of the thermal reactions of several complexes of the general structure $(PMe_3)_4Ru(X)(H)$, where X is an aryl or benzyl group, have been investigated. The mechanism of decomposition depends critically on the structure of the complex and the medium in which the thermolysis is carried out. For example, thermolysis of the benzyl hydride complex $(PMe_3)_4Ru(CH_2Ph)(H)$ (**1**) leads to reductive elimination of toluene directly from the 18-electron complex and yields the intermediate $(PMe_3)_4Ru$ which undergoes intramolecular oxidative addition of a phosphine C-H bond. Heating the phenyl hydride complex $(PMe_3)_4Ru(Ph)(H)$ (**5**) in cyclohexane also leads to reductive elimination to form $(PMe_3)_4Ru$. In contrast, allowing **5** to decompose in arene solvents leads to exchange of the arene ring by an intermolecular C-H activation mechanism involving the intermediate $(PMe_3)_3Ru(Ph)(H)$ formed by rapid, reversible phosphine dissociation. Thermolysis of $(PMe_3)_4Ru(H)_2$ does not result in the formation of H_2 and $(PMe_3)_4Ru$, but instead it undergoes only H/D exchange with C_6D_6 solvent via the intermediate $(PMe_3)_3Ru(H)_2$. Thus, the intermediate $(PMe_3)_4Ru$ gives rise to products resulting from intramolecular C-H activation, whereas $(PMe_3)_3Ru(Ph)(H)$ and $(PMe_3)_3Ru(H)_2$ lead only to products resulting from intermolecular C-H activation.

Introduction

Reductive elimination from alkyl(hydrido)metal complexes to form C-H bonds has been shown to be an important step in several catalytic processes.[1] Careful studies of this reaction have revealed different mechanisms for the process.[2,3] For example, studies with metals in the platinum triad have shown that reductive elimination can be induced by ligand dissociation as well as by ligand association. A saturated Ir^{III} system with labile ligands was shown to undergo a reductive elimination reaction induced both thermally[2j,k] and photochemically[2g] by ligand dissociation.

The microscopic reverse of this reaction, oxidative addition of C-H bonds, has also been looked at extensively in recent years in the hope of designing a system that will catalytically functionalize saturated hydrocarbons.[4] One approach to this problem involves oxidative addition of an alkane to the transition-metal center followed by coordination of an unsaturated organic molecule, migratory insertion, and reductive elimination of the functionalized alkane. In fact, homogeneous catalytic systems that functionalize arenes (albeit with low turnover numbers) have been achieved both thermally and photochemically by this route.[5]

Several electron rich late transition metal systems are now known which undergo oxidative addition of hydrocarbon C-H bonds, leading to alkyl hydride complexes.[2b-f,4,6] Many of these metal systems contain ancillary ligands that do not dissociate easily, and this has limited the ability of these complexes to open a coordination site and undergo insertion reactions into the alkyl or hydride ligand. Most recently, dihydride and alkyl hydride complexes that activate hydrocarbons and contain potentially labile phosphines as the other ligands have been identified.[6b-e,j] In these complexes, phosphine dissociation potentially provides a site of unsaturation for potential modification of the alkyl substituent. Examples include $(DMPE)_2Fe(H)_2$ (DMPE = (dimethylphosphino)ethane), which oxidatively adds alkanes upon photochemical loss of H_2,[6d] and $(DMPE)_2Ru(aryl)(H)$, which has been shown to undergo exchange of the aryl group with arene solvent.[6k] However, a common problem with polyphosphine systems has been the observation of intra- rather than intermolecular C-H oxidative addition reactions.[2b-f,6,7] Moreover, systems with chelating phosphines do not provide an open site as readily as those with

(1) Masters, C. *Homogeneous Transition-Metal Catalysis*; Chapman and Hall: New York, 1981. Yamamoto, A. *Organotransition Metal Chemistry*; John Wiley and Sons, Inc.: New York, 1986.

(2) (a) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1978**, *10*, 343 and references therein. (b) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1346. (c) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 7964. (d) Harper, T. G.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915. (e) Ermer, S. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *Organometallics* **1989**, *8*, 1337. (f) Shinomoto, R. S.; Desrosiers, P. J.; Harper, G. P.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704. (g) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1986**, *108*, 4838. (h) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (i) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (j) Basato, M.; Morandini, F.; Longato, B.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 649. (k) Basato, M.; Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 3972. (l) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831. (m) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915. (n) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221.

(3) (a) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181. (b) Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466. (c) DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601. (d) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (e) Stille, J. K.; Gillie, A. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (f) Akermark, B.; Johansen, H.; Roos, B.; Wahlgren, U. *J. Am. Chem. Soc.* **1979**, *101*, 5876. (g) Akermark, B.; Ljungqvist, A. *J. Organomet. Chem.* **1979**, *182*, 59. (h) Akermark, B.; Ljungqvist, A. *J. Organomet. Chem.* **1978**, *149*, 97. (i) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 1892. (j) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255. (k) Kuch, P. L.; Tobias, R. S. *J. Organomet. Chem.* **1976**, *122*, 429.

(4) For recent reviews on C-H oxidative additions see: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Green, M. L. H.; O'Hare, D. *Pure. Appl. Chem.* **1985**, *57*, 1897. (c) Halpern, J. *Inorg. Chem. Acta* **1985**, *100*, 41. (d) Bergman, R. G. *Science* **1984**, *223*, 902.

(5) (a) Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047. (b) Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764. (c) Kunin, A. J.; Eisenberg, R. *Organometallics* **1986**, *7*, 2124. (d) Kunin, A. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1986**, *108*, 535. (e) Gordon, E. M.; Eisenberg, R. *J. Mol. Catal.* **1988**, *45*, 57. (f) Sakakura, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1987**, 758. (g) Maguire, J. A.; Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1989**, *111*, 7088.

(6) (a) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (b) Hackett, M.; Ibers, J. A.; Whitesides, G. *J. Am. Chem. Soc.* **1988**, *110*, 1436. (c) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449. (d) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433, 7436. (e) Antberg, M.; Dahlenberg, L. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 260. (f) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620. (g) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508. (h) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726. (i) Ghosh, C. K.; Rodgers, D. P. S.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1988**, 1511. (j) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352; **1983**, *105*, 3929. (k) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 6073.

(7) (a) Werner, H.; Gotzig, J. *Organometallics* **1983**, *2*, 547. (b) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*, C60. (c) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272. (d) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637.

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monodentate phosphines, and they make mechanistic studies difficult because the dissociation of one end of the phosphorus ligand is difficult to detect kinetically. The $(PMe_3)_4Os(R)(H)$ system (which possesses monodentate phosphine ligands) has been shown to cleanly insert into the C–H bond of benzene, but intramolecular insertion into the C–H bond of the phosphine is competitive with insertion into the C–H bond of methane.[2b]

We have studied the analogous ruthenium system $(PMe_3)_4Ru(R)(H)$ in order to improve the understanding of factors that control inter- and intramolecular oxidative addition reactions in systems containing labile phosphine ligands. Kinetic and labeling studies provide evidence for the generation of two types of intermediates, one of which yields products resulting from entirely intramolecular oxidative addition and the other exclusively from intermolecular addition. Moreover, these studies indicate that reductive elimination of alkane from the alkyl hydride complexes proceeds by a simple one-step mechanism, unusual for most d^6 and d^8 metal systems possessing labile ligands.

Results

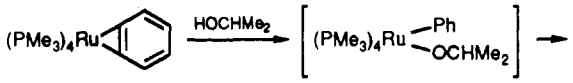
Synthesis of Tetrakis(trimethylphosphine)ruthenium Alkyl Hydride and Deuteride Complexes. The benzyl hydride complex $(PMe_3)_4Ru(CH_2Ph)(H)$ (**1**) was synthesized as shown in eq 1.

$$cis\text{-}(PMe_3)_4Ru(Me)(Cl) \xrightarrow[Et_2O/-CH_4]{H_2\ (3\ atm)} cis\text{-}(PMe_3)_4Ru(H)(Cl) \xrightarrow[Et_2O]{PhCH_2MgCl} cis\text{-}(PMe_3)_4Ru(H)(CH_2Ph) \quad (1)$$

3 **2** **1**

The known methyl chloride complex **2**[8] was exposed to 3 atm of hydrogen in ether to yield hydrido chloride **3**[9] as the only compound observed by $^{31}P\{^1H\}$ NMR spectrometry. Attempts to isolate the hydrido chloride gave low yields; an insoluble light yellow precipitate was obtained upon removal of the ether solvent under vacuum. Therefore, **2** was used in situ. Treatment with 1.1 equiv of benzylmagnesium chloride followed by crystallization from pentane gave **1** in 67% yield. The ^1H NMR spectrum of the benzyl hydride complex displayed a doublet of doublet of triplets in the hydride region of the ^1H NMR spectrum and an A_2BC pattern in the $^{31}P\{^1H\}$ spectrum, indicating a cis octahedral geometry. The benzyl deuteride was prepared in comparable yield by an analogous route, using 3 atm of deuterium in the first step. Neither the EI nor FAB mass spectroscopy provided a molecular ion for the benzyl hydride complex, so the isotopic purity of the benzyl deuteride could not be determined by this method. However, a minimum isotopic purity could be determined by ^1H and ^2H NMR spectroscopy. The ^2H NMR spectrum of a 0.043 mmol benzene solution of **1**-d_1 showed only a signal corresponding to the deuteride resonance, and the ^1H NMR spectrum of a 0.029-mmol solution of **1**-d_1 showed no signal for the hydride resonance. A 0.0014-mmol solution of **1**-d_0 did show a detectable hydride resonance by ^1H NMR spectroscopy, providing a lower limit of 95% for the isotopic purity for **1**-d_1.

The phenyl hydride complex $(PMe_3)_4Ru(Ph)(H)$ (**5**) was most conveniently prepared by room temperature addition of 1 equiv of isopropyl alcohol to a pentane solution of the recently reported[10] benzyne complex, $(PMe_3)_4Ru(\eta^2\text{-}C_6H_4)$ (**4**) (eq 2). Concentration



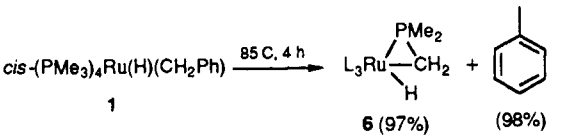
4

$$cis\text{-}(PMe_3)_4Ru(H)(Ph) + Me_2CO \quad (2)$$

5

of the solution and cooling to −40 °C gave **5** in 48% yield. The phenyl deuteride complex was synthesized by the addition of methanol-d_3 to a benzene solution of the benzyne complex and was crystallized from pentane to give **5**-d_1 in 43% yield. Only a signal corresponding to the deuteride resonance was observed in the ^2H NMR spectrum, and no signal for the hydride resonance was observed in the ^1H NMR spectrum, again indicating >95% isotopic purity. The resonances in the phenyl region of the ^1H and $^{13}C\{^1H\}$ NMR spectra of **5** at room temperature were broad, but sharpened upon cooling to −40 °C, at which point rotation of the phenyl ring was slow on the ^1H and $^{13}C\{^1H\}$ NMR time scales. The hydride resonance in the ^1H NMR spectrum again appears as a doublet of doublet of triplets pattern, and the room temperature $^{31}P\{^1H\}$ NMR spectrum displayed an A_2BC pattern, indicating a cis geometry as was observed for the benzyl hydride complex **1**.

Thermolysis and Isotope Exchange Reactions. Thermolysis of the benzyl hydride complex in C_6D_6 solvent at 85 °C for 5 h yielded toluene and the cyclometalated complex $Ru(CH_2PMe_2)(PMe_3)_3(H)$ (**6**) in 97% yield (^1H NMR spectroscopy) resulting from oxidative addition of the ligand C–H bond to the metal center (eq 3). This compound was reported by Werner

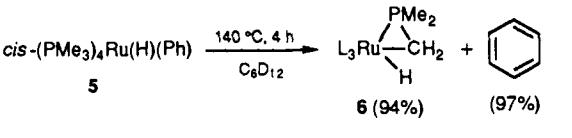


1 **6** (97%) (98%) (3)

as the product of the reduction of $Ru(PMe_3)_4(Cl)_2$ with Na/Hg.[7b] The $^{31}P\{^1H\}$ and ^1H NMR spectra of the product obtained from the thermolysis of **1** were identical with those of an independently prepared sample of **6** prepared in 22% yield by the method of Werner. The $^{31}P\{^1H\}$ NMR spectrum of the product showed an ABCD pattern and a characteristic high-field resonance at −29 ppm for the phosphine in the metalated ring. No evidence for addition of solvent C–H bonds was observed in the thermolysis of **1**.

Thermolysis of the benzyl deuteride complex **1**-d_1 in cyclohexane yielded **6** in 97% yield and exclusively toluene-d_1, as determined by comparison to an authentic sample prepared by the addition of D_2O to a solution of $PhCH_2MgBr$. The ^2H NMR spectrum of the reaction mixture showed no hydride signal, and GC/MS analysis of the volatile materials showed that the toluene consisted of only toluene-d_1. The reaction was run in cyclohexane so that the aromatic and methyl regions of the toluene could be integrated in the ^2H NMR spectrum of the final reaction solution. The ratio of the signal for the methyl group on the product toluene-d_1 to the signal for the ortho position was 11:1. This small degree of deuteration in the aryl ring presumably occurred by reversible ortho metalation of the aryl C–H bond to the metal center, consistent with other ortho metalation reactions in this system[10,11] and others.[12]

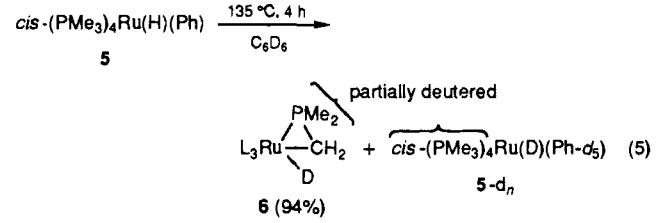
Thermolysis of the phenyl hydride complex **5** in cyclohexane-d_{12} at 135 °C for 8 h again yielded the cyclometalated complex **6** in 94% yield by ^1H NMR spectroscopy (eq 4). However, thermolysis



5 **6** (94%) (97%) (4)

of **5** in C_6D_6 at 140 °C for 8 h yielded the cyclometalated deuteride complex $Ru(CH_2PMe_2)(PMe_3)_3(D)$ (**6**-d_1) in 90% yield by ^1H NMR spectroscopy with deuterium incorporated into the hydride position (eq 5). When this reaction was run in C_6D_6 and monitored after 4 h at 135 °C, the ^1H NMR spectrum showed an absence of both the aromatic signals and the hydride signal of

(8) Statler, J. A.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 1731.
(9) Jones, R. A.; Mayor Real, F.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 551.
(10) (a) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717. (b) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3404.
(11) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Organomet. Chem.* **1990**, *394*, 417.
(12) (a) Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983. (b) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 6713. (c) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713. For reviews of cyclometalation reactions see: (d) Constable, E. C. *Polyhedron* **1984**, *3*, 1037. (e) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. (f) Shilov, A. E.; Steinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97.



the residual starting material and an increase in the solvent benzene peak (eq 5). The $^{31}P\{^1H\}$ NMR spectrum of the residual starting material exhibited the A_2BC part of an A_2BCX pattern, where X = D. The ^2H NMR spectrum contained resonances corresponding to the aromatic and hydride hydrogens of **5** in a ratio of 5:1, consistent with complete exchange of deuterated benzene into **5**. These data indicate that the rate of exchange between **5** and solvent benzene-d_6 is greater than the rate of reductive elimination to form **6**. Deuterium incorporation was also observed in the phosphine ligands by ^2H NMR spectroscopy; the ratio of deuterium in the phosphine region to deuterium in the hydride position was roughly 1:1.

Thermolysis of phenyl deuteride complex **5** was conducted in toluene at 140 °C, monitoring the reaction by ^2H NMR spectrometry over the course of 4 h, followed by determination of the isotopic distribution in the benzene product by GC/MS of the volatile materials and determination of the conversion of phenyl hydride to tolyl hydride by addition of acid to the organometallic products. Monitoring the reaction by ^2H NMR spectroscopy showed a decrease in the hydride (deuteride) signal, an increase in the benzene resonance, and the appearance of signals for the phosphine region. However, the ratio of deuterium in the phosphine region to deuterium in the benzene product was small, between 1:4 and 1:5 throughout the thermolysis. Analysis of the volatile materials showed that the ratio of benzene-d_0 to benzene-d_1 was significantly greater than these values. The thermolysis was conducted twice, and the ratio of benzene-d_0 to benzene-d_1 was found to be 1:0.86 and 1:0.67 by GC/MS.

The extent of conversion of phenyl deuteride to tolyl hydride could not be simply determined by ^1H or $^{31}P\{^1H\}$ NMR spectroscopy because of the similar NMR spectra of the starting complex **5** and the arene exchange products. Instead, the conversion was determined by treating a portion of the nonvolatile products with methanesulfonic acid in ether and determining the ratio of benzene to toluene by GC analysis. The ratio of phenyl to tolyl groups was found to be 1:2.85 and 1:2.05 by this method for the two experiments. To confirm that all of the solvent toluene had been removed, a portion of the nonvolatile materials which were not treated with acid was analyzed by ^1H NMR spectroscopy in C_6D_6. The spectrum contained no toluene resonances, but it did contain a resonance at δ 2.40 and 2.37 corresponding to the methyl groups of the metal-bound tolyl groups, presumably meta and para substituted.

Thermolysis of the known $Ru(PMe_3)_4(H)_2$ in benzene-d_6 at 135 °C for 9.5 h yielded $Ru(PMe_3)_4(D)_2$ quantitatively by ^1H and ^2H NMR spectroscopy (eq 6). The hydride resonance was absent

$$cis\text{-}(PMe_3)_4Ru(H)_2 \xrightarrow[C_6D_6]{135\ ^\circ C,\ 4\ h} cis\text{-}(PMe_3)_4Ru(D)_2 \quad (6)$$

in the ^1H NMR spectrum of the reaction mixture after the thermolysis, indicating at least 95% deuterium incorporation, and the deuteride signal was the only resonance observed in the ^2H NMR spectrum after the solvent was replaced with C_6H_6. The EI mass spectrum of the reaction product showed only a parent ion for $Ru(PMe_3)_4(D)_2$. No peak for $Ru(PMe_3)_4(H)_2$ or $Ru(PMe_3)_4(D)(H)$ was observed, indicating *complete* deuteration of the hydride position. Neither H_2 nor cyclometalated hydride, known to be stable at this temperature, was observed by ^1H NMR spectrometry. In fact, the dihydride complex remained unchanged in alkane solvent up to 180 °C. Thermolysis of the dihydride in *n*-pentane-d_{12} did not yield a decrease in the hydride signal or an increase in the residual pentane resonances of the ^1H NMR spectrum. In addition, no deuteride resonances were observed in the ^2H NMR spectrum of the thermolysis reaction when the deuterated solvent was removed under vacuum and replaced with undeuterated *n*-pentane.

Table I. Rate Constants for the Thermolysis of **1** in the Presence of Added Trimethylphosphine (L)

$10^{-4}k_{obs}$, s^{-1}	[L], M	$10^{-4}k_{obs}$, s^{-1}	[L], M
1.26 ± 0.19	0.0410	1.14 ± 0.17	no added phosphine,
1.35 ± 0.20	0.123		[1] = 0.0412 M
1.22 ± 0.18	0.246	1.38 ± 0.21	no added phosphine,
1.59 ± 0.24	0.492		[1] = 0.0121 M

Table II. Rate Constants for the Thermolysis of **5** in the Presence of Added Phosphine

$10^{-5}k_{obs}$, s^{-1}	[L], mM	$10^{-5}k_{obs}$, s^{-1}	[L], mM
2.93 ± 0.44	4.10	2.73 ± 0.41	27.9
2.26 ± 0.34	8.36	2.87 ± 0.43	86.8
3.06 ± 0.46	13.1		

Kinetic Studies. The thermolysis of **1** in benzene-d_6 was conducted at 80 °C in NMR tubes sealed under vacuum. The course of the reaction was monitored by removing the tubes, cooling them quickly, and then obtaining ^1H NMR spectra at ambient temperature. The growth of the methyl group resonance of the toluene product and the disappearance of the methylene resonance of the starting ruthenium complex were integrated against a ferrocene internal standard and provided identical rates. For one set of experiments, the reaction was run in 0.041–0.25 M solutions of trimethylphosphine in benzene-d_6 with a constant concentration of 0.041 M ruthenium complex. Linear first-order plots were obtained for greater than 3 half-lives at all concentrations. No intermediates were detected. To confirm the first-order behavior of the reductive elimination, the reaction was also run with an initial metal concentration of 0.0121 M. Within experimental error, the rate constants for all concentrations of phosphine and starting ruthenium complex were identical (Table I).

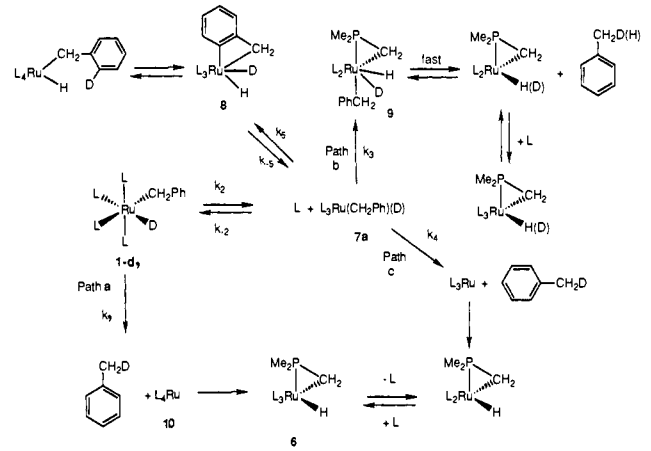
To check for rapid dissociation of phosphine ligand, compound **1** was heated to 60 °C in the presence of 4.0 equiv of PMe_3-d_9 in benzene-d_6 for 12 h. The initial solution showed only PMe_3-d_9 in the free phosphine region of the $^{31}P\{^1H\}$ NMR spectrum (the isotope shift of 0.26 ppm for each deuterium is large enough that all possible isotopes of PMe_3-d_0 to PMe_3-d_9 can be observed by $^{31}P\{^1H\}$ NMR spectrometry). Less than 10% conversion of **1** to **6** and toluene was observed after the 12 h of thermolysis. However, the $^{31}P\{^1H\}$ NMR spectrum showed a 0.86:1.0 mixture of free PMe_3-d_9 and PMe_3-d_0. Although quantitative rate studies were not carried out on this substitution reaction, these observations make it clear that the rate of phosphine dissociation is much faster than the rate of reductive elimination.

A quantitative study of the rate of reductive elimination of benzene from phenyl hydride **5** at 135 °C demonstrated that the rate was independent of phosphine concentration, as was the case for the reductive elimination of toluene from **1** at 80 °C. The thermolysis of **5** was conducted in cyclohexane-d_{12}, a solvent which does not react with **5**. The rate of the reaction was measured at 135 °C by removing the samples and monitoring the disappearance of a phosphine methyl resonance of starting material **5** by ambient temperature ^1H NMR spectroscopy. The samples contained 0.0082 M **5** and between 0.0041 and 0.087 M added phosphine. All reactions were monitored for at least 3 half-lives and provided first-order plots with correlation coefficients greater than 0.988. The rate constants were identical within experimental error at all phosphine concentrations, as shown in Table II.

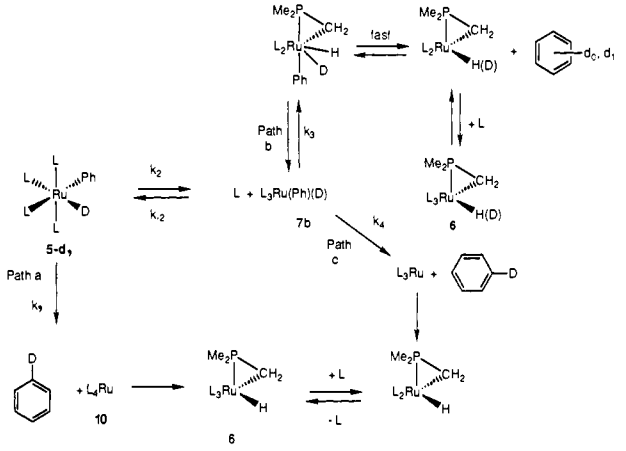
Obtaining quantitative rate data in benzene solvent was complicated by the two competing processes, exchange forming **5**-d_6 and reductive elimination forming **6**. We did, however, obtain the following qualitative information which is consistent with a phosphine-independent rate for the reductive elimination process to form **6** and a phosphine-dependent rate for the arene exchange process to form **5**-d_6.

Thermolysis of the phenyl hydride complex **5** in benzene-d_6 was conducted at 135 °C for 12 h in two NMR tubes, side by side,

Scheme I



Scheme II



one containing no additional phosphine and one containing 2 equiv of PMe_3 (0.23 M solution). The amount of conversion of **5** to **6** after 12 h of thermolysis at 135 °C was nearly identical for the two samples: the one containing no added phosphine showed 55% conversion, while the one containing 0.23 M PMe_3 showed 56% conversion by $^{31}P\{^1H\}$ NMR spectroscopy. In contrast to the formation of **6** in either cyclohexane or benzene, the rate of arene exchange was strongly dependent on phosphine concentration. No signal in the hydride or phenyl region was observed in the ^1H NMR spectrum of the sample containing no added phosphine, indicating that complete exchange had occurred with solvent benzene. However, resonances in both regions were observed for the sample containing 0.234 M phosphine.

In an attempt to assure ourselves that phosphine inhibition was due to shifting of the preequilibrium involving phosphine dissociation, rather than scavenging of some unknown trace catalyst by the added ligand, we attempted to run the thermolysis of phenyl hydride **5** in benzene-d_6 in the presence of a phosphine which would trap such a species but which would not be incorporated into **5**. Unfortunately, even addition of the larger tri-*n*-butylphosphine (4 equiv) led to substantial substitution for trimethylphosphine. Similarly, addition of the poorer electron donor triphenylphosphine led to free trimethylphosphine and a different (as yet unidentified) material, perhaps formed by ortho metalation of the ligand aryl substituents. These results clearly confirm that PMe_3 dissociation occurs rapidly, and though we have not demonstrated absolutely that this step is required for the arene exchange process, this conclusion is strongly suggested.

Like the rate of H/D exchange of phenyl hydride complex **5** with benzene, the rate of H/D exchange of the dihydride complex with benzene-d_6 appeared to depend on the concentration of phosphine. The exchange with benzene-d_6 was run at 135 °C for 9.5 h in two NMR tubes, side by side, one with no added phosphine and one with 10 equiv of PMe_3 (0.39 M). (As noted above, the dihydride is stable at these temperatures.) Again, a marked decrease in the rate of exchange was observed for the tube containing added phosphine. The ^1H NMR spectrum of the sample with no added phosphine contained no hydride resonances, while the sample with added phosphine did contain a hydride resonance.

Discussion

Mechanism of $(PMe_3)_4Ru(CH_2Ph)(H)$ Thermolysis. Three possible mechanisms for reactions induced by thermolysis of the benzyl hydride complex (illustrated for the corresponding deuteride **1**-d_1) are shown in Scheme I. Pathway a involves reductive elimination directly from the coordinatively saturated 18-electron starting material. Both pathway b and pathway c are initiated by a rapid phosphine-dissociation preequilibrium. In the pathway b branch, oxidative addition of a ligand C–H bond to the ruthenium center is followed by reductive elimination to form toluene. Pathway c involves the same 5-coordinate ruthenium(II) unsaturated intermediate, but reductive elimination to form toluene precedes oxidative addition of the ligand C–H bond.

The distribution of deuterium observed during the thermolysis of **1**-d_1 provides information that supports pathway a as the dominant route to **6**. As shown in Scheme I, pathway a would yield deuterium only in the methyl group of the toluene product with none in the final ruthenium complex. If reversible ortho metalation were occurring competitively (for example, by competitive loss of L, generating **7a** and then **8**) it would scramble deuterium into the phenyl ring of the benzyl group. Even if this ortho metalation occurs, elimination by pathway a would yield exclusively toluene-d_1. In pathway c, reductive elimination occurs from the unsaturated species **7a** before any ligand oxidative addition occurs, and so this mechanism also predicts that deuterium would be observed only in the toluene. Pathway b gives rise to intermediate **9** which contains a hydride and a deuteride on the same 7-coordinate metal center as the benzyl group. From this intermediate, reductive elimination of either toluene-d_1 or toluene-d_0 can occur, yielding products which contain deuterium both in the hydride position on the ruthenium and in the methyl group of the toluene. The formation of only toluene-d_1 or **6**-d_0 in the thermolysis of **1**-d_0 eliminates pathway b.

Our kinetic studies provided a means of distinguishing the two remaining mechanisms a and c and are consistent only with pathway a. Pathway a predicts a simple first-order rate expression, assuming that the ratio of k_2/k_{-2} is small. Consistent with this assumption, no free phosphine was observed when monitoring this reaction at 85 °C by either ^1H or $^{31}P\{^1H\}$ NMR spectrometry. Reaction by either pathway b or pathway c would be inhibited by added phosphine, if k_{-2} is fast compared to k_3 or k_4, and would show a linear inverse dependence on phosphine concentration (eq 7). At 60 °C free labeled phosphine exchanges with coordinated

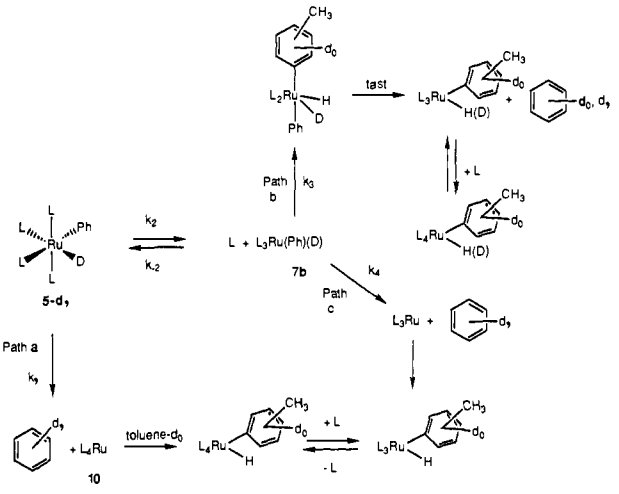
$$\frac{d[6]}{dt} = \frac{k_2k_3[1]}{k_3 + k_{-2}[L]} \qquad k_{obs} = \frac{k_2k_3}{k_3 + k_{-2}[L]} \tag{7}$$

phosphine at a much faster rate than reductive elimination occurs, demonstrating that k_{-2} is indeed larger than k_3 or k_4. Consequently, the identical rates at all concentrations of phosphine rules out both pathways b and c. Thus, rapid dissociation of phosphine occurs, but does *not* lie on the pathway to formation of **6**. Instead, reductive elimination occurs directly from the coordinatively saturated complex **1** to form the 16-electron intermediate $(PMe_3)_4Ru$ (**10**), which oxidatively adds the ligand C–H bond.

Mechanism of $(PMe_3)_4Ru(Ph)(H)$ Thermolysis. Mechanisms analogous to those shown in Scheme I for the benzyl deuteride complex are shown for the phenyl deuteride complex **5** in Scheme II. Again, the three pathways are distinguishable with use of kinetic and labeling studies. In contrast to the behavior of **1**, the thermolysis of **5** follows two of the three pathways: reductive elimination of benzene proceeds via pathway a and leads to intramolecular oxidative addition of the ligand C–H bond. In contrast, H/D exchange with aromatic solvent proceeds by pathway b as shown in Scheme III.

The mechanisms of the intramolecular C–H activation processes are shown in Scheme II. Formation of **6** from **5** in cyclohexane

Scheme III



occurred without any intermolecular arene ring exchange with solvent. In all solvents, exchange of phosphine occurred at temperatures much lower than either arene ring exchange or formation of **6**. Quantitative rate data in cyclohexane demonstrated that the rate of formation of **6** was independent of phosphine concentration, consistent with pathway a.

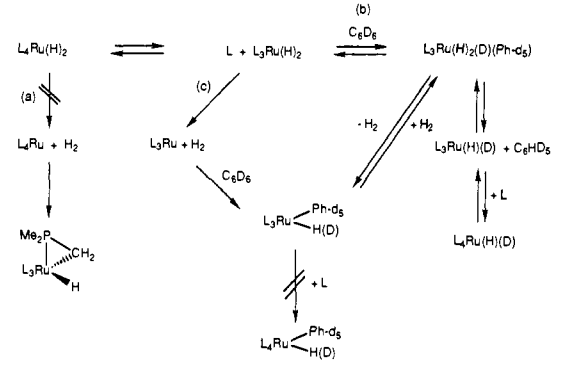
The intermolecular C–H activation processes are shown in Scheme III. In contrast to the behavior observed for the reductive elimination reactions, the rate of H/D exchange of **5** with aromatic solvents *was* inhibited by added phosphine. Thus, this reaction most likely involves rapid initial dissociation of PMe_3, leading to **7b**. Assuming that the selectivity of the reactive intermediate L_4Ru does not change significantly between 85 and 135 °C, intermolecular C–H activation of solvent benzene *must* occur by way of an intermediate different from **10** because our results with benzyl hydride complex **1** demonstrated that intermediate **10** reacts exclusively intramoleularly in arene solvents. As pointed out by a referee, the ratio of deuterium in the phosphine to deuterium in the eliminated benzene leads to the conclusion that the rate of intermolecular oxidative addition in $L_3Ru(Ph)(D)$ is 4–5 times larger than the rate of intramolecular oxidative addition.

Although pathways b and c are kinetically indistinguishable, they do predict different results for the labeling experiments. If pathway b operates, the thermolysis of **5**-d_1 in toluene would result in the formation of both benzene-d_0 and benzene-d_1, whereas pathway c would lead to formation of only benzene-d_1. The observation of both benzene-d_1 and benzene-d_0 in roughly equal amounts after 67–74% conversion to tolyl hydride complexes in the exchange of **5**-d_1 with toluene rules out c as the exclusive pathway.

Finally, the phosphine inhibition of H/D exchange of the dihydride complex $(PMe_3)_4Ru(H)_2$ with benzene solvent indicates that this process occurs by pathway b or c. As pictured in Scheme IV, pathway a would yield H_2 and cyclometalated product **6**. Pathway c involves reductive elimination of dihydrogen from the five-coordinate intermediate followed by successive oxidative addition of benzene and dihydrogen. Although our results do not rule out pathway c, a simpler mechanism is pathway b, and it is analogous to the mechanism of H/D exchange with phenyl hydride **5**. This mechanism involves reversible oxidative addition of benzene to the five-coordinate dihydride to form a trihydride intermediate which allows for exchange, and this seems to be the most likely mechanism.

Selectivities. Our results suggest that the propensity of the benzyl hydride, phenyl hydride, and dihydride complexes to undergo intramolecular or intermolecular oxidative addition can be traced to their abilities to undergo reductive elimination. The activation energy required to eliminate toluene from the saturated complex **1** is lower than the total activation energy required to dissociate PMe_3 and then add solvent or ligand to the resulting 5-coordinate intermediate **7a**, so C–H oxidative addition in **1** occurs via L_4Ru intermediate **10**. In contrast, the barrier to

Scheme IV



reductive elimination from the phenyl hydride complex is higher than it is from the benzyl hydride complex. As a result, phosphine dissociation followed by oxidative addition to the corresponding 5-coordinate species **7b** is competitive with direct reductive elimination. Because the barrier to reductive elimination of dihydrogen is too high to observe, even up to 180 °C, only the 5-coordinate intermediate $L_3Ru(H)_2$ is accessible in this case.

The inter- vs intramolecular selectivity in benzene solvent is markedly different for the 5-coordinate Ru^{II} and 4-coordinate Ru^0 species which are generated by the thermolyses of these three compounds: the 4-coordinate L_4Ru (**10**) chooses only intramolecular reactivity, whereas the 5-coordinate $L_3Ru(R)(H)$ is capable of both intra- and intermolecular reactivity. Typically, systems are thought to be driven toward intramolecular reactivity when the metal center is sterically encumbered.[13] We propose that the intermediates with the higher coordination numbers in this study actually possess metal centers that are sterically *less* encumbered because they contain three rather than four bulky trimethylphosphine ligands.

Comparison of the Reductive Elimination Mechanism with Those in Other Systems. The reductive elimination reactions of d^6 metal systems that possess labile ligands are often accelerated by ligand dissociation. For example, elimination of maleic anhydride from the Ir(III) complexes, Ir(H)[σ-$CHCH_2C(O)OC(O)$](σ-carborane)(CO)(PhCN)(PPh_3),[2k] and of carborane from Ir(H)(Cl)(σ-carborane)(CO)(PPh_3)$_2$[2j] has been shown to involve predissociation of ligand. Reductive elimination of ketone from a rhodium enolate hydride complex involves predissociation of phosphine ligand,[2n] and photolytic elimination of dihydrogen from a series of Ir(III) and Rh(III) complexes involves initial photodissociation of ligand, followed by thermal elimination of H_2.[2g] In addition, some C–C reductive elimination reactions are accelerated by ligand dissociation.[2a,3] In contrast, the rates of several other C–H reductive elimination reactions are independent of free ligand concentration, because dissociation occurs more slowly than reductive elimination.[2h,j] For the ruthenium system discussed here, dissociation of phosphine was shown to occur more rapidly than reductive elimination, but the elimination process occurred directly from the saturated $L_4Ru(CH_2Ph)(H)$ and $L_4Ru(Ph)(H)$ species. Thus, this study presents an unusual case of a transition-metal complex which undergoes rapid ligand dissociation, but which displays a preference for reductive elimination from the saturated 18 e^- species over reductive elimination from unsaturated 16 e^- species.

Comparison to $(PMe_3)_4Os(CH_2CMe_3)(H)$. Our results indicate that differences in the mechanisms for the ruthenium and osmium systems stem from the greater bond strengths[14] and more accessible M^{IV} oxidation state[15] of the third row over the second row transition metals. The differences in bond strength are manifested in the faster rate of reductive elimination directly from the saturated alkyl hydride complex for the ruthenium system and in

(13) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.
(14) (a) Pearson, R. G. *Chem. Rev.* **1986**, *85*, 41. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *84*, 245.
(15) Cotton, F. A.; Wilkinson, G. *Advanced Organometallic Chemistry*; John Wiley and Sons: New York, 1980; p 912.

the different oxidation potentials which result in a slower rate of oxidative addition by the ruthenium(II) intermediate $(PMe_3)_3Ru(R)(H)$ to form the ruthenium(IV) intermediate $(PMe_3)_3Ru(R)(R')(H)_2$. Thus, thermolysis of the ruthenium alkyl hydride complex results exclusively in formation of $(PMe_3)_4Ru$ (**10** in Scheme I), while the osmium system reacts predominantly by oxidative addition of benzene solvent to the $(PMe_3)_3Os^{II}(R)(H)$ intermediate, forming $(PMe_3)_3Os^{IV}(R)(Ph)(H)_2$. Oxidative addition to the L_3Ru^{II} intermediate occurs only above 135–140 °C as compared to oxidative addition to L_3Os^{II} observed at 80 °C.

A final difference between these two group 16 metal systems is their propensity to react via the $(PMe_3)_3M$ intermediate. Our labeling studies with $(PMe_3)_4Ru(Ph)(D)$ indicate that the major intermolecular pathway involves $(PMe_3)_3Ru(D)(Ph)$ and not $(PMe_3)_3Ru$. Flood and his co-workers have concluded from kinetic isotope experiments that the osmium system undergoes activation of methane, mesitylene, and tetramethylsilane by way of $(PMe_3)_3Os$, although aryl ring exchange with benzene occurs via $(PMe_3)_3Os(CH_2CMe_3)(H)$. Although evidence has been presented that the 14-electron, three-coordinate intermediate is important in the osmium system, we believe our labeling results rule out this species as part of any major reaction pathway for the ruthenium system.

Experimental Section

General. Unless otherwise noted, all manipulations were carried out under an inert atmosphere in a Vacuum Atmospheres 553-2 drybox with attached M6-40-1H Dritrain, or by using standard Schlenk or vacuum line techniques.

^1H NMR spectra were obtained on either the 300-, 400-, or 500-MHz Fourier transform spectrometers at the University of California, Berkeley (UCB), NMR facility. The 300-MHz instrument was constructed by Mr. Rudi Nunlist and interfaced with a Nicolet 1280 computer. The 400- and 500-MHz instruments were commercial Bruker AM series spectrometers. ^1H NMR spectra were recorded relative to residual protiated solvent. In some second-order spectra resonances are observed patterns rather than true multiplicity patterns. In these cases the values are reported as "*N*" for separation of lines rather than "*J*" for true coupling constants. $^{13}C\{^1H\}$ NMR spectra were obtained at either 75.4, 100.6 MHz or 125.7 MHz on the 300-, 400-, or 500-MHz instruments, respectively, and chemical shifts were recorded relative to the solvent resonance. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane. $^{31}P\{^1H\}$ NMR spectra were obtained at either 121.6 or 162.1 MHz on the 300- or 400-MHz instruments, respectively, and chemical shifts were recorded in units of parts per million downfield from 85% H_3PO_4. ^2H NMR spectra were recorded at 153.4 MHz on the 500-MHz instrument and chemical shifts are reported in units of parts per million downfield from tetramethylsilane.

IR spectra were obtained on a Perkin-Elmer Model 283 infrared spectrometer or on a Perkin-Elmer Model 1550 or 1750 FT-IR spectrometer with potassium bromide solution cells (0.1 or 0.025 mm path length) or potassium bromide ground pellets. Mass spectroscopic (MS) analyses were obtained at the UCB mass spectrometry facility on AEI MS-12 and Kratos MS-50 spectrometers. GC/MS results were obtained with either a gas chromatograph in series with the Kratos MS-50 or a Hewlett-Packard 5890A gas chromatograph in series with a Hewlett-Packard 5970 mass selective detector with a 30-m column (0.25 mm i.d., 0.25 m film thickness), DB1701 from J&W Scientific. Elemental analyses were obtained from the UCB Microanalytical Laboratory.

Sealed NMR tubes were prepared by fusing Wilmad 505-PP and 504-PP tubes to ground glass joints which were then attached to a vacuum line with Kontes stopcocks, or alternatively, the tubes were attached via Cajon adapters directly to Kontes vacuum stopcocks.[16] High pressure valve NMR tubes refer to Wilmad Cat. No. 522-PV. Known volume bulb vacuum transfers were accomplished with an MKS Baratron attached to a high-vacuum line.

Unless otherwise specified, all reagents (including Grignard reagents) were purchased from commercial suppliers and used without further purification. PMe_3 (Strem) was dried over NaK or a Na mirror and vacuum transferred prior to use. Ferrocene (Aldrich) was sublimed prior to use. Methanesulfonic acid was dried by azeotroping with benzene with use of a Dean-Stark trap followed by vacuum distillation under argon. Pentane, hexane, and cyclohexane (UV grade, alkene free) were distilled from $LiAlH_4$ under nitrogen. Benzene, toluene, diethyl ether, and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Isopropyl alcohol and methanol-d_3 were dried over sodium and vacuum distilled. Deuterated solvents for use in NMR experiments were dried as their protiated analogues but were vacuum transferred from the drying agent. $(PMe_3)_3Ru(\eta^2\text{-}CH_2PMe_2)(H)$ was prepared by the method of Werner but was isolated by sublimation at 85 °C, followed by crystallization from pentane at −40 °C.

$(PMe_3)_4Ru(Me)(Cl)$. We found the procedure provided here to be more convenient than the published procedure.[17] In a 250-mL round-bottom flask, 1.50 g of $(PMe_3)_4Ru(OAc)(Cl)$[17] was dissolved in 100 mL of toluene. To this stirred solution was added, at room temperature over 3 min, 0.50 mL (0.33 equiv) of $AlMe_3$ as a 2.0 M solution in toluene. The solution was stirred for 1 h at room temperature over which time a fine white powder formed. The volume of the solution was reduced to 5–10 mL under vacuum and filtered while still cold from solvent removal in order to remove all aluminum salts. The resulting yellow solution was then layered with pentane to yield 0.629 g (46% yield) of yellow blocks. The supernatant was then cooled to −40 °C to obtain an additional 0.246 g (18%) of product. ^1H NMR (C_6D_6) δ 1.27 (t, 18 H, N = 5.8) 1.20 (d, 9 H, N = 5.4), 0.91 (d, 9 H, N = 7.6), 0.27 (m, 3 H); $^{31}P\{^1H\}$ NMR A_2BC, δ_A = −5.65, δ_B = 15.16, δ_C = −16.09, J_{AB} = 34.5, J_{AC} = 24.4, J_{BC} = 18.3. Lit. ^1H NMR (C_6D_6) δ 1.27 (t, 18 H, N = 6), 1.19 (d, 9 H, N = 5), 0.90 (d, 9 H, N = 8), 0.29 (m, 3 H); $^{31}P\{^1H\}$ NMR A_2BC δ_A = −5.8, δ_B = 14.9, δ_C = −16.3, J_{AB} = 34, J_{AC} = 24, J_{BC} = 18.

$Ru(PMe_3)_4(H)_2$. Into a 250-mL round-bottom flask was weighed 1.00 g (2.00 mmol) of $(PMe_3)_4Ru(OAc)(Cl)$.[17] Ether (100 mL) was added. To the stirred solution was added 0.250 mL (1.00 mmol) of a 2.0 M solution of lithium aluminum hydride in ether. The initial yellow solution became clear and contained a white precipitate after 15 min. After allowing the reaction to stir for an additional 1 h, the solvent was removed under reduced pressure and the residue extracted with pentane (3 × 50 mL). The pentane was removed to yield 0.540 mg (66% yield) of a white powder which ^1H and $^{31}P\{^1H\}$ NMR spectroscopy showed to be pure **7**, as determined by comparison to literature data.[16] ^1H NMR (C_6D_6) δ 1.37 (t, 18 H, N = 5.2), 1.24 (d, 18 H, N = 5.0), −9.71 (m, 2 H); $^{31}P\{^1H\}$ NMR A_2B_2, δ_A = 0.12, δ_B = −7.41, J_{AB} = 26.1. Lit. ^1H NMR (C_6D_6) δ 1.37 (t, 18 H, N = 5), 1.27 (d, 18 H, N = 5), −10.1 (m, 2 H); $^{31}P\{^1H\}$ NMR A_2B_2 δ_A = 2.7, δ_B = −4.8, J_{AB} = 26.4.

$Ru(PMe_3)_4(CH_2Ph)(H)$ (1). A Fisher-Porter bottle was charged with 1.11 g (2.44 mmol) of $Ru(PMe_3)_4(Me)(Cl)$[8] in 10 mL of tetrahydrofuran in the drybox and then was filled with 100 psi of H_2. The solution was stirred for 12 h at room temperature. The vessel was brought into the drybox, and 1.24 mL of 2.0 M $PhCH_2MgBr$ in THF was added to the reaction solution. This mixture was stirred for 5 h, after which time the solution had turned clear and a white solid had precipitated. The solvent was removed under vacuum and the residue extracted with 50-, 25-, and 25-mL portions of pentane. The pentane extracts were combined and filtered; concentrated to ~7 mL under vacuum, and cooled to −40 °C to yield 0.681 g (55.0%) of analytically pure, white crystals. A second crop, also pure by ^1H NMR spectroscopy, yielded 0.152 mg of white crystals (12.3%). ^1H NMR (C_6D_6) δ 7.90 (d, 7.6, 2 H), 7.29 (t, 7.4, 2 H), 7.04 (t, 7.8, 1 H), 2.25 (m, 2 H), 1.21 (t, N = 4.7, 18 H), 1.15 (d, N = 5.5, 9 H), 1.05 (d, N = 4.9, 9 H), −9.49 (ddt, J = 89.8, 29.7, 22.1, 1 H); $^{31}P\{^1H\}$ A_2BC, δ_A = −1.40, δ_B = −7.56, δ_C = −13.11, J_{AB} = 26.4, J_{AC} = 26.4, J_{BC} = 19.9; $^{13}C\{^1H\}$ δ 158.45 (d, 6.7), 132.41 (s), 127.11 (s), 121.63 (s), 28.26 (d, 18.6), 24.74 (tt, 12.4, 3.3), 22.79 (dq, 14.6, 2.7), 15.99 (dtd, 46.9, 13.4, 6.4); IR 1856 (M − H, s); MS (EI) m/e 406 (M − CH_2Ph). Anal. Calcd for $C_{19}H_{44}P_4Ru$: C, 45.87; H, 8.91. Found: C, 45.70; H, 8.81.

$Ru(PMe_3)_4(CH_2Ph)(D)$ (1-d_1). A procedure identical with that for the preparation of $Ru(PMe_3)_4(CH_2Ph)(H)$ was followed except D_2 was substituted for H_2, and the reaction was run with 255 mg of $Ru(PMe_3)_4(Me)(Cl)$ to yield 116 mg (41.6%) of product in one crop. ^{1}NMR (C_6D_6) δ 7.90 (d, 7.6, 2 H), 7.29 (t, 7.4, 2 H), 7.04 (t, 7.8, 1 H), 2.25 (m, 2 H), 1.21 (t, N = 4.7, 18 H), 1.15 (d, N = 5.5, 9 H), 1.05 (d, N = 4.9, 9 H); $^2H\{^1H\}$ NMR δ −9.49 (dq, J = 15, 4); $^{31}P\{^1H\}$ NMR A_2BCX, δ_A = −1.40, δ_B = −7.56, δ_C = −13.11, J_{AB} = 26.4, J_{AC} = 26.4, J_{AX} = 3.9, J_{BC} = 19.9; J_{BX} = 0, J_{CX} = 13.8; IR 1333 ($\nu_{M\text{-}D}$).

$Ru(PMe_3)_4(Ph)(H)$ (5). To a solution of 300 mg (0.627 mmol) of $Ru(PMe_3)_4(\eta^2\text{-}C_6H_4)$ in 5 mL of pentane was added 47.7 μL (0.627 mmol) of isopropyl alcohol in 0.5 mL of pentane at room temperature. After allowing the mixture to react for 1 h, the volume was reduced under vacuum to 1 mL and cooled to −40 °C to yield 145 mg (48.2%) of white crystals. ^1H NMR (THF-d_8, −55 °C) δ 7.75 (m, 1 H), 7.45 (m, 1 H), 6.60 (m, 3 H), 1.38 (d, N = 5.4, 9 H), 1.35 (d, N = 5.8, 9 H), 1.10 (t, N = 5.2, 18 H), −9.50 (dtd, J = 92.6, 18.3, 18.3); $^{31}P\{^1H\}$ NMR A_2BC,

(16) Bergman, R. G.; Buchanan, J. M.; McGhee, W. D.; Periana, R. A.; Seidler, P. F.; Trost, M. K.; Wenzel, T. T. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Ser. No. 357; American Chemical Society: Washington, DC, 1987; p 227.

(17) Mainz, V. V.; Andersen, R. A. *Organometallics* **1984**, *3*, 675.

δ_A = −1.356, δ_B = −10.59, δ_C = −17.18, J_{AB} = 24.5, J_{AC} = 26.7, J_{BC} = 18.9; $^{13}C\{^1H\}$ NMR (THF-d_8, −55 °C) δ 174.20 (m), 153.10 (s), 146.55 (d, 8.8), 125.32 (s), 124.84 (s), 119.69 (s), 27.96 (d, 18.0), 24.67 (m), 23.59 (t, 12.2); IR 3060 (m), 2981 (m), 2966 (m), 1859 (M − H, s), 1561 (m), 1424 (m), 1419 (m), 1295 (s), 1278 (m), 940 (s); MS (EI) *m/e* 406 (M − C_6H_6), 330 (M − C_6H_6 − PMe_3). Anal. Calcd for $C_{18}H_{42}P_4Ru$: C, 44.71; H, 8.62. Found: C, 44.82; H, 8.83.

Ru(PMe$_3$)$_4$(Ph)(D) (5-d_1). To a solution of 100 mg (0.209 mmol) of Ru(PMe$_3$)$_4$(η^2-C_6H_4) in 3 mL of benzene was added 18 μL of MeOH-d_3 in 0.5 mL of pentane. After the mixture was allowed to react for 1 h, the benzene was removed under vacuum, and the residue was crystallized from pentane at −40 °C to yield 43.6 mg (43.4%) of white crystals. ^1H NMR (THF-d_8, −55 °C) δ 7.75 (m, 1 H), 7.45 (m, 1 H), 6.60 (m, 3 H), 1.38 (d, *N* = 5.4, 9 H), 1.35 (d, *N* = 5.8, 9 H), 1.10 (t, *N* = 5.2, 18 H); $^2H\{^1H\}$ NMR (THF, 20 °C) δ = −9.58 (dq, *J* = 14.3, 4.0); $^{31}P\{^1H\}$ NMR δ 0 −1.356 (br t, *J* = 25, 2 P), −10.59 (m), −17.18 (m); IR 3036 (m), 2981 (m), 2966 (m), 1561 (s), 1424 (m), 1420 (m), 1337 (M − H, m), 1295 (s), 1279 (s) 939 (s).

Thermolysis of Ru(PMe$_3$)$_4$(CH$_2$Ph)(D) in Cyclohexane. The ruthenium complex (15.0 mg, 0.0302 mmol) was dissolved in cyclohexane (0.7 mL), and the solution was transferred to an NMR tube. The sample was degassed and sealed under vacuum. The NMR tubes were heated by submerging them completely in an oil bath heated to 85 °C. $^{31}P\{^1H\}$ NMR spectroscopy showed quantitative conversion to **6**, determined by comparison with a sample of **6** independently prepared as described in the general section. ^2H NMR spectroscopy showed an 11:1 integrated ratio of the methyl peak to aryl peaks of the toluene product. The tube was then cracked open under vacuum and the volatile materials collected in a glass tube cooled in a liquid nitrogen bath. GC/MS analysis of the volatile materials showed the absence of toluene-d_0. Only toluene-d_1 was detected, as determined by comparison of the mass spectrum of the toluene peak to that obtained for a sample of toluene-d_1 obtained by treating benzylmagnesium chloride with D_2O (99.8% isotopic purity).

Kinetic Evaluation of the Thermolysis of Ru(PMe$_3$)$_4$(CH$_2$Ph)(H) in C_6D_6. Into a 5.00-mL volumetric flask was weighed 102 mg (0.205 mmol) of Ru(PMe$_3$)$_4$(CH$_2$Ph)(H) and 28 mg of ferrocene as an internal standard. C_6D_6 was added to the flask, making a 0.0412 M solution. In a typical experiment, 0.700 mL of this solution was added by syringe to a thin-walled, 9-in. NMR tube. In an experiment to confirm the first-order nature of the reaction, 4.2 mg (0.0084 mmol) of ruthenium complex was weighed into an NMR tube. To this tube was added 0.7 mL of C_6D_6 by syringe. Each tube was degassed, the appropriate amount of PMe_3 was condensed into it, and the tube was flame sealed to give a length of 8.5 in. The tubes were heated at 80 ± 0.1 °C in a factory-calibrated Neslab Exocal Model 251 constant temperature bath filled with Dow Corning 200 silicone Fluid and frozen rapidly in ice water after removal from the bath. All reactions were monitored to greater than 3 half-lives by ambient-temperature ^1H NMR spectrometry by integrating the methylene protons of the benzyl group vs the ferrocene internal standard. The spectra were taken with a single acquisition and double checked with a second acquisition after a delay of at least $10T_1$. Formation of **6** was confirmed by comparing the ^1H NMR spectrum with that of an independently prepared sample of **6** as described in the general section. Rate constants are given in Table I; all kinetic plots displayed excellent linearity with correlation coefficients of 0.95 or better.

Exchange of PMe$_3$-d_9 with Ru(PMe$_3$)$_4$(CH$_2$Ph)(H). A sample of 11.0 mg (0.0221 mmol) of Ru(PMe$_3$)$_4$(CH$_2$Ph)(H) was dissolved in C_6D_6 and transferred to an NMR tube. The tube was degassed and 0.0885 mmol of PMe$_3$-d_9 was added by vacuum transfer. The tube was sealed under vacuum and heated to 60 °C for 12 h. $^{31}P\{^1H\}$ NMR spectrometry showed a ratio of 1:0.8 for the peak at 61.44 (PMe_3) and 64.05 (PMe_3-d_9).

Thermolysis of Ru(PMe$_3$)$_4$(Ph)(H) in C_6D_6. The ruthenium complex (10.8, 0.0224 mmol) was dissolved in 0.7 mL of C_6D_6 and 2 mg of ferrocene was added as an internal standard. The solution was transferred to an NMR tube which was degassed and sealed under vacuum. The tube was submerged completely in a 140 °C bath for 18 h, and ^1H NMR spectroscopic analysis of the resulting solution showed formation of **6** in 90‰ yield.

Thermolysis of Ru(PMe$_3$)$_4$(Ph)(H) in C_6D_6 with and without Added PMe$_3$. The ruthenium complex (22.6 mg, 0.0464 mmol) was dissolved in 1.5 mL of C_6D_6 and the solution was divided into two NMR tubes. One tube was degassed and sealed under vacuum, and the other was degassed and sealed under vacuum after the addition of 2 equiv (0.0464 mmol) of PMe_3. The tubes were heated at 135 °C for 9.5 h. Conversions for the two samples were determined by $^{31}P\{^1H\}$ NMR spectroscopy since the resonances are well-separated. Approximate conversions of 55% for the sample with no added phosphine and 56% for the sample with 2 equiv of phosphine were determined by comparing the total of all integrals for the two compounds. ^1H NMR spectroscopy showed no hydride or aromatic resonances for the sample containing no additional PMe_3. Only the phosphine resonances corresponding to **5** and **6** were observed. A hydride resonance and aryl resonances were observed for the sample containing 2 equiv of PMe_3.

Thermolysis of Ru(PMe$_3$)$_4$(Ph)(H) in Cyclohexane-d_{12}. The ruthenium complex (11.0 mg, 0.0228 mmol) was dissolved in 0.7 mL of cyclohexane and 2 mg of ferrocene was added as an internal standard. The solution was transferred to an NMR tube which was degassed and sealed under vacuum. The tube was submerged completely in a 135 °C bath for 18 h, and ^1H NMR spectroscopic analysis of the resulting solution showed formation of **4** in 94% yield and benzene in 97% yield.

Kinetic Evaluation of the Thermolysis of Ru(PMe$_3$)$_4$(Ph)(H) in Cyclohexane-d_{12}. Into a 5.00-mL volumetric flask was weighed 19.8 mg (0.0410 mmol) of Ru(PMe$_3$)$_4$(CH$_2$Ph)(H) and 20 mg of mesitylene as an internal standard. Cyclohexane-d_{12} was added to the flask, making a 8.20 mM solution. In a typical experiment, 0.700 mL of this solution was added by syringe to a thin-walled, 9-in. NMR tube. The tube was degassed, the appropriate amount of PMe_3 was condensed and the tube was flame sealed to give a length of 8.5 in. The tubes were heated at 80 ± 0.1 °C in a factory-calibrated Neslab Exocal Model 251 constant temperature bath filled with Dow Corning 200 silicone Fluid and frozen rapidly in ice water after removal from the bath. All reactions were monitored to greater than 3 half-lives by ambient-temperature ^1H NMR spectrometry by integrating the resonance due to the mutually trans phosphines of **5** vs the mesitylene internal standard. The spectra were taken with a single acquisition and double checked with a second acquisition after a delay of at least $10T_1$. Rate constants are given in Table II; all kinetic plots displayed excellent linearity with correlation coefficients of 0.98 or better.

Thermolysis of Ru(PMe$_3$)$_4$(Ph)(D) in Cyclohexane. The ruthenium complex (25.2 mg, 0.0517 mmol) was dissolved in 0.7 mL of cyclohexane. The solution was transferred to an NMR tube which was degassed and sealed under vacuum. The tube was submerged completely in a 140 °C bath for 8 h, and ^2H NMR spectroscopic analysis of the sample was conducted every 2 h during the thermolysis. The spectra showed a decrease in the hydride resonance for **5** and an increase in the resonances for benzene at 7.11 ppm and for the PMe_3 groups of **5** between 1.1 and 1.4 ppm. The integrated ratio of the benzene and phosphine signals in the final reaction mixture was roughly 2:1; an accurate value for this ratio could not be obtained due to overlap of the PMe_3 resonances with the cyclohexane solvent resonance. No signals were observed in the hydride region.

Thermolysis of Ru(PMe$_3$)$_4$(Ph)(D) in Toluene. Two samples of the ruthenium complex (14.2 and 15.6 mg) were dissolved in toluene (0.7 mL) and transferred to NMR tubes which were then freeze–pump–thawed through three cycles. Each sample was heated for 4 h at 140 °C, after which time the NMR tube was cracked open under vacuum. The volatile materials were collected in a glass tube cooled with liquid nitrogen and analyzed by GC/MS at 90 eV. Two spectra were taken for each experiment, and the ratios agreed within 1–2%. Using the *m/e* = 78 and 79 peaks the ratio of benzene-d_1 to benzene-d_0 was calculated to be 0.86:1 for one experiment and 0.67:1 for the other. The remaining material was exposed to high vacuum for 4 h, dissolved in 1 mL of hexamethyldisiloxane, and exposed to high vacuum for 8 h to remove any residual solvent. The solid was dissolved in ether and >3 equiv of methanesulfonic acid in ether was added. A white solid rapidly formed, and the resulting solution was filtered through a plug of Celite and analyzed by gas chromatography to determine the ratio of toluene to benzene as 2.85:1 in one experiment and 2.05:1 in the other.

Thermolysis of Ru(PMe$_3$)$_4$(H)$_2$ in C_6D_6 with and without Added Phosphine. The ruthenium complex (22.0 mg, 0.0543 mmol) was dissolved in 1.5 mL of C_6D_6, 2 mg of ferrocene was added, and the solution was divided into two NMR tubes. One tube was degassed and sealed under vacuum, and the other tube was degassed and sealed under vacuum after the addition of 10 equiv (0.272 mmol) of PMe_3 to give a PMe_3 concentration of 0.36 M. The tubes were heated at 135 °C for 9.5 h. ^1H NMR spectroscopy showed a hydride signal for the sample containing 10 equiv of PMe_3 but no hydride signal for the sample containing no additional PMe_3.

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