Mechanism of a Directly Observed β-Hydride Elimination Process of Iridium Alkoxo Complexes†

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Received July 15, 1994. Revised Manuscript Received November 28, 1994®

Abstract: The octahedral alkoxo complexes *mer-cis*-HIr(OR)Cl(PR'_3)$_3$ (R = Me, Et, *i*-Pr; R′ = Me, Et; H *trans* to Cl) decompose at room temperature in an alcohol/benzene solution, forming the dihydrido products *mer-cis*-H_2IrCl(PR'_3)$_3$ and the corresponding aldehyde or ketone. The reaction rate is of first order in the iridium complex and of 1.33 order in the alcohol, which serves as a catalyst. The rate depends on the nature of the phosphine (PEt_3 > PMe_3), on the alkyl substituent of the alkoxide (Me > Et ≫ *i*-Pr), and on the medium (benzene > *N*-methylpyrrolidone) but is not effected by excess phosphine. The activation parameters obtained for the decomposition of *mer-cis*-HIr(OCH_3)Cl(PMe_3)$_3$ are $\Delta H^{\ddagger}_{obs}$ = 24.1 ± 1.8 kcal mol^{-1}, $\Delta S^{\ddagger}_{obs}$ = 0.6 ± 5.9 eu, and $\Delta G^{\ddagger}_{obs}$ (298 K) = 23.9 ± 3.6 kcal mol^{-1}. The kinetic isotope effect (combined primary and secondary effects) for the decomposition of *mer-cis*-DIr(OCD_3)Cl(PMe_3)$_3$ at 22 °C is k_H/k_D = 2.45 ± 0.10, and the secondary kinetic isotope effect for the decomposition of DIr(OCH_3)Cl(PMe_3)$_3$ at 22 °C is 1.10 ± 0.06. Both DIr(OCH_3)Cl(PMe_3)$_3$ and HIr(OCD_3)Cl(PMe_3)$_3$ produce only the two *mer-cis* isomers of HDIrCl(PMe_3)$_3$, but in different ratios. The following steps are involved in the β-hydride elimination process: (a) pre-equilibrium generation of a free coordination site by chloride dissociation, which is induced by hydrogen bonding of a methanol molecule to the chloride; (b) irreversible rate-determining β-C−H cleavage through the *sterically* favored transition state; (c) facile, irreversible dissociation of the aldehyde; (d) ligand rearrangement; and (e) irreversible reassociation of the chloride. Selective deuterium labeling enables the elucidation of a competing minor mechanism through the *electronically* favored transition state, operative for the trimethylphosphine complex only.

Late transition metal alkoxides are suggested as intermediates in various catalytic reactions such as carboalkoxylation of olefins and alkyl halides,[1] hydrogenation of carbon monoxide,[1] ketones, and aldehydes,[1] dehydrogenation of alcohols,[1] transesterification,[2] and hydrogen transfer from alcohols to ketones.[2] While the late transition metal−alkoxide homolytic bond strength is comparable to that of metal−alkyls,[3] isolation of the alkoxo complexes is considered more difficult, even in apolar media where heterolysis of the alkoxide does not take place.[1] The decomposition of these alkoxo complexes to metal hydrides, presumably by β-H elimination,[4] is held responsible for their scarcity.[5,6] Kinetically stabilized metal alkoxides having β-hydrogens have been isolated.[7] Complexes with electron-withdrawing substituents,[8] *tert*-butoxide,[8d] hydroxide,[1,9] aryloxide,[1,10] and γ-fluoroalkoxide[11] are relatively stable.

The only mechanistically characterized β-hydride elimination from a metal alkoxide that we know of involves the square planar (dppe)Pt(OCH_3)$_2$.[4b] This decomposition involves a reversible β-C−H cleavage (without a preceding ligand dissociation)[12] followed by a rate-determining release of the organic products. β-Hydride eliminations from alkoxo complexes in which the C−H cleavage is rate limiting are not known and are rare even for the analogous metal−alkyls.[13] Mechanistic studies of β-hydride eliminations from octahedral alkyl complexes are also rare.[14,15] We now report a detailed mechanistic study of β-H elimination from *mer-cis*-HIr(OCH_3)Cl(PR_3)$_3$ (**1**, R = Me; **10**, R = Et). This process takes place by a rate-determining β-C−H cleavage. The results obtained allow us to suggest differences and similarities between the β-hydrogen eliminations from metal alkyls and from metal alkoxides.

Results

1. Decomposition of *mer-cis*-HIr(OCH_3)Cl(PMe_3)$_3$ (1). Complex **1**, which is obtained by methanol oxidative addition to (C_8H_{14})IrCl(PMe_3)$_3$ (**2**),[16,17] decomposes at room temperature in a methanolic (2.24 M, 9% by volume) benzene solution. It generates *mer-cis*-H_2IrCl(PMe_3)$_3$ (**3**) as the single metal complex product (eq 1). The presence of formaldehyde and its oligomers was verified by the chromotropic acid test.[18] These results suggest that **1** decomposes by β-hydride elimination from the

† Dedicated to Prof. J. Blum on the occasion of his 60th birthday.

® Abstract published in *Advance ACS Abstracts*, April 1, 1995.

(1) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

(2) Kim, Y. J.; Osakada, K.; Takenaka, A.; Yamomoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096 and references cited therein.

(3) (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444. (b) *Polyhedron* **1988**, *7*, 1441.

(4) The β-hydride elimination was confirmed in only a few cases: (a) A Re−OiPr homoleptic cluster was found to be in equilibrium with acetone and the H−Re elimination product: Hoffman, D. M.; Lappas, D.; Wierda, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 1531. (b) Other mechanisms were eliminated for the decomposition of Pt(dppe)(OCH_3)$_2$ [dppe = 1,2-bis(diphenylphosphino)ethane]: Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805. (c) The reactivity observed is probably not compatible with any other mechanism: Blum, J.; Sasson, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 309.

(5) Reactions of late transition metals with alcohols usually lead to aldehydes or ketones and hydrido products (which are not always stable), without observation of an (alkoxo) intermediate: (a) Many earlier examples of such reactions are cited in the following: Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231. (b) Schunn, R. A. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; p 203. (c) Recent examples closely related to our work: Gotzig, J.; Werner, R.; Werner, H. *J. Organomet. Chem.* **1985**, *290*, 99. (d) Reference 3a.

(6) A hydrido carbonyl product is sometimes observed instead of the separate aldehyde and hydrido metal. It is most common when methanol is used. For leading references, see: (a) Morton, D.; Cole-Hamilton, D. J.; Utuk, I. D.; Paneque-Sosa, M.; Lopez-Poveda, M. *J. Chem. Soc., Dalton Trans.* **1989**, 489. (b) Portnoy, M.; Frolow, F.; Milstein, D. *Organometallics* **1991**, *10*, 3960.

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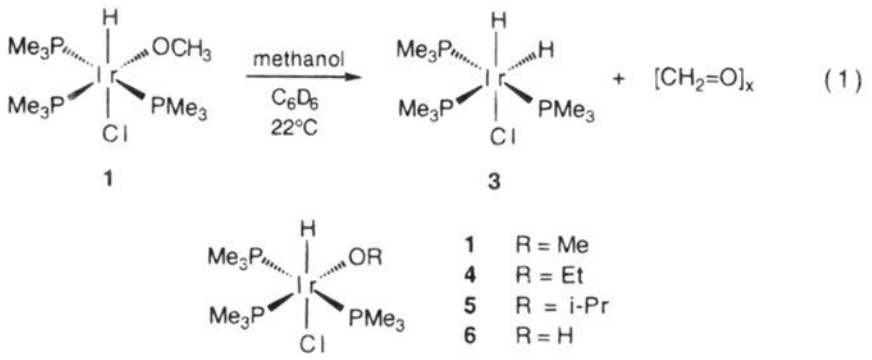


methoxo ligand. We observed similar reactivity for the ethoxo **4** and isopropoxo **5** derivatives, which were obtained by reaction of **2** with the appropriate alcohol.[16] The qualitative decomposition rates observed were **1** > **4** ≫ **5**.[19] The hydroxo derivative **6** was stable under similar conditions.[20] Recently, the analogous stable aryloxo and carboxylato *mer-cis*-HIr(OR)Cl(PMe_3)$_3$ derivatives, which do not contain β hydrogens, were reported.[10c] These stabilities suggest that Ir−O bond homolysis is an unlikely mechanism for reaction 1.

Thermolysis kinetics measured by $^{31}P\{^1H\}$ NMR in a 2.24 M methanolic solution in benzene show that reaction 1 is first order in **1** from 14 to 50 °C (Figure 1, Table 1). **1** was found indefinitely stable at −30 °C in methanolic toluene under otherwise the same conditions.

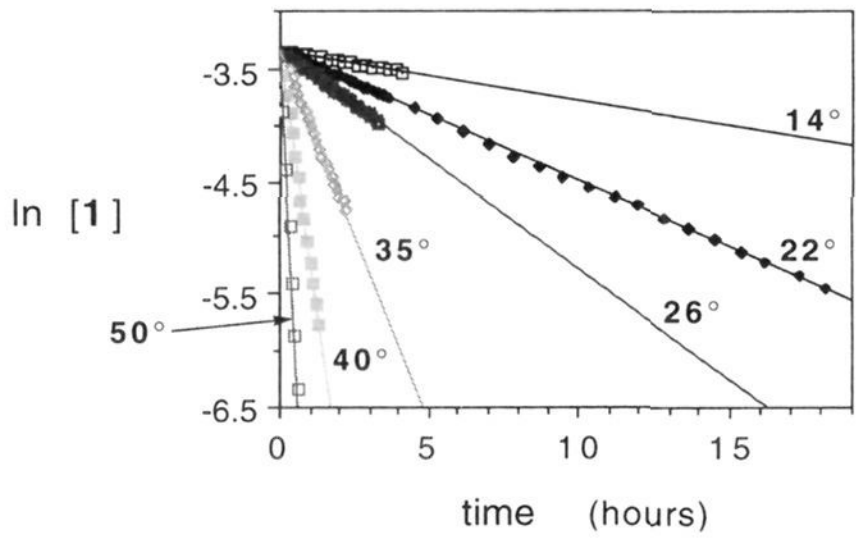


Figure 1. Pseudo-first-order plots for the decomposition of **1** in benzene-d_6: [MeOH] = 2.24 M, $[\mathbf{1}]_0$ = 36.1 ± 1.6 mM. The thermolysis process was followed for at least three half-lives of **1** at 22, 40, and 50 °C.

Table 1. Observed Rate Constants for the Thermolysis of **1** in Benzene-d_6 ($[\mathbf{1}]_0$ = 36.1 ± 1.6 mM)

		pseudo-first-order	
T, °C (±0.5 °C)	[MeOH], M	k_{obs},[a] s^{-1}	k_{obs},[a] s^{-1} $M^{-1.33}$
14	2.24	1.26×10^{-5}	4.31×10^{-6}
22	2.24	3.28×10^{-5}	1.12×10^{-5}
26	2.24	5.43×10^{-5}	1.86×10^{-5}
35	2.24	1.82×10^{-4}	6.23×10^{-5}
40	2.24	5.19×10^{-4}	1.77×10^{-4}
50	2.24	1.37×10^{-3}	4.68×10^{-4}
22	0	0[b]	0[b]
22	0.09	0[b]	0[b]
22	0.45	0[b]	0[b]
22	1.12	1.76×10^{-5}	1.51×10^{-5}
22	3.37	6.09×10^{-5}	1.21×10^{-5}
22	6.73	1.55×10^{-4}	1.23×10^{-5}
7	6.73	1.66×10^{-5}	1.31×10^{-6}
40	6.73	1.40×10^{-3}	1.11×10^{-4}

[a] The largest variation found in the reproducibility of k_{obs} was 11%. Each single measurement gave no more than 0.3% (usually 0.1%) of the error in the rates derived (R^2 > 0.997). [b] Only **1** was observed by $^{31}P\{^1H\}$ NMR after 12 h.[21]

A plot of the pseudo-first-order k_{obs} vs the methanol concentration to the power of 1.33 yields linear correlation (Table 1, Figure 2).[22] Reaction 1 is, therefore, methanol catalyzed. The uncatalyzed reaction does not contribute to the reaction rate.

(7) (a) Cp*IrH(OEt)PPh_3: Glueck, D. S.; Newman-Winslow, L. J.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462. (b) $HOs(OCH_3)Cl(NO)(PMe_3)_2$, in which the chloride is *trans* to the weak σ-donating methoxide: Werner, H.; Michenfelder, A.; Schultz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 596. (c) $L_2Pt(C_6H_9)(OMe)$ is stable against β-hydride elimination when L_2 is the 1,2-bis(diphenylphosphino)ethane chelate but not when L is PPh_3: Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750. (d) $Os(OEt)(\eta^2\text{-}S_2CN(CH_3)_2)(PMe_2Ph)_3$: Cole-Hamilton, D. J.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1976**, 2396. (e) $HOs_3(OEt)(CO)_{10}$: Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1328. (f) $[Cp^*Ru(OMe)]_2$: Kang, B. S.; Koelle, U.; Thewalt, U. *Organometallics* **1991**, *10*, 2569. (g) Chelate-stabilized *fac*-$(CO)_3M(OR)$-(dppe) (R = Me, Et; M = Mn, Re): Mandal, S. K.; Ho, D. M.; Orchin, M. *Inorg. Chem.* **1991**, *30*, 2244. (h) *fac*-$(CO)_3ReL_2(OR)$ (L_2 = a chelating bis-phosphine or bis-arsine, R = Me, Et, *i*-Pr; L_2 = $2PMe_3$, R = Me) are thermally stable. When a different phosphine is used (such as PPh_3), the M−OR complexes are not isolated: Simpson, R. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 781. (i) Ir(OR)(cycloocta-1,5-diene)(PCy_3) (R = Et, Cy; Cy = cyclohexyl) is stable, but when the smaller OMe is used, the complex decomposes: Fernandez, J. M.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1989**, *8*, 1158. (j) In bis-chelating alkoxo complexes, such as Pt-$(\eta^2\text{-}P(Ph_2)CH_2CH_2O)_2$, the geometry is unfavorable for β-H elimination: Alcock, N. W.; Platt, A. W. G.; Pringle, P. G. *J. Chem. Soc., Dalton Trans.* **1989**, 139. (k) Substitutionally inert Pt(IV) alkoxides: Akl, N. S.; Tayim, H. A. *J. Organomet. Chem.* **1985**, *297*, 371 and (l) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444. (m) M(II)−methoxy-(octaethylporphyrin) complexes (M = Ru, Os): Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015. (n) Our $[HIr(OMe)(PMe_3)_4]PF_6$ was previously communicated. Its stability against β-H elimination is discussed here: Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387. (o) *trans*-$(PEt_3)_2Pt(C_6H_5)(OCH_3)$ is stable at room temperature, even in basic methanolic solution. Compare with ref 7c: Coulson, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3111.

(8) (a) $[Ir(OR)(NO)(PPh_3)_2]^+$ (R = Et, Pr): Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1014. (b) $M(OMe)R(PPh_3)_2$ (M = Pt, Pd) were isolated for R = C_6F_5 and $CCl{=}CCl_2$ but not for R = $CH{=}CCl_2$: Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993. (c) $Pt(OMe)RL_2$ (R = CF_3, L = PPh_3, $^1/_2Ph_2PCH{=}CHPPh_2$; R = CH_2CN, L = $^1/_2Ph_2PCH{=}CHPPh_2$) (compare these compounds to ref 4b): Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175*, 239. (d) *trans*-(CO)Ir(OR)$(PPh_3)_2$ (R = Me, *n*-Pr, *i*-Pr) is stable at room temperature: Bernard, K. A.; Rees, W. M.; Atwood, J. D. *Organometallics* **1986**, *5*, 390. (e) Non-phosphinic alkoxo bridged dimers of the platinum group metals are reviewed: Mehrotra, R. C.; Agarwal, S. K.; Singh, Y. P. *Coord. Chem. Rev.* **1985**, *68*, 101.

(9) For recent examples: (a) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3404. (b) Green, L. M.; Meek, D. W. *Organometallics* **1989**, *8*, 659.

(10) Metal phenoxides were reviewed: (a) Malhotra, K. C.; Martin, R. L. *J. Organomet. Chem.* **1982**, *239*, 159. (b) For recent examples see: Simpson, R. D.; Bergman, R. G. *Organometallics* **1992**, *11*, 3980 and references cited therein. (c) Ladipo, F. T.; Kooti, M.; Merola, J. S. *Inorg. Chem.* **1993**, *32*, 1681.

(11) These ligands have β-hydrogens but are resistant to β-H elimination due to either the stronger C−H bond or the electron-withdrawing CF_2R neighboring group(s). For leading references, see: (a) Osakada, K.; Kim, Y. J.; Tanaka, M.; Ishiguro, S.; Yamamoto, A. *Inorg. Chem.* **1991**, *30*, 197. (b) Johnson, T. J.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1992**, *114*, 2725.

(12) Since the analogous non-chelated complexes could not be prepared, a partial dissociation of the chelating diphosphine prior to the C−H cleavage may be considered.

(13) (a) Ikaria, T.; Yamamoto, A. *J. Organomet. Chem.* **1976**, *120*, 257. (b) Evans, J.; Schwartz, J.; Urquhart, P. W. *J. Organomet. Chem.* **1974**, *81*, C37.

(14) (a) Reference 13a. (b) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1104.

(15) Cyclopentadienyl complexes: (a) Reger, D. L.; Culberston, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789. (b) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 3973. Bryndza, H. E.; Evitt, E. R.; Bergman, R. G. *Ibid.* **1980**, *102*, 4948.

(16) Blum, O.; Milstein, D. Submitted.

(17) Complex **2** was first reported: Herskovitz, T.; Guggenberger, L. *J. Am. Chem. Soc.* **1976**, *98*, 1615.

(18) Feigel, F. *Spot Tests in Organic Synthesis*, 5th ed.; Elsevier: New York, 1956; p 331.

(19) Similar observations are reported: (a) Reference 7c. (b) Reference 7i.

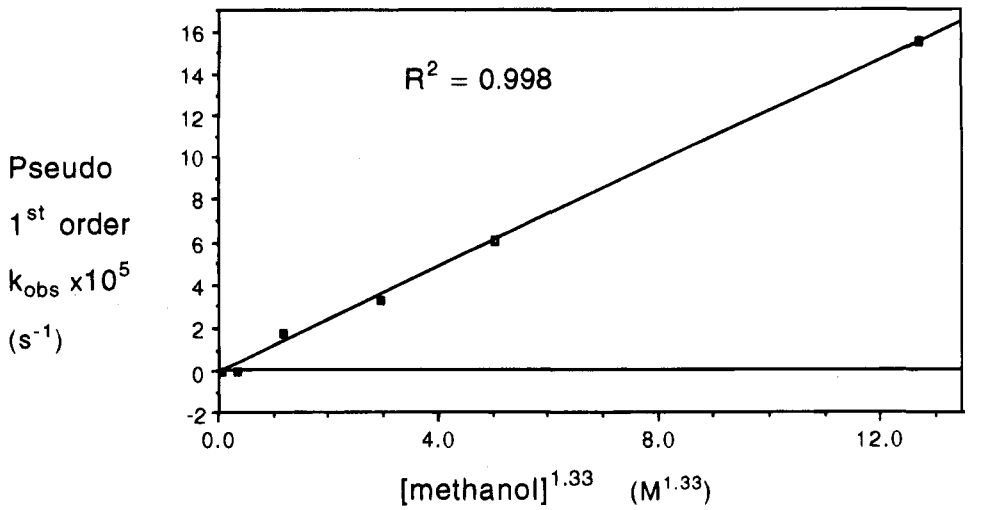


Figure 2. Dependence of the pseudo-first-order rate constant of the thermolysis of **1** at 22 °C on the methanol concentration to the power of 1.33 in benzene-d_6: $[\mathbf{1}]_0 = 36.1 \pm 1.6$ mM.

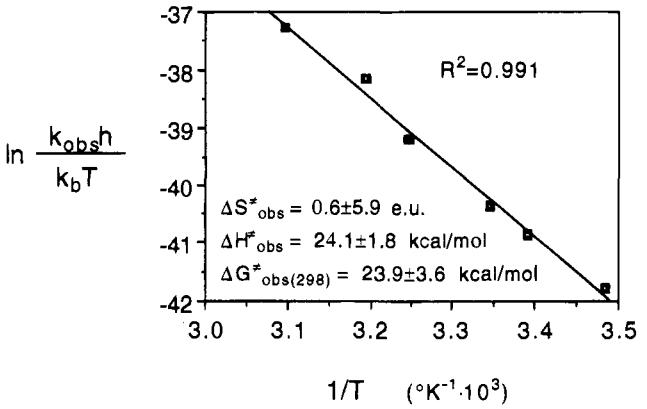
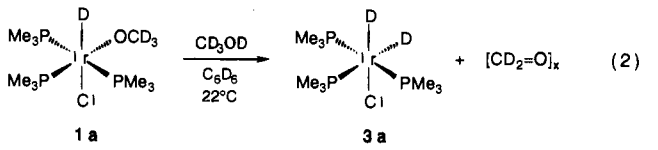


Figure 3. Eyring plot for the methanol-catalyzed decomposition of **1** between 14 and 50 °C: $[\mathbf{1}]_0 = 36.1 \pm 1.6$ mM; [MeOH] = 2.24 M.

The activation parameters obtained for the process (Figure 3) are $\Delta H^{\ddagger}_{obs} = 24.1 \pm 1.8$ kcal mol^{-1},[23] $\Delta S^{\ddagger}_{obs} = 0.6 \pm 5.9$ eu,[23] and $\Delta G^{\ddagger}_{obs}(298) = 23.9 \pm 3.6$ kcal mol^{-1}. The same values (within the experimental error) were obtained in different methanol concentrations (2.24 M, Figure 3; 6.73 M, rate constants in Table 1, $R^2 = 0.999$).[24] The close to zero entropy of activation observed suggests that the process is comprised of more than a single basic reaction and that the rate determining step (RDS), for which these parameters are derived, is not the initial one.[25] Single step dissociative and associative reactions are usually characterized by significantly positive or negative activation entropies, respectively, and so are isomerization processes.[26]

The effect of deuterium substitution on the thermolysis rate was determined by comparing the decompositions of **1** (eq 1) and of *mer-cis*-DIr(OCD$_3$)Cl(PMe$_3$)$_3$ (**1a**) (eq 2). We obtained $k_{obs}(\mathbf{1})/k_{obs}(\mathbf{1a}) = 2.45 \pm 0.10$[27] at 22 °C. Comparing the disappearance rates of **1** and of *mer-cis*-DIr(OCH$_3$)Cl(PMe$_3$)$_3$ (**1b**) under the same conditions (eq 9) yielded the secondary kinetic effect caused by a deuterium substitution on the metal. A value of $k_{obs}(\mathbf{1})/k_{obs}(\mathbf{1b}) = 1.10 \pm 0.06$ was measured.[28] We did not determine the effect of the two geminal deuterons on the thermolysis rate of **1a**. It is expected to be small enough[29] to render the significance of the $k_{obs}(\mathbf{1})/k_{obs}(\mathbf{1a})$ value as a normal primary kinetic isotope effect beyond doubt. This result strongly implies that the C−H bond cleavage is either involved in the RDS or precedes it.



To our knowledge, (dppe)Pt(OCH$_3$)$_2$ is the only transition metal alkoxo complex for which β-hydride elimination was kinetically studied.[4b] No kinetic isotope effect was found there. Significant normal kinetic deuterium isotope effects are also not common among β-hydride elimination from metal−alkyls. The only two reports are $k_H/k_D = 2.30$ both for $(CX_3CH_2)_2Co(acac)(PMe_2Ph)_2$ (X = H, D; acac = acetylacetonate)[13a] and for the square planar $C_6H_{13}CH(D)CH_2Ir(CO)(PPh_3)_2$.[13b] This value is remarkably similar to ours.

Reaction 1 is solvent dependent. It proceeds faster in C_6D_6 than in the aprotic, rather polar but slightly coordinating

(20) But a water/THF (1/10, v/v) solution was used. When an alcohol is introduced, the hydroxo ligand is substituted by an alkoxide: (a) Reference 3a. (b) Reference 7h and references cited therein. (c) Reference 7n.

(21) When no methanol was present, degradation products started to appear after about 1 week. However, even after 1 month, **3** was not observed. *mer-cis*-HIrCl$_2$(PMe$_3$)$_3$ (**7**) (Zlota, A. A.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1826) and *cis*-[H$_2$Ir(PMe$_3$)$_4$]$^+$ (**8**) (Behr, A.; Herdtweck, E.; Herrmann, W. A.; Keim, W.; Kipshagen, W. *Organometallics* **1987**, *6*, 2307) are among the decomposition products found.

(22) A plot of the pseudo-first-order k_{obs} vs [methanol] results in far less good correlation ($R^2 = 0.981$). It also yields a hard to explain threshold of 0.73 M methanol for the β-H elimination from **1** in benzene-d_6.

(23) The error in the curve fit is small ($R^2 = 0.991$). The uncertainties are derived from the maximum and minimum slopes.

(24) The activation parameters obtained for the process in 6.73 M methanolic solution in C_6D_6 are $\Delta H^{\ddagger}_{obs} = 22.8 \pm 1.4$ kcal mol^{-1}, $\Delta S^{\ddagger}_{obs} = -3.8 \pm 4.6$ eu, and $\Delta G^{\ddagger}_{obs}(298) = 23.9 \pm 1.8$ kcal mol^{-1}.

(25) The observed activation parameters are comprised of an algebraic sum of the different equilibrium values of all the basic transformations occurring prior to the RDS plus the activation value for the RDS.

(26) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: Weinheim, Germany, 1991. Activation energies of different processes are cited in Chapters 4−7.

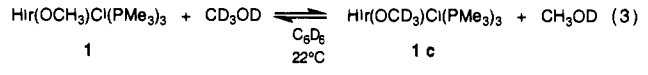
(27) Arithmetically corrected for 1% non- or partially deuterated **1** and **1b** in the reaction mixture.

(28) Arithmetically corrected for 4% non-deuterated **1** in the reaction mixture.

(29) Secondary kinetic deuterium isotope effects resulting from geminal deuterium substitutions are generally small. Some of the higher valves ($1.15 < k_H/k_D < 1.25$ per deuterium) are associated with processes involving sp^3 to sp^2 rehybridization at the carbon during the RDS: (a) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; p 210. (b) Maskill, H. *The Physical Basis of Organic Chemistry*, 1st ed.; Oxford: Oxford, U.K., 1990 (reprint); p 386. (c) Streitwieser, A., Jr.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326.

N-methylpyrrolidone (NMP),[30,31] both containing the same methanol concentration. A similar inhibition of the β-hydride elimination from metal−alkoxides and metal−alkyls by coordinating solvents was observed.[32]

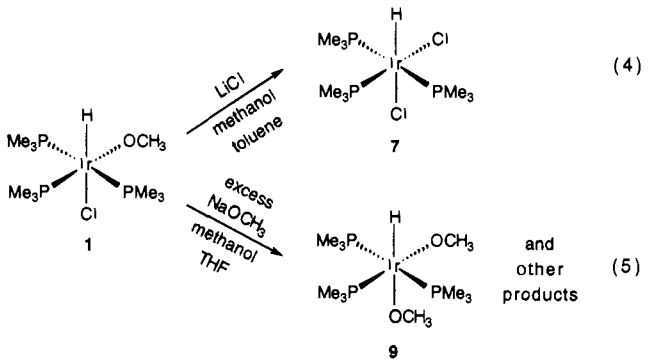
Heterolysis of a methoxide from **1** was probed by the exchange reaction 3.[33] The pseudo-first-order rate constant for



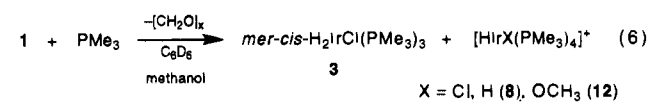
the methoxide exchange between **1** and methanol-d_4 was found to be ca. 24 times larger than the pseudo-first-order rate constant for the generation of **3** and formaldehyde in C_6D_6/methanol-h_4 under otherwise the same conditions ([methanol] = 2.24 M).[34] The process is slow in the 400 MHz ^{1}H NMR time scale, as the coupling between the methoxo protons and the phosphorous *trans* to it is the same in a methanolic benzene solution as in pure benzene.

Notably, the methoxide exchange also proceeds in methanol concentrations or at temperatures (−30 °C, albeit slow) in which reaction 1 does not take place. This indicates that methoxide exchange does not follow the same mechanistic pathway as reaction 1. Retention of most of the metal-bound hydrides[35] shows that reaction 3 does not proceed by a reductive elimination oxidative addition sequence. The anionic ligand exchange is thought to be predominantly associative, mediated by hydrogen bonding between the lone pairs of the alkoxo oxygen and the H−X proton.[2,11a] Yet, the exchange of the methoxo ligand for a chloride in the presence of LiCl takes place rapidly (eq 4). A dissociative anionic metathesis with OCD_3^- may therefore account for at least some of the exchange during reaction 1.

Reaction of **1** with methoxide anion leads to chloride substitution (eq 5), thus preventing a study of its effects on the decomposition of **1**.

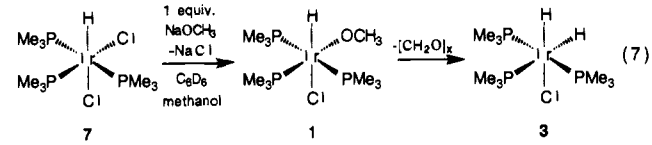


Thermolysis of **1** in the presence of trimethylphosphine resulted in a mixture containing **3** and cationic ligand substitution products (eq 6).[36] Phosphine association was observed also when β-hydride elimination from (octyl)Ir(CO)$(PPh_3)_2$ was



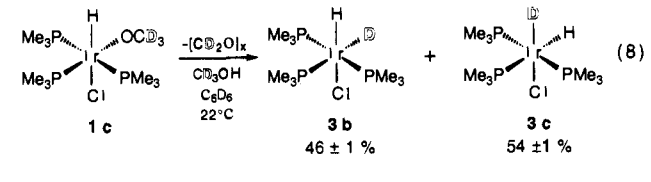
studied.[37] Repeating reaction 6 in the presence of trimethylphosphine-d_9 revealed that no labeled phosphine was incorporated into **3**, suggesting that no phosphine dissociation takes place upon degradation of **1**.

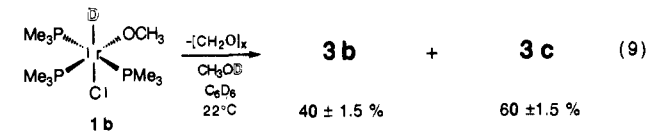
An attempt to study the influence of added chloride on the thermolysis of **1** was hindered by reaction 4. We could only show that Ir−Cl bond cleavage does take place in the analogous complex **7**,[21a,38] even in the presence of a weaker binding alkoxide (eq 7). This bimolecular anionic exchange reaction



was faster than the decomposition of **1** at the beginning, but turned to be rate-determining when most of the $NaOCH_3$ was consumed. Heterolysis of a chloride from the analogous benzoato complex was observed.[36]

In order to evaluate the reversibility of the C−H scission from the methoxo ligand of **1**, we analyzed the final products of the decomposition of *mer-cis*-HIr(OCD_3)Cl$(PMe_3)_3$ (**1c**) and *mer-cis*-DIr(OCH_3)Cl$(PMe_3)_3$ (**1b**) (eqs 8 and 9). Inclusion of more





than one deuteride per product in reaction 8 or less than one in reaction 9 would imply that the C−H cleavage is reversible. By arithmetically correcting for the initial non- (or partially) deuterated reactants present, integration of the hydrides of **3b,c** together totaled 50 ± 2% of what was expected for the non-deuterated **3**.[39] We conclude that the deuteride of **1b** is not incorporated into the aldehyde released and that only $[CD_2{=}O]_x$ is lost from **1c**. In most β-H eliminations studied, the C−H bond cleavage was found to be reversible. The exceptions are the two examples for which a significant kinetic deuterium isotope effect was found.[13]

It should be noted that the incorporation of the hydride into the product in reactions 8 and 9 was not stereospecific, resulting in complexes **3b,c**. In both reactions, **3c** is formed in a slight excess but the product ratios are different. In reaction 9, **3c** corresponds to the original deuteride *trans* to chloride stereo-

(30) The pseudo-first-order rate constant of reaction 1 in 1:1 NMP:C_6D_6 was found to be 1.68×10^{-5} s^{-1}, while in a C_6D_6 solution, it is doubled ($k = 3.28 \times 10^{-5}$ s^{-1}) ([methanol] = 2.24 M).

(31) We were unable to examine the influence of protic solvents on the reaction since they replace the methoxide ligand by an anionic ligand exchange (e.g., all other alcohols, *vide infra*).

(32) (a) Cp*IrH(OEt)$(PPh_3)_3$ is stable in ethanol but undergoes β-H elimination in benzene: ref 7a. (b) β-H elimination from (dppe)Pt$(OCH_3)_2$ is faster in noncoordinating solvents: ref 4b. (c) Reference 13a.

(33) For references about alkoxide exchange reactions, see refs 2, 4b, 7a, and 20.

(34) The pseudo-first-order rate constant for the forward process of reaction 3 under these conditions is 7.85×10^{-4} s^{-1}.

(35) The 2 orders of magnitude slower IrD to Ir−H exchange is observed: Blum, O.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 229. In refs 7a,n, a full retention of the metal-bound hydride is observed.

(36) Reaction of the benzoato analog to **1** with 1.1 equiv of PMe_3 yielded pure chloride dissociation products: ref 10c.

(37) Schwartz, J.; Cannon, J. B. *J. Am. Chem. Soc.* **1974**, *96*, 2276.

(38) Heterolysis of a halide was directly demonstrated for *trans*-RuX_2-$(dcpe)_2$ (X = Br, I; dcpe = bis(dicyclohexylphosphino)ethane): Mezzetti, A.; Del Zotto, A.; Rigo, P.; Bresciani-Pahor, N. *J. Chem. Soc., Dalton Trans.* **1989**, 1045.

(39) According to the ratio between the trimethylphosphine protons and the hydrides.

Table 2. Kinetic Data for the Decomposition of **10** at 22 °C in a 0.449 M Methanolic Solution in C_6D_6 ($[\mathbf{10}]_0 = 31.2 \pm 0.8$ mM)

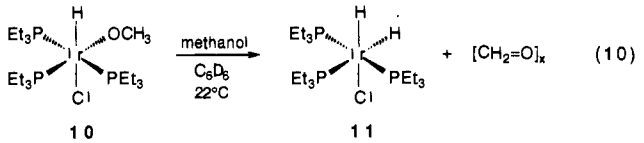
$[\mathbf{10}]_0$, M × 10^{-2}	$[PEt_3]$, M	pseudo-first-order k_{obs},[a] $s^{-1} \times 10^{-4}$
3.12 ± 0.08	0	2.12
3.12 ± 0.08	0.308 ± 0.008	2.83

[a] The largest variation found in the reproducibility of k_{obs} was 10%. See also note under Table 1.

chemistry, whereas it does not in reaction 8, and a somewhat lower amount of it is generated.

It must be noted that the product ratios in reactions 8 and 9 are reproducible[40] and do not change with time. Therefore, an equilibrium mixture is most probably not obtained in these reactions.

2. Decomposition of *mer-cis*-HIr(OCH$_3$)Cl(PEt$_3$)$_3$ (10). The thermolysis of **10** (eq 10) seems similar to that of **1** but is more than an order of magnitude faster (compare Tables 1 and 2). Degradation of **10** takes place even at −30 °C (in toluene/

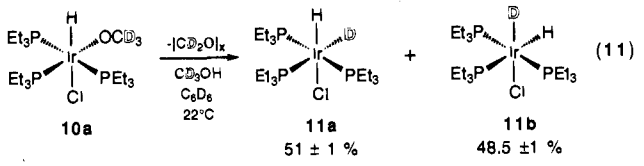


10 **11**

methanol, 10/1) or in neat benzene, conditions under which **1** is stable. In order to follow reaction 10 conveniently by $^{31}P\{^1H\}$ NMR, we used 0.449 M methanolic solution in benzene (instead of the 2.24 M methanolic solution used to study the decomposition of **1**).

The larger cone angle of PEt_3 as compared to PMe_3[41] prevents the generation of a tetraphosphine product upon exposure of **10** to excess PEt_3, enabling examination of the effect of added ligand. Interestingly, adding 10 equiv of triethylphosphine did not retard the decomposition of **10** (Table 2) but rather caused a slight acceleration.

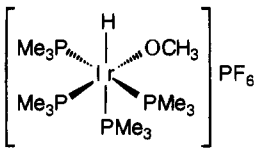
Decompositions of *mer-cis*-HIr(OCD$_3$)Cl(PEt$_3$)$_3$ (**10a**) (eq 11) yielded the *cis*-hydrido−deuterido complexes **11a,b**. Unlike reactions 8 and 9, a practically 1:1 product ratio was obtained in reaction 11.[40,42]



10a **11a** 51 ± 1 % **11b** 48.5 ±1 %

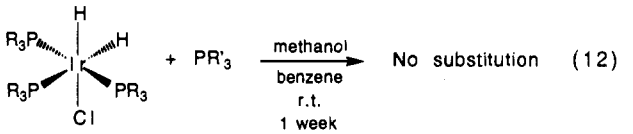
Although triethylphosphine does not retard reaction 10, complex **10** does undergo phosphine exchange reactions.[43] When reacted with 10 equiv of P(*n*-Bu)$_3$, a mixture of complexes was obtained and free triethylphosphine was clearly observed.[44]

3. *cis*-[HIr(OCH$_3$)(PMe$_3$)$_4$]PF$_6$ (12). The synthesis of **12** from *cis*-[HIr(OH)(PMe$_3$)$_4$]PF$_6$ and methanol was communicated by us.[7n] Heating **12** in THF at 70 °C for 24 h resulted in no change. **12** is stable also in a 2.24 M methanolic solution in benzene at room temperature.



12

4. Additional Relevant Results. Of relevance to understanding some of the factors governing the observed dissociation reactions and to determining the mechanistic sequence of reaction 1 is the behavior of complexes **3** and **11**. These complexes differ from **1** and **10** by having a strong σ-donating hydride in place of the π-donating methoxide. **3** is substitutionally inert toward P(CD$_3$)$_3$ in a 2.24 M methanolic solution in benzene at room temperature for at least 1 week (eq 12). Likewise, **11** is substitutionally inert toward P(*n*-Bu)$_3$ in a 0.449 M methanolic solution in benzene at room temperature for a month.



R = CH$_3$ (**3**); R' = CD$_3$

R = Et (**11**); R' = n-Bu

Discussion

General Mechanism. Four possible mechanisms were considered for the decomposition of the methoxo complexes **1** and **10**: (a) homolysis of the Ir−O bond, followed by abstraction of a hydrogen atom from the OCH$_3$ radical, (b) base-catalyzed abstraction of a proton from the methoxo ligand, (c) hydride abstraction from a dissociated alkoxide, and (d) β-hydride elimination from a coordinated alkoxo ligand.

A radical mechanism is considered unlikely.[45] Solvent dependence is not expected in such a mechanism, and a negative $\Delta S^{\ddagger}_{obs}$ does not fit Ir−O bond homolysis as the RDS. Hydrogen atom abstraction as RDS will cause deviations from the observed first-order dependence on **1**. Also, the absence of H/D scrambling between the hydride and the organic product, as well as the stability of the analogous carboxylato,[10c] aryloxo,[10c] and hydroxo derivatives, does not fit a radical mechanism.

The results presented here were reproduced by different batches of complexes and solvents, thus rendering base catalysis by contaminations improbable. CH_3O^- or traces of the Ir^I complex are conceivable basic catalysts, but in both cases, deviation from the first-order dependence on **1** and **10** would be expected.[46]

A bimolecular mechanism in which the methoxide anion serves as a hydride donor[47] would not be in keeping with either the observed steric demands of the reaction (rate **10** > **1**), the stability of *cis*-[HIr(OMe)(PMe$_3$)$_4$]PF$_6$ (**12**), or the molecularity observed for the decomposition. We also expect the kinetic product of this mechanism to place the abstracted hydride at the vacant position generated by the dissociation of the methoxide. The deduced intermediacy of a *trans*-dihydride

(40) The error bars originate from averaging four repeated experiments.

(41) The cone angles for PEt_3 and PMe_3 are 132° and 118°, respectively: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(42) An expected 10% excess of hydrides was observed in the products. ^2H NMR confirmed that no deuterium was incorporated into the phosphines. Since the alkoxide exchange of **10** is much faster than that of **1**, it is likely that this excess is due to the faster decomposition of an IrOCH(D)$_2$ species.

(43) Similarly, *mer-cis*-HIrCl$_2$(PEt$_2$Ph)$_3$ undergoes exchange with PMe$_2$Ph, also resulting in a mixture: Powell, J.; Shaw, B. L. *J. Chem. Soc. (A)* **1968**, 617.

(44) Mono-, di-, and tri-P(*n*-Bu)$_3$ substituted complexes were obtained.

(45) A radical mechanism en route from Cu(I)−alkoxides to Cu(I)−hydrides is reported: Whitesides, G. M.; Sadowski, J. S.; Lilburn, J. *J. Am. Chem. Soc.* **1974**, *96*, 2829.

(46) The phosphine or hydride ligands are also basic, but much weaker than either methoxide or Ir^I. β-H elimination from metal−alkyls catalyzed by a tethered aminic base is reported: (a) Grate, J. H.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1979**, *101*, 4601. (b) *Ibid.* **1981**, *103*, 541.

(47) Examples from organic chemistry are known. (a) In solution: Swain, C. G.; Powel, A. L.; Lynch, T. J.; Alpha, S. R.; Dunlap, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 3584. (b) In the gas phase: Ingemann, S.; Kleingeld, J. C.; Nibbering, N. M. M. *J. Chem. Soc., Chem. Commun.* **1982**, 1009.

complex (**19**), which isomerizes only afterward to the expected product **3**, contradicts this prediction.

β-Hydride elimination remains the only mechanism which does not contradict our experimental findings. This mechanism[4b] (along with its microscopic reverse[48]) was shown to be a viable reaction pathway for the late transition metal alkoxides.

Basic Steps of the β-Hydride Elimination Mechanism. The accepted mechanism for β-hydride eliminations from metal alkoxides[4b] and metal alkyls[49] comprises three elementary reaction steps: (a) generation of a free *cis coordination* site, (b) β-hydride elimination, and (c) product release. We observed an additional step, the intramolecular rearrangement of the ligands after release of the aldehyde.

Generation of a Free Coordination Site. Since β-hydride elimination *must* involve a free coordination site into which the hydride can enter, the saturated octahedral complexes **1** and **10** must dissociate a ligand prior to undergoing such a process. Either chloride or phosphine is likely the candidate for dissociation.

Phosphine dissociation is not on the mechanistic pathway of the β-hydride elimination from either **1** or **10**. Conversion of **10** to the dihydrido **11** did not slow down in the presence of 10 equiv of triethylphosphine. It even accelerated slightly.[50] Although a similar experiment for **1** was impossible (eq 6), it is clear that phosphine detachment from **1** during β-hydride elimination does not take place, since there was no incorporation of labeled phosphine into **3** when reaction 6 was carried out in the presence of $P(CD_3)_3$.

Other d^6 complexes of third row transition metals also undergo no trimethylphosphine dissociation. This fact is manifested by the unique stability of some *cis*-hydrido−alkyl complexes of iridium.[51] Substitutionally inert d^6 complexes of other phosphine ligands are also reported, though less frequently.[52]

Interestingly, phosphine dissociation from **10** does take place as confirmed by the substitution of triethylphosphine in **10** by tri-*n*-butylphosphine, which has a similar cone angle.[53] Similarly, *mer-cis*-$HIrCl_2(PR_3)_3$ (R = PEt_3, PEt_2Ph), which like **10**, has two π-donors, undergoes exchange with PMe_2Ph.[43]

A study of the chloride dissociation from **1** was hampered by the fast generation of **7** upon exposure of **1** to chloride anion (eq 4). The generation of **1** and **3** from **7** in the presence of $NaOCH_3$ (eq 7) indicates that Cl^- dissociation from **1** is possible.[10c,38,54] The fact that **1** is observed as an intermediate indicates that at least under the conditions of reaction 7, chloride heterolysis from **7** is faster than the β-hydride elimination from **1**.

Generation of small amounts (up to 2%) of *mer-cis*-$HIrCl_2(PR_3)_3$ (R = Me, **7**; R = Et[55]) during the decomposition of **1** or **10** (eqs 1 and 10) is in accord with the presence of dissociated chloride. Also indicative of the importance of chloride dissociation for the β-H elimination is the stability of **12**. A rate-determining anionic ligand dissociation was reported for the β-H elimination from *trans*-$EtPd(PMe_3)_2X$ (X = anionic ligand).[56]

As practically identical activation values were obtained for reaction 1 in different methanol concentrations, the rate dependence on methanol is not likely to be a result of a change in the properties of the medium (e.g., the dielectric constant). We attribute the catalytic role of methanol in reaction 1 to hydrogen bonding to the chloro ligand prior to its dissociation, thus weakening the Ir−Cl bond and facilitating its heterolysis. Possibly, some of the molecules of **1** bind two methanol molecules to the chloro ligand during the Ir−Cl heterolytic cleavage, thus accounting for the observed reaction order of greater than one in methanol. Otherwise, this order in methanol may reflect the solvolysis of the chloride-bound methanol by other methanol molecules.

Hydrogen bonding between a phosphate and a platinum-bound hydroxide was suggested to activate the hydroxo group to substitution.[57] It is possible that the correlation between the anionic ligand rate of heterolysis from *trans*-$EtPt(PMe_3)_2X$ and the pK_a of HX originates from hydrogen bonding of the solvent (water) to X during its dissociation.[56] A protic solvent catalysis by hydrogen bonding was demonstrated for the hydration of aldehydes.[58]

Role of the Methoxide Ligand in the Chloride Dissociation. Complexes **3** and **11**, which have only a single π-donating substituent undergo neither phosphine nor chloride substitution in the presence of 10 equiv of $P(CD_3)_3$ and $P(n\text{-}Bu)_3$, respectively (eq 12). Under the same conditions, the analogous **1**, **10**, and **7**, which have two π-donor ligands, undergo β-hydride elimination (eq 1), phosphine association (eq 6), or methoxide coordination (eq 7) following heterolysis of a chloride.[59] Substitution of the chloride in **3** by PMe_3 *does* take place in protic solutions (such as THF/methanol, 1:1) albeit slowly. In contrast, the tetraphosphine products of reaction 6 are all resistant to phosphine loss, even at elevated temperatures.[60] These demonstrate that the stabilities of **3** and **11** toward ligand substitution in reaction 12 are kinetic in origin and are associated with difficulties in chloride dissociation. We also note that some of the substitutionally inert d^6 iridium trimethylphosphine complexes mentioned above[51] have a single chloro ligand. None of them, however, have any other π-donating ligand.

We suggest that it is the π-donating methoxide which facilitates the chloride dissociation from **1** and **10** by stabilizing both the unsaturated pentacoordinate product and the product-like late transition state. It has been claimed that this π-effect can lower the activation enthalpies for ligand dissociation considerably. For example, the phosphine dissociation from $Cp^*Ru(OH)(PMe_3)_2$ has $\Delta H^{\ddagger}$ lower by as much as 10 kcal mol^{-1} than that from $Cp^*Ru(CH_3)(PMe_3)_2$.[61] The substitutional resistance of complexes such as **3**, *fac*-$H_2IrCl(PMe_3)_3$,[60] or other

(48) Tani, K.; Tanigawa, E.; Tatsuno, Y.; Otsuka, S. *J. Organomet. Chem.* **1985**, *279*, 87.

(49) Cross, R. J. In *The Chemistry of the Metal Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985, Vol. 2, p 559.

(50) This acceleration may be ascribed to inhibition of the competing triethylphosphine dissociation from **10**.

(51) (a) Thorn, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 7109. (b) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448. (c) Thorn, D. L. *Organometallics* **1982**, *1*, 197. (d) Milstein, D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3773. (e) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221.

(52) (a) *mer-cis*-$H_2IrCl(PEt_2Ph)_3$ does not exchange with PMe_2Ph in benzene, even after several days at 100 °C: ref 43. (b) Exchange of PPh_3 by a different phosphine in $Cp^*Ir(PPh_3)Me(NHPh)$ takes place by an associative mechanism, utilizing unsaturation created by the Cp* ligand: Glueck, D. S.; Bergman, R. G. *Organometallics* **1991**, *10*, 1479.

(53) θ of PEt_3 is 132°. θ of P(n-Bu)$_3$ is 136°: Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758.

(54) Apart from the presence of the salt, the conditions employed for this experiment are the same as those used for the study of the decomposition of **1**.

(55) Chatt, J.; Coffey, R. S.; Shaw, B. L. *J. Chem. Soc.* **1965**, 7391.

(56) Kawataka, F.; Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Organometallics* **1994**, *13*, 3517.

(57) Orton, D. M.; Green, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1612.

(58) Reference 29b, pp 334−335 and references cited therein.

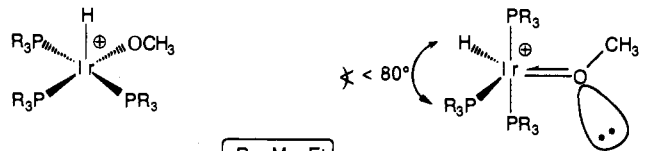
(59) In reaction 6, it is mainly the replacement of the methoxide which is observed. However, *cis*-$[HIr(OMe)(PMe_3)_4]^+$ (**12**), which is the chloride replacement product, is present as well. It is also possible that a secondary anionic ligand exchange brings about the final product distribution.

(60) Blum, O.; Milstein, D. Unpublished results.

(61) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379.

monochloro d^6 iridium trimethylphosphine complexes[51] can be rationalized by the absence of a stabilizing π-donor ligand in the transition state of chloride heterolysis. Other experimental examples for the stabilization of unsaturated complexes by π-donation are rare.[7f,52b,62-64]

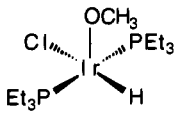
Unsaturated Product Generated by the Chloride Dissociation. The initial product of chloride dissociation from **1** or **10** is a square pyramidal complex with a hydride at the apical position (**13**). **13** is expected to be of a transient nature and is probably very close in structure and energy to the transition state of the whole decomposition process (*vide infra*). An analogous, calculated square pyramid $H_2Ir(OMe)(PH_3)_2$ is *not* a minimum on the potential energy surface.[65]



13 R = Me, Et **14**

The structure of π-donor-stabilized pentacoordinate complexes is a distorted trigonal bipyramid, having the two best σ-donors and the π-donor in the equatorial plane.[66] It was calculated that by this geometry the π-donation to the metal can be maximized.[67] On these grounds, the distorted trigonal bipyramidal **14** has the structure which is expected to be the most stable for the chloride dissociation product.[68] **14** is expected to be as much as 10 kcal mol^{-1} more stable than **13**.[65] Although **14** is not on the reaction coordinate, it serves as a more accessible reservoir for the transient **13** than the saturated **1** or **10**.

It is puzzling why the PEt_3 dissociation from **10** does not lead to β-H elimination. The product of phosphine dissociation (**15**) is expected to be less sterically crowded than the chloride dissociation product **13**. Retardation of β-H elimination from platinum alkyls by bulky phosphines was reported.[69] It is most likely that steric factors account for the phosphine dissociation from **10**, since it does not take place from **1**. As the phosphine *trans* to the alkoxide is the most sterically encumbered, **15** is the expected structure after phosphine dissociation from **10**. Since **15** has no free coordiantion site *cis* to the alkoxide, it cannot undergo β-hydride elimination. Unlike pentacoordinate d^6 complexes having only one π-donor, the square pyramidal geometry becomes more stable when additional π-donor(s) are present,[70,71] making rearrangement through the required geometry difficult. We suggest that **15**, which retains its two



15

π-donors, is not found en route from **10** to **11**, due to a higher barrier for the combined $\Delta G°$ of the PEt_3 dissociation and the consequent $\Delta G^‡$ of the rearrangement, as compared to the $\Delta G°$ of the chloride dissociation from **10**, followed by $\Delta G^‡$ for β-H elimination.

C−H Bond Cleavage. The rate dependence of the β-hydride elimination on the alkoxide, $MeO^- > EtO^- \gg i\text{-}PrO^-$,[19] clearly indicates the C−H cleavage to be rate-determining. This trend is opposite to that observed for the catalytic reduction of ketones by hydrogen transfer from alcohols.[72] Neither the homolytic strength of the C−H bond cleaved[73] nor the stability of the pro ducts $[(CH_2O)_x$, acetaldehyde, and acetone, respectively] can account for our findings. Steric factors satisfactorily explain the trend observed only if the C−H cleavage is rate-determining. A bulky alkoxo group will retard the formation of the M···H−C agostic interaction. The prior generation of unsaturation, the Ir−O bond cleavage, and the final detachment of the aldehyde or ketone are all expected to be facilitated by bulky alkoxides. Additional support for this view is found in the significant, normal primary kinetic deuterium isotope effect observed for the decomposition of **1**, as well as in the solvent effect. The retardation of reaction 1 by NMP is readily explained by its coordination to **13**, which blocks the required coordination site.

It is, therefore, to the C−H cleavage process that we relate the activation parameters observed. Considering the preceding chloride dissociation (for which a positive $\Delta H°$ is expected) and since $\Delta H^‡_{obs} = \Delta H°_{diss} + \Delta H^‡_{C-H\ cleavage}$, the activation enthalpy for the C−H bond cleavage is low (even lower than the measured value: $\Delta H^‡_{obs}(\mathbf{1}) = 24.1 \pm 1.8$ kcal mol^{-1}). Our value is somewhat lower than those obtained by Yamamoto for the analogous process involving octahedral $Co-C_2H_5$ complexes.[74] The observed activation entropy, which is close to zero ($\Delta S^‡_{obs}(\mathbf{1}) = 0.6 \pm 5.9$ eu) reflects a predicted positive $\Delta S°$ of the dissociation step and an expected negative $\Delta S^‡$ for the C−H bond cleavage. Yamamoto's activation entropies are unequivocally positive.[74]

(62) Darensbourg, D. J.; Sanchez, K. M.; Reibenspies, J. H.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 7094.
(63) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1351.
(64) (a) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160. (b) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.
(65) Riehl, J. F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729.
(66) All structures (except the last one) were crystallographically determined. (a) Werner, H.; Höhn, A.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1090. (b) Fryzuk, M. D.; MacNeil, P. A.; Ball, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6414. (c) Reference 38. Note that even though two bulky phosphines share the small equatorial plane, the P−Ru−P bond is only 93.1°! (d) Westcott, S. A.; Taylor, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1991**, 324. (e) Lunder, D. M.; Lobkovsky, E. B.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1991**, *113*, 1837. (f) Reference 11b. (g) Briggs, J. C.; McAuliffe, C. A.; Dyer, G. *J. Chem. Soc., Dalton Trans.* **1984**, 423.
(67) (a) Thorn, D. L.; Hoffmann, R. *New J. Chem.* **1979**, *3*, 39. (b) Daniel, C.; Koga, N.; Han, J.; Fu, X. Y.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3773. (c) Rachidi, I. El-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671. (d) Reference 65.
(68) Note that the O−C bond shares the P−Ir−P plane: (a) Reference 66e. (b) Reference 11b. (c) Reference 65.
(69) Reversible β-hydride elimination from $Pt(C_2H_5)$−phosphine complexes is favored when the phosphines are smaller: (a) Mole, L.; Spencer, J. L.; Carr, N.; Orpen, A. G. *Organometallics* **1991**, *10*, 49. (b) Carr, N.; Dunne, B. J.; Mole, L.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1991**, 863.
(70) While the pentacoordinate (diphosphino)Ir($N(SR_3)_2$)(CH_3)(C_5H_{11}) has a single π-donor and a distorted trigonal bipyramidal structure (ref 66b), upon replacement of the neopentyl group with an iodide, a square pyramidal geometry is observed, with the best σ-donor, the methyl ligand, at the apical position: Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1986**, *5*, 2469. Other such compounds are known. For example, d^6 $RuCl_2(PPh_3)_2$ has a square pyramidal structure: La Placa, S. J.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 778.
(71) The calculated structure of the analogous $RuCl(OCH_3)(PH_3)_3$ is a square pyramid. It was calculated to be less stable than any of the transient states leading from it to the product of the C−H cleavage. An agostic interaction exists between the methoxide and the ruthenium atom, but only when the methoxide is *trans* to a phosphine: Itagaki, H.; Koga, N.; Morokuma, K.; Saito, Y. *Organometallics* **1993**, *12*, 1648.
(72) (a) Imai, H.; Nishiguchi, T.; Fukuzumi, K. *J. Org. Chem.* **1976**, *41*, 665. (b) Fernandez, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A. *J. Organomet. Chem.* **1986**, *316*, 343. (c) Smith, T. A.; Maitlis, P. M. *J. Organomet. Chem.* **1985**, *289*, 385. (d) Farnetti, E.; Vinzi, F.; Mestroni, G. *J. Mol. Catal.* **1984**, *24*, 147.
(73) $D(H-C(CH_3)_2OH) = 91 \pm 1$ kcal mol^{-1}; $D(H-CH_2OH) = 94 \pm 2$ kcal mol^{-1}: Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.
(74) $\Delta H^‡_{obs}$ is between 30.0 and 34.1 kcal mol^{-1}. $\Delta S^‡_{obs}$ is between 31.6 and 39.9 eu. This is the only other case of β-hydride elimination (although from metal−alkyls) in which the activation parameters can be connected with an RDS, which is the C−H cleavage: ref 13a.

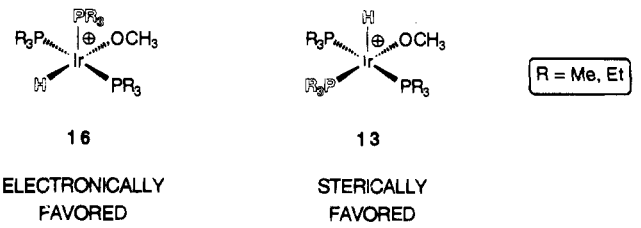
The low $\Delta H^{\ddagger}$ for the C−H cleavage in **1** suggests that the C−H bond is only slightly stretched in the transition state.[73] This picture fits the description of an agostic C−H···M structure[75] as not being far from the geometry of the actual transition state of the β-H elimination process.[76] A theoretical treatment of the β-H elimination from $HRh(C_2H_5)Cl(PH_3)_3$ also concludes that the transition state is relatively early.[67b]

The "early" nature of the transition state for the C−H cleavage is also corroborated by the small secondary kinetic isotope effect caused by the deuteride in **1b** ($k_H/k_D = 1.10 \pm 0.06$). In the transition state, a certain degree of Ir−H is formed.[77] As the new bond is generated *trans* to the hydride (*vide infra*), the existing Ir−H bond elongates, giving rise to the effect observed. A secondary isotope effect of 1.44 was ascribed to the stretching of a Pt−D bond during the associative replacement of the chloride by pyridine in *trans*-$XPtCl(PEt_3)_2$ (X = H, D).[78]

We correlate the transition state with the actual formation of the agostic interaction between the methoxide and the iridium, at a position *trans* to a hydride (*vide infra*). A theoretical study of the β-hydride elimination from $Ru(OCH_3)(CH_3OH)Cl(PH_3)_3$ resulted in a similar conclusion.[71] Generating an agostic interaction *trans* to a strong σ-donor is calculated to be unfavorable.[67b,71,76c]

Since both the 2.24 M (9%) and the substantially more polar 6.73 M (27%) methanolic benzene solutions yield practically the same activation parameters, it seems as if the medium contribution to the activation parameters is small.[79] Hence, the deduced negative activation entropy for the C−H cleavage is mostly intrinsic to the decomposing complex and fits a strained, multicenter transition state. A $C(\delta^+)\cdots H(\delta^-)$ polarization in the transition state of the β-hydride elimination from copper and silver adsorbed β-fluorinated ethoxides was recently suggested.[80] The small (if any) effect of the solvent polarity[81] on the rate-determining C−H scission points against such polarization in our case.

Stereochemical Course of the C−H Cleavage. In order to have a *cis* coordination site, the trigonal bipyramidal complex must rearrange into a square pyramid. The viable transient structures are **13** and **16**.[82]

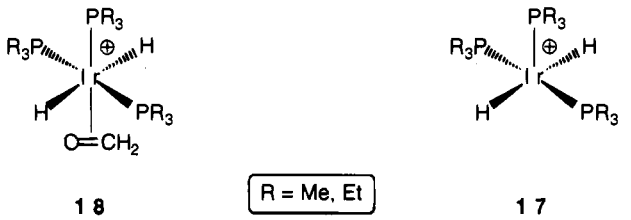


On the basis of *electronic* considerations, **16** will give rise to a transition state more stable than will **13**. Since a phosphine has a weaker *trans* influence compared to that of a hydride,[83] the agostic interaction generated in **16** will be stronger than in **13**.[71] However, the energy difference will not be large, since the trialkylphosphines are also good σ-donors.[84]

13 will generate the *sterically* more stable transition state, since its three phosphines have a neighboring free coordination site, while the apical phosphine in **16** has instead a methoxide at a *cis* position. The steric favoring of **13** will increase with the cone angle of the phosphine.

Upon decomposition of the partially deuterated **1b** (eq 9), **1c** (eq 8), and **10a** (eq 11), we noticed no H/D scrambling between the deuteride and the two hydrogens left on the generated aldehyde. However, we found almost complete H/D scrambling between the two nonequivalent positions of the products. Hydride rearrangement after generation of the final product can be excluded, since no change in the H/D distribution was found during the decomposition of **1b** (eq 9). The kinetic inertness of **3** (eq 12) corroborates this conclusion.

This H/D scrambling process suggests an intermediate in which the hydride and the deuteride occupy symmetrically equivalent positions. Only the *trans* dihydride structure **17** can fulfill this requirement. Since **17** is the least stable isomer of



the pentacoordinate $[H_2Ir(PR_3)_3]^+$, it is reasonable to conclude that it is generated by detachment of the aldehyde from the *trans* dihydride **18**. The C−H cleavage takes place, therefore, through the sterically favored transient **13** and the *trans* dihydride−η^2-aldehyde[85] complex **18**, which is the direct product of the β-H elimination from **14**.

18 is expected to be unstable. *Trans* dihydride complexes of the late transition metals are rare,[86,87] probably due to the

(75) Reviews: (a) Brookhardt, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (c) Ginzburg, A. *Russ. Chem. Rev.* **1988**, *57*, 1175.

(76) Theoretical treatments concerning the role of agostic interactions in β-hydride eliminations (a) of a Ru−alkoxide: ref 71 and (b) from metal−alkyls: Koga, N.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4625. (c) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *Ibid.* **1985**, *107*, 7109. (d) Reference 67b.

(77) We note that a small kinetic isotopic effect can also reflect a very late transition state: ref 29a, p 208.

(78) Falk, C. D.; Halpern, J. *J. Am. Chem. Soc.* **1965**, *87*, 3003.

(79) Although canceling out the solvent effects on ΔS° of the chloride dissociation and on $\Delta S^{\ddagger}$ of the C−H cleavage cannot be ruled out. The contribution of the solvent to $\Delta S^{\ddagger}_{obs}$ was expected to stem from the ΔS° of solvation of the chloride anion and of the organometallic cation.

(80) Gellman, A. J.; Dai, Q. *J. Am. Chem. Soc.* **1993**, *115*, 714.

(81) Probed by different methanol concentrations, as well as by the comparison between NMP and C_6D_6.

(82) An isomer with an apical methoxide is excluded, since the β-hydride elimination takes place into a free *cis* position. A facial isomer with an apical phosphine is unlikely, due to steric considerations.

(83) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(84) In view of the strong *trans* influence of PH_3 (which is a weaker σ-donor than PMe_3 or PEt_3), the stabilization of $Ru(OCH_3)Cl(PH_3)_3$ by an agostic interaction *trans* to a phosphine is only 0.7 kcal mol^{-1}, while *trans* to a chloride this interaction stabilizes this complex by 6.3 kcal mol^{-1}: ref 71.

(85) A π-bound η^2-aldehyde complex is the initial product of the C−H cleavage, since that is the microscopic reverse of aldehyde insertion into M−H bonds. We also assume η^2 bonding of the aldehyde to be the more stable structure of **18**. Aldehydes and electron-rich complexes exhibit η^2-bonding modes while ketones and electron-deficient species bind through the oxygen lone pairs: (a) Quirós Méndez, N.; Seyler, J. W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2323. (b) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439. (c) Powell, D. W.; Lay, P. A. *Inorg. Chem.* **1992**, *31*, 3542. (d) A theoretical treatment: Delbecq, F.; Sautet, P. *J. Am. Chem. Soc.* **1992**, *114*, 2446.

(86) *trans*-$H_2Pt(PCy_3)_2$ must obtain this geometry due to the bulkiness of the tricyclohexylphosphines: (a) Immirzi, A.; Musco, A.; Carturan, G.; Belluco, U. *Inorg. Chim. Acta.* **1975**, *12*, L23. (b) Green, M.; Howard, J. A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 3. (c) *trans*-H_2PtL_2 (L = bulky trialkylphosphines): Shaw, B. L.; Uttley, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 918. (d) *trans*-$H_2Ir(PPh_3)_2$(acac): Araneo, A. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2925. (e) *trans*-$H_2Pt(C_6H_5)(SnMe_3)(PEt_3)_2$ is identified at −78 °C: Arnold, D. P.; Bennet, M. A. *Inorg. Chem.* **1984**, *23*, 2110.

(87) When more than two hydrides are present, a configuration of a hydride *trans* to a hydride is more common. For example, *mer*-$H_3Ir(PEt_3)_3$: Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1970**, 846.

strong *trans* influence of the hydride ligand. Formaldehyde complexes of the late transition metals are also not common.[88]

Since no H/D scrambling was found between the deuterides of **3b**, **3c**, **11a**, and **11b** and the two protons remaining on the generated aldehyde (eqs 8, 9, and 11), *the C−H scission is irreversible.*[89] It reflects a substantially lower energy barrier for product release (*vide infra*) as compared to the reverse insertion of the aldehyde into the Ir−H bond. Indeed, the microscopic reverse formation of metal alkoxides from aldehydes and metal hydrides is relatively rare and takes place either when electron-withdrawing substituents are at an α-position to the aldehyde carbonyl[90] or when less electron-rich complexes are employed.[91]

Product Release. Generation of the final products from *trans*-dihydride **18** proceeds through three basic steps: (a) detachment of formaldehyde, (b) isomerization within the pentacoordinate intermediate, and (c) reassociation of the chloride.

The dissociation of the aldehyde from **18** is presumed to be facile, since it competes so efficiently with the insertion of the aldehyde into the M−H bond (*vide supra*). η^2-bound olefins are better π-acids compared to η^2-bound aldehydes.[85c,92] This may be the reason why most β-eliminations from metal−alkyls studied have the product release as their rate-determining step.[49]

The *cis* dihydride geometry of the final products **3** and **11** implies that a ligand rearrangement takes place within the unsaturated square pyramidal *trans* dihydride intermediate **17**, generated by the aldehyde detachment. Since the products **3** and **11** (eq 12)[93] are substitutionally inert, it is clear that the rearrangement within the pentacoordinate intermediate **17** is much faster than the reassociation of the chloride. When substituted by the bulkier PEt_3, the isomerization of **17** is expected to be faster than when PMe_3 is coordinated due to the steric congestion within **17**.[94] As a result, the final products **11a,b** are formed in practically a 1:1 ratio, irrelevant of the deuterium labeling site in the reactants (eq 11). The relatively slow rearrangement within PMe_3-substituted **17** allows smaller energy differences to be expressed.

The higher amount of **3c** in reactions 8 and 9 is likely to be due to the higher *trans* influence of the deuteride compared to the hydride. However, **17** is thought to be the common intermediate for both reactions 8 and 9. Since the ratio of the products in reactions 8 and 9 is reproducible and does not change with time, it is clear that an equilibrium mixture is not obtained in either reaction. The dependence of the products ratio on the deuterium labeling site in the reactant can only be explained by the existence of a competing mechanistic pathway of minor importance, which is effective only for the trimethylphosphine derivatives of **1**.

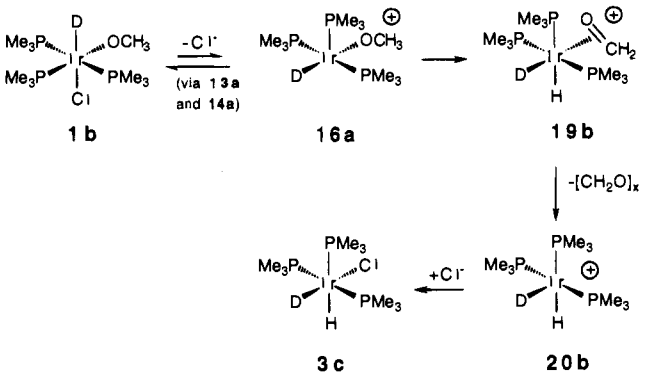


Figure 4. β-H elimination from the mono-deuterated **1b** through transient **16a** (the competing minor mechanism).

Competing Minor Mechanism. β-Hydride elimination from intermediate **14** via the *electronically* favored **16** can account for the observations. It will generate only **3c** from **1b** (Figure 4) and, similarly, only **3b** from **1c**. No significant isomerization is expected within the pentacoordinate intermediate **20** formed by formaldehyde dissociation from **19**, since it is both the electronically and sterically[94] favored structure of this complex.

Upon decomposition of **1b** (eq 9), the stronger *trans* influence of the deuteride and the competing mechanism will be additive, generating an excess of the thermodynamic product **3c** larger than the excess created by a single factor operating alone. Upon decomposition of **1c** (eq 8), the two factors will cancel out. Since we obtain 54 ± 1% of **3c** from **1c** (eq 8) and 60 ± 1.5% of **3c** from **1b** (eq 9), it can be easily calculated that, for a first approximation,[95] the larger *trans* influence of the deuteride accounts for ca. 14%[96] of the excess of **3c** in both reactions and the minor mechanism is responsible for ca. 6% of the products.

Since **16** is more sterically congested than **13**, its generation with PEt_3 ligands will be even less favored than for PMe_3 ligands. For this reason, the decomposition of **10** through **16** takes place only via the *sterically* favored pathway. In accord with our findings, calculations show that for the analogous intermediate $Ru(OCH_3)Cl(PH_3)_3$, which has much smaller phosphine substituents, the β-hydride elimination proceeds only via the *electronically* favored intermediate.[71]

Conclusions

The octahedral alkoxo complexes *mer-cis*-$HIr(OCH_3)Cl(PR_3)_3$ (**1**, R = Me; **10**, R = Et) decompose to the dihydrido products *mer-cis*-$H_2IrCl(PR_3)_3$ (**3**, R = Me; **11**, R = Et) by β-hydride elimination. The plausible mechanism of the decomposition is depicted in Figure 5.[97] The initial step is a pre-equilibrium generation of a free coordination site by a methanol-assisted dissociation of a chloride. The pentacoordinate dissociation

(88) (a) $H_2W(\eta^2\text{-}CH_2O)(PMe_3)_4$ was obtained directly from a reaction with methanol, probably by β-hydride elimination from a methoxide precursor: Green, M. L. H.; Parkin, G.; Moynihan, K. J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1540. (b) For reviews of other aldehyde and ketone complexes: Huang, Y.-H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298. (c) Shambayati, S.; Schreiber, S. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 1, Chapter 1.10, p 283.

(89) Some reversible β-hydride eliminations from metal−alkoxides were observed: (a) refs 4a−c. (b) Gaus, P. L.; Jones, L. M.; Zamiska, L. A. *Polyhedron* **1989**, *8*, 653.

(90) (a) Hayashi, Y.; Komiya, S.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1984**, 1363. (b) Reference 48.

(91) (a) Labinger, J. A.; Komadina, K. H. *J. Organomet. Chem.* **1978**, *155*, C25. (b) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428. (c) van der Zeijden, A. A. H.; Bosch, H. W.; Berke, H. *Organometallics* **1992**, *11*, 2051.

(92) The thermodynamically preferred binding sites in α,β-unsaturated aldehydes and ketones are the carbon−carbon multiple bond units: (a) Harman, W. D.; Schaefer, W. P.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2682. (b) Wang, Y.; Agbossou, F.; Dalton, D. M.; Liu, Y.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2699.

(93) Similarly, *mer-cis*-$H_2IrCl(PEt_2Ph)_3$ does not exchange with PMe_2Ph: ref 43.

(94) In **17**, the apical phosphine has two phosphines and two hydrides at *cis* positions instead of two phosphines, a hydride, and *a vacant position* at the isomerization product **20**.

(95) Ignoring the influence of (a) isotopic effects prior to the generation of **17** and (b) isotopic effects within the minor route.

(96) If only this factor was operating, we would have expected for a first approximation[95] 57% of **3c** and only 43% of **3b** upon decomposition of either **1b** or **1c** at 22 °C (eqs 8 and 9).

(97) The rate law for the process was derived, utilizing the fact that the C−H cleavage is rate-determining:

$$\text{rate} = k_{\text{diss}}[\mathbf{1}][\text{methanol}]^{1.33}\left\{1 - \frac{k_{\text{reassoc}}[Cl^-]}{k_{\text{reassoc}}[Cl^-] + k_{\text{C-H cleavage}}}\right\}$$

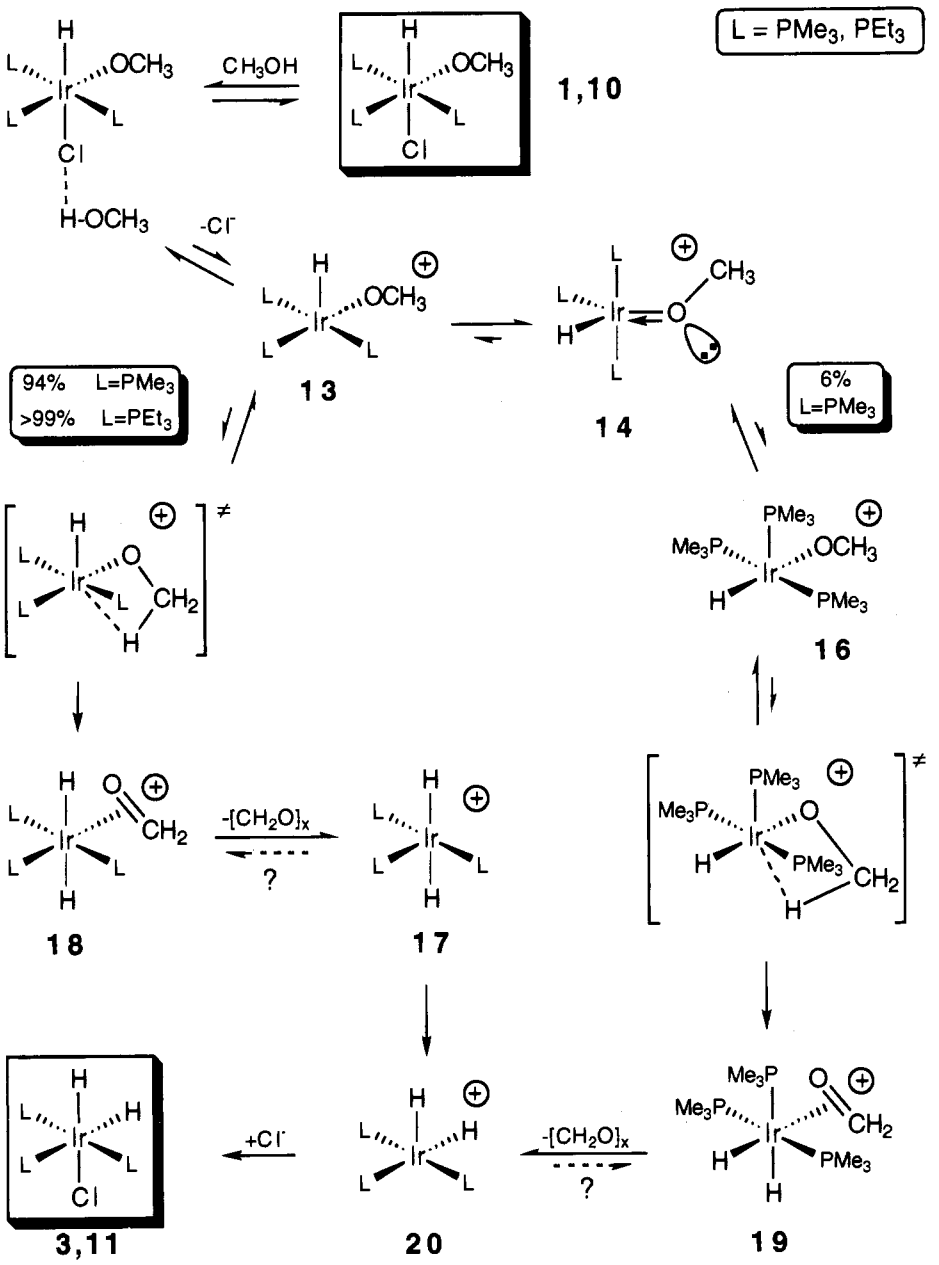


Figure 5.

product and the transition state leading to it are probably stabilized by π-donation from the coordinated methoxide. The rate-determining step is an irreversible scission of the β-C−H bond, which has a relatively early transition state. This process is of low activation energy ($\Delta H^{\ddagger}_{obs} = \Delta H^{\circ}_{diss} + \Delta H^{\ddagger}_{C-H\ cleavage}$ = 24.1 ± 1.8 kcal mol^{-1}; $\Delta S^{\ddagger}_{obs} = \Delta S^{\circ}_{diss} + \Delta S^{\ddagger}_{C-H\ cleavage}$ = 0.6 ± 5.9 eu). **10** and most of **1** (94% at 22 °C) undergo β-hydride elimination via the *sterically* favored geometry of the transition state (which is the electronically less stable geometry). The unstable η^2-formaldehyde *trans*-dihydrido intermediate formed (which was not observed) undergoes a facile product release process, which includes detachment of the π-coordinated aldehyde, fast isomerization within the pentacoordinate intermediate, and an irreversible reassociation of the chloride to obtain **3** or **11**. Under the conditions employed, 6% of **1** (in which the phosphines are less bulky than in **10**) decompose via the *electronically* favored (sterically destabilized) transition state, generating the *cis*-dihydride geometry directly. Following this trend, calculations indicate that the β-H elimination proceeds only via the electronically favored transition state when three of the even smaller PH_3 ligands are present.[71]

Although the alkoxo octahedral complexes **1** and **10** undergo β-hydride elimination by an essentially similar mechanism to that accepted for octahedral alkyl complexes,[14,15] our results suggest significant differences and similarities between the reactions. Stabilization of the unsaturated dissociation product and the transition state leading to it by π-donation of the alkoxide may facilitate the generation of the necessary vacant coordination site in alkoxo complexes compared to alkyl analogs.

It is difficult to draw conclusions from a comparison of the concomitant C−H and M−X cleavages (X = OR, CH_2R) in alkoxo− and alkyl−metal complexes. We found this step to be rate-determining and involving an asymmetric transition state (since it is slower with bulky alkoxides, although the Ir−OR bond cleavage is expected to become easier). The only octahedral transition metal complex for which the C−H scission was found to be rate-determining shows an opposite dependence

on the bulk of the alkyl groups (faster β-H elimination from bulkier alkyls).[13a]

An olefin is a stronger π-acid than the analogous aldehyde.[85c,92] Hence, the product release is expected to be slower with alkyl complexes, particularly in electron-rich systems. Consequently, while the C−H scission from our alkoxo complexes is rate-controlling, the product release was found to be the slowest step in the β-hydride elimination from most transition metal−alkyls studied.

Experimental Section

General Considerations. All syntheses and chemical manipulations were carried out under nitrogen in a Vacuum Atmospheres DC-882 drybox, equipped with an oxygen/water scrubbing recirculation MO-40 "Dri-Train", or under argon, using high vacuum and standard Schlenk techniques.

Materials. All solvents were refluxed on proper drying agents, distilled under argon, and stored over activated 4 Å molecular sieves (150 °C under vacuum for 12 h): toluene (Frutarom, Na/benzophenone), pentane (Merck, Na/benzophenone/tetraglyme), THF (Biolab, prepurified by passing through a column of basic alumina, Na/benzophenone), dioxane (Frutarom, predried over KOH pellets, Na/benzophenone), NMP (Aldrich, distilled), methanol, ethanol, and 2-propanol (Biolab or Fluka, Mg alkoxide; methanol was kept over 3 Å molecular sieves). All deuterated solvents were purchased from Aldrich, degassed, and dried over 3 Å molecular sieves for at least 1 week before use. Trimethylphosphine (Aldrich) and LiCl and LiBr (Merck) were used as received. $NaOCH_3$ was prepared from sodium and methanol under nitrogen. Excess methanol was removed under vacuum at 70 °C for 48 h. $P(CD_3)_3$ was prepared according to a literature method,[98] using CD_3I (Aldrich). $IrCl_3 \cdot 3H_2O$ was supplied by Engelhardt.

Physical Measurements. Infrared spectra were recorded with a Nicolet Spectrometer using NaCl plates either as Nujol mulls or as neat films. Gas chromatographic analyses were performed with a Varian 3700 instrument, equipped with a 10% SE30 on Anakron G80/100 mesh column. Elemental analyses were performed at the Hebrew University of Jerusalem, Israel.

^1H, ^{31}P, ^{13}C, and ^2H NMR spectra were recorded at 400.19, 161.9, 100.6, and 61.4 MHz, respectively, using a Bruker AMX 400 spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si (^1H, ^{13}C) or $(CD_3)_4Si$ (^2H) and referenced to the residual solvent-h_1 (^1H), *all-d*-solvent (^{13}C) and natural abundance solvent-d_1 (^2H) or downfield from external H_3PO_4 85% in D_2O (^{31}P).

Solutions for the kinetic experiments were prepared in the drybox using standard dilution techniques and a Mettler PM200 (1 mg) balance. Gilson pipettes were used to add the solutions at room temperature to 5 mm pyrex NMR tubes, and the height of the solution in the tubes was checked for consistency. Additional solvent was added to attain the desired solvent volume (usually 550 μL). ^{31}P spin−lattice relaxation times (T_1, s) were determined by standard spin inversion/recovery methods for *mer-cis*-$HIr(OCH_3)Cl(PMe_3)_3$ (**1**).

Spectra were recorded in standard pulsed FT mode using 90° (or less) pulses and at least five T_1 periods between pulses to assure reliable quantitative results. When tip angles smaller than 90° were employed, calculated[99] delay times were used. Only the faster relaxing signals of the phosphorus *trans* to phosphorus were used as data sources. These signals are also larger and less split than the triplets of the unique phosphorus atom. Thus, their integration is less sensitive to the noise. In all cases integration was referenced to that of the initial spectrum. In each set of experiments, the acquisition parameters were left constant. However, the intervals between the acquisition of single spectra were changed as needed.

Syntheses. Syntheses and characterization of the hydrido alkoxy complexes are described elsewhere.[16]

***mer-cis*-$H_2IrCl(PMe_3)_3$ (3).** A 50 mg sample of $(C_8H_{14})IrCl(PMe_3)_3$[17] (**2**) was dissolved in 3 mL of benzene at room temperature. Ethanol (300 μL) was added, resulting in quick bleaching. After 30 min, the solvents were stripped off under high vacuum, yielding a yellowish solid, which was crystallized from toluene/pentane at −30 °C. ^1H NMR (C_6D_6): 1.47 (t, $^{virt}J_{H-P}$ = 3.5 Hz, 18H, $2P(CH_3)_3$), 1.23 (d, $^2J_{H-P}$ = 7.5 Hz, 9H, $P(CH_3)_3$ trans to H), −10.35 (dtd, $^2J^d_{H-P,trans}$ = 138.2 Hz, $^2J_{H-P,cis}$ = 23.5 Hz, $^2J^d_{H-H,cis}$ = 5.9 Hz, 1H, P−Ir−*H*), −22.96 (tdd, $^2J_{H-P,cis}$ = 15.8 Hz, $^2J^d_{H-P,cis}$ = 12.0 Hz, $^2J^d_{H-H,cis}$ = 5.8 Hz, 1H, Cl−Ir−*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): −42.90 (d, $^2J_{P-P,cis}$ = 24.1 Hz, 2P), −49.16 (t, $^2J_{P-P,cis}$ = 21.4 Hz, 1P). ^{31}P NMR (C_6D_6): −42.9 (m, 2P), −49.2 (d of m, $^2J_{P-H,trans}$ = 135 Hz, 1P, H−Ir−*P*). IR (neat): 2150 cm^{-1} (s, ν(Ir−H) trans to Cl), 2000 cm^{-1} (s, ν(Ir−H) trans to P). Elemental analysis. Calcd: C, 23.61%; H, 6.38%. Found: C, 23.91%; H, 6.50%.

***mer-cis*-$H_2IrCl(PEt_3)_3$ (11).**[100] A 50 mg sample of $IrCl(PEt_3)_3$[101] was dissolved in 3 mL of benzene and transferred to a Schlenk tube. The solution was frozen (liquid N_2), and the nitrogen atmosphere was replaced by ca. 1 atm of H_2. The reaction mixture was left to warm to room temperature, and the excess H_2 was released. An almost immediate color change (red to yellow) occurred. The solution was stirred for 30 min, after which the hydrogen was released and the solvent was stripped off under high vacuum, yielding a yellowish oil. ^1H NMR (C_6D_6): 1.94 (m, 6H, $P(CH_2CH_3)_3$ trans to H), 1.65 (m, $J_{apparent}$ = 7.1 Hz, 12H, $2P(CH_2CH_3)_3$), 1.01 (apparent quintet (dt), J = 7.3 Hz, 18H, $2P(CH_2CH_3)_3$), 0.96 (m, $J_{apparent}$ = 7.2 Hz, 9H, $P(CH_2CH_3)_3$ trans to H), −11.66 (dtd, $^2J^d_{H-P,trans}$ = 130.0 Hz, $^2J_{H-P,cis}$ = 21.7 Hz, $^2J^d_{H-H,cis}$ = 3.5 Hz, 1H, P−Ir−*H*), −23.65 (apparent qd (dtd), $^2J^q_{H-P,cis}$ = 14.6 Hz, $^2J^d_{H-H,cis}$ = 3.5 Hz, 1H, Cl−Ir−*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): −7.5 (d, $^2J_{P-P,cis}$ = 17 Hz, 2P), −18.4 (t, $^2J_{P-P,cis}$ = 17 Hz, 1P). ^{31}P NMR (C_6D_6): −7.5 (m, 2P), −18.4 (dm, $^2J_{H-P,trans}$ = 128 Hz, 1P, *P* trans to H). IR (neat): 2275 cm^{-1} (m, ν(Ir−H) trans to Cl), 2070 cm^{-1} (s, ν(Ir−H) trans to P). Elemental analysis. Calcd: C, 37.01%; H, 8.11%. Found: C, 37.26%; H, 8.21%.

Physical Experiments. Decomposition of *mer-cis*-$HIr(OCH_3)Cl(PMe_3)_3$ (1). A C_6D_6 solution of **1** was prepared and partitioned among several NMR tubes, as described above. Each tube contained 10 mg of **1** in 500 μL of C_6D_6. The NMR tubes were kept frozen (−30 °C) in the drybox. Before the measurement, 50 μL of methanol was added on top of the frozen solution in the drybox. The tube was kept frozen (liquid N_2) for a few more minutes, then warmed to room temperature (1.5 min) and placed in the thermostated NMR probe. There they remained until the end of the decomposition process. The spectra were recorded as described. The decomposition was followed by $^{31}P\{^1H\}$ NMR for approximately three half-lives of **1** at 22, 40, and 50 °C, for which there was no deviation from the first-order dependence of the rate on [**1**]. At 14, 26, and 30 °C, this was followed for approximately one half-life of **1**. In all reactions (except the one at 50 °C), only the starting material **1**, *mer-cis*-$H_2IrCl(PMe_3)_3$ (**3**), and small amounts (<2%) of *mer-cis*-$HIrCl_2(PMe_3)_3$ (**7**)[21a] were observed. The presence of formaldehyde and its oligomers was confirmed by the chromotropic acid test.[18] All values were reproducible (at least twice) with less than 8% inaccuracy.

1 was stable at −30 °C in otherwise the same conditions (only that benzene is replaced by toluene) or even in neat, methanol.

The above procedure was repeated using 400 μL of C_6D_6 and 150 μL of methanol. The decomposition of **1** was followed at 7, 22, and 40 °C.

Kinetic Deuterium Isotope Effects in the Decomposition of 1. The decomposition rates of *mer-cis*-$HIr(OCH_3)Cl(PMe_3)_3$ (**1**) and of *mer-cis*-$DIr(OCD_3)Cl(PMe_3)_3$ (**1a**) (99% D) were compared at 22 °C. The procedure described above was used here as well. A value of $k_1/k_{1a} = 2.45 \pm 0.1$ was obtained after repeating this experiment three times (and mathematically correcting for 1% non-deuterated **1** in the initial solution of **1a**). The value obtained is a combination of primary (C−H cleavage) and secondary (Ir−D bond and two geminal C−D bonds) kinetic deuterium isotope effects (see text).

A similar procedure was used for $DIr(OCH_3)Cl(PMe_3)_3$ (**1b**) except that both $^{31}P\{^1H\}$ and ^1H NMR spectra were alternatingly recorded.

(98) Luetkens, M. L., Jr.; Sattelberger, A. P.; Murray, H. H.; Basil, J. D.; Fackler, J. P., Jr. *Inorg. Synth.* **1990**, *28*, 305.

(99) Martin, M. L.; Martin, G. J.; Delpuech, J.-J. *Practical NMR Spectroscopy*; Hyden: London, 1980; p 353.

(100) This compound was prepared by a different method before, but spectroscopic characterization was not reported: Lehner, H.; Matt, D.; Tongi, A.; Thouvenot, R.; Venanzi, L. M.; Albinati, A. *Inorg. Chem.* **1984**, *23*, 4254.

(101) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738.

This experiment was repeated four times (and corrected for 4% non-deuterated **1**), yielding the secondary kinetic effect caused by a deuterium substitution on the metal $k_1/k_{1b} = 1.10 \pm 0.06$.

Methanol Dependence of the Decomposition Rate of 1. The decomposition rates of 10 mg of **1** in 550 μL solutions containing various methanol to benzene-d_6 ratios were compared at 22 °C: 0 μL of CH_3OH/550 μL of C_6D_6; 2/548; 10/540; 25/525; 50/500; 75/475; 150/400; 550/0. The 25, 50, 75, and 150 μL methanolic solutions in C_6D_6 gave a linear plot of k_{obs} vs methanol concentration. The decomposition in pure methanol was too fast to follow. In the other three less polar media, **1** was the only compound observed after 12 h. A few days later, signals of other products appeared, due to other chemical processes. Among them, we could identify *mer-cis*-$HIrCl_2(PMe_3)_3$ (**7**),[21a] *cis*-$[H_2Ir(PMe_3)_4]^+$ (**8**),[21b] and a singlet in $^{31}P\{^1H\}$ NMR at −15 ppm, which is possibly due to a product with only two trimethylphosphines on a metal (probably a chloro (or methoxo) bridged dimer). It is possible that ligand disproportionation processes take place.

Aprotic Solvent Dependence of the Decomposition Rate. The above procedure was repeated at 22 °C using a 1:1 *N*-methylpyrrolidone (NMP):C_6D_6 solution instead of the 500 μL C_6D_6 solution.

Exchange of 1 with Methanol. Two NMR tubes containing frozen (−30 °C) solutions of 3 mg of **1** in 500 μL of benzene were prepared. To one, a solution of 2 μL of methanol-d_4 in 48 μL of benzene-d_6 was added, and to the other, a solution containing 25 μL of methanol-d_4 and 25 μL of benzene-d_6. A 50 μL portion of methanol-d_4 was added to a third tube containing 10 mg of **1** in 500 μL of frozen C_6D_6. Disappearance of the methoxy peak relative to the signals of the aliphatic phosphines was monitored by ^1H NMR at 22 °C. First-order dependence on [**1**] was observed in all the experiments for three half-lives of **1**. In the first tube, where only 2 μL of methanol-d_6 were added, the exchange rate was too slow, so only initial rates were observed (less than one half-life of **1**). A very slow exchange of the hydride to a deuteride was observed in all cases as well.

The methoxide exchange reaction was examined (but not followed by NMR) at −30 °C. The above amounts were used here too, except that the benzene was replaced by toluene. After 6 h, the solvents were stripped off at −30 °C. We found 49% of Ir−OCH_3. Again, a small percentage of the hydrides was replaced by deuterides.

Decomposition of 1 in the Presence of LiCl. (a) At −30 °C. A 10 mg sample of **1** was dissolved in 500 μL of toluene, and the solution was cooled to −30 °C. Next, 2.5 mg of LiCl (3 mol equiv) dissolved in 50 μL of methanol was added, forming two phases. The reaction was shaken periodically for 2 h, after which the liquids were stripped off at −30 °C under high vacuum and the residue was extracted with benzene. Only *mer-cis*-$HIrCl_2(PMe_3)_3$ (**7**)[21a] was observed. To prevent the generation of two phases, the above procedure was repeated using THF instead of toluene. Again, **7** was the only product observed.

(b) At room temperature. The above procedure was repeated in dioxane at room temperature, using 1 equiv of LiCl. Initially (after 10 min) 60% of **7** was present along with 40% of **1**. Generation of **3** was slower than in the absence of LiCl. After 16 h, only 35% of **7** and 65% of **3** were present. **7** was observed for 2 more days before it disappeared, leaving **3** as the single product. Repeating the last procedure in a biphasic benzene/methanol + LiCl led to similar observations. When 3 mol equiv of LiCl were used, **7** was fast and irreversibly generated.

Decomposition of 1 in the Presence of $NaOCH_3$. A 10 mg sample of **1** was dissolved in 500 μL of THF. Then, 5.5 mg of NaOMe (5 mol equiv) dissolved in 50 μL of methanol was added at room temperature. ^{31}P and ^1H NMR of the solution revealed the formation of a mixture. Among the products we could identify, *mer-cis*-$HIr(OMe)_2(PMe_3)_3$ (**9**) was the most abundant product. After the solvents were stripped off and the residue was redissolved in C_6D_6, the relative amount of **9** in the mixture decreased. Spectroscopic characterization of **9** was as follows. ^1H NMR (C_6D_6): 4.10 (d, $^4J_{H-P,trans} = 5.5$ Hz, 3H, OCH_3 trans to PMe_3), 3.89 (s, 3H, OCH_3 trans to PMe_3), 1.36 (t, $^{virt}J_{H-P} = 3.5$ Hz, 18H, $2P(CH_3)_3$), 1.13 (d, $^2J_{H-P} = 9.4$ Hz, 9H, $P(CH_3)_3$), −23.09 (dt, $^2J^d_{H-P,cis} = 18.7$ hz, $^2J'_{H-P,cis} = 15.9$ Hz, 1H, Ir−*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): −29.4 (d, $^2J_{P-P,cis} = 19.6$ Hz, 2P), −52.8 (br m, 1P). **9** is not stable and decomposes further in C_6D_6.

Decomposition of 1 in the Presence of PMe_3. A 10 mg sample of **1** was dissolved in 400 μL of C_6D_6. Then, 50 μL of methanol was added to the frozen solution, followed by 1.3 μL of PMe_3 (2 mol equiv) dissolved in 100 μL of C_6D_6. ^1H NMR of the solution, after warming to 22 °C, revealed formation of a mixture containing **3** (ca. 20%, its amount changed with time) in addition to the following cationic complexes (the nature of the anion, Cl^- or OCH_3^-, is not known): *cis*-$[HIr(OCH_3)(PMe_3)_4]^+$ (**12**),[7n] *cis*-$[H_2Ir(PMe_3)_4]^+$ (**8**),[21b] small amounts of $HIr(PMe_3)_4$,[21b] and approximately 60% of the *cis* (50%) and *trans* (10%) isomers of $[HIrCl(PMe_3)_4]^+$. These two compounds were also prepared separately.[16]

Repetition of the above procedure using $P(CD_3)_3$ resulted in the same product distribution. Notably, ^1H and ^2H NMR revealed that no labeled phosphine was incorporated into **3**.

Decomposition of *mer-cis*-$DIr(OCH_3)Cl(PMe_3)_3$ (1b) has already been described for obtaining the kinetic deuterium isotope effect of the decomposition of **1**. Integration of the signals of the two hydrides of **3** and of the trimethylphosphine protons (serving as an internal reference) revealed that (a) after mathematically correcting the results for 99% D in the starting material (and/or the consequent complications caused by isotope effects in the preparation of **1b**[16] and its further reactivity, i.e. β-hydride elimination and alkoxide exchange), only 50 ± 3% of the total hydrides (as compared to $H_2IrCl(PMe_3)_3$) were observed, i.e. there was no loss (or gain) of deuterium during decomposition; (b) the average integration ratio between the two hydride signals was 60 ± 1.5% (H *trans* to P, **3c**) to 40 ± 1.5% (H *trans* to Cl, **3b**); and (c) this ratio did not change during the decomposition process. Leaving the solution for an additional 24 h showed neither loss of the deuteride nor any change in the ratio between the integrations of the two hydride signals. At this point, the solvents were stripped off and the residues redissolved in C_6D_6. A two-dimensional H−H correlation spectrum (COSY-90) was measured, revealing practically no cross peaks between the hydrides. We conclude that only the two isomers of *mer-cis*-$H(D)IrCl(PMe_3)_3$ (**3b,c**) were obtained without any additional amounts of *mer-cis*-$H_2IrCl(PMe_3)_3$ (**3**) and *mer-cis*-$D_2IrCl(PMe_3)_3$ (**3a**). This conclusion is strengthened by the well-defined shape of the hydride signals that did not seem to fit the superposition of the hydride, i.e. the dihydrido complex **3** is not present in substantial amounts.

Decomposition of *mer-cis*-$HIr(OCD_3)Cl(PMe_3)_3$ (1c). The procedure employed for decomposing **1b** was repeated, except that no kinetic follow up of the decomposition in the NMR was performed. Again, no loss (or gain) of deuterium was observed. The average integration ratio (of four experiments) between the two hydride signals was 54 ± 1% (H *trans* to P, **3c**) to 46 ± 1% (H *trans* to Cl, **3b**). As in the decomposition of **1b**, the ratio of the products did not change with time and a two-dimensional H−H correlation spectrum confirmed that only **3b,c** (but not **3** or **3a**) were formed.

Reaction of *mer-cis*-$HIrCl_2(PMe_3)_3$ (7) with 1 Equiv of $NaOCH_3$. A 1.1 mg (1 mol equiv) sample of $NaOCH_3$ dissolved in 50 μL of methanol was added to 10 mg of **7** dissolved in 500 μL of benzene-d_6. Periodic examination of the reaction showed slow formation of **3**. **1** was generated as well, but it decomposed afterward to give **3**.

Stability of *mer-cis*-$HIr(OH)Cl(PMe_3)_3$ (6).[16] A solution of 10 mg of **6** in 50 μL of water and 500 μL of THF was left at room temperature for 1 month. No change was apparent in the NMR.

Decomposition of *mer-cis*-$HIr(OEt)Cl(PMe_3)_3$ (4).[16] **4** was left to decompose at 22 °C in a manner similar to the decomposition of **1**, except that ethanol replaced methanol as a cosolvent. **3** was the only metal complex product observed.

Decomposition of *mer-cis*-$HIr(O\text{-}i\text{-}Pr)Cl(PMe_3)_3$ (5).[16] A solution of **5** (in a mixture with **3**) in concentrations similar to those used for the decomposition of **1** (except that 2-propanol replaced methanol) showed almost no generation of **3**. Even in a solution containing 100 μL of 2-propanol and 450 μL of THF, the thermolysis of **5** was not completed in 2 days at 22 °C. **5** and **3** were the only complexes observed in solution. GC analysis of the volatiles confirmed the presence of acetone.

Decomposition of *mer-cis*-$HIr(OCH_3)Cl(PEt_3)_3$ (10). The compound decomposes even in a 10 μL of methanol/540 μL of toluene solution at −30 °C, albeit slowly. Therefore, some (less than 10%) decomposites were present in the starting solutions.

In a neat benzene solution, 10 mg of **10** disappear within 2 days, generating mainly *mer-cis*-$H_2IrCl(PEt_3)_3$ (**11**). Small amounts of $HIrCl_2(PEt_3)_3$[55] and $H_3Ir(PEt_3)_3$[87,102] were also present.

When repeated under the same conditions where **1** decomposes [i.e., a solvent of methanol/benzene (1/10 v/v)], the decomposition of **10** was too fast to follow up by NMR. Therefore, a less polar methanol/benzene (1/54, v/v) medium was used for the thermolytic kinetics of **10**. The decomposition of 10 mg of **10** at 22 °C in 10 μL of methanol and 540 μL of benzene was performed in a manner otherwise analogous to the decomposition of **1**.

Decomposition of 10 in the Presence of Excess PEt_3. A 100 μL C_6D_6 solution containing 25 μL of PEt_3 (10 mol equiv) was added to 10 mg of **10** dissolved in 40 μL of C_6D_6. The solution was frozen (−30 °C), and 10 μL of methanol was added. The decomposition was monitored at 22 °C by $^{31}P\{^1H\}$ NMR. **11** was the only transition metal product. The rate constant for this thermolysis was found to be a little *larger* than that of the analogous decomposition in the absence of excess PEt_3.

Decomposition of *mer-cis*-$HIr(OCD_3)Cl(PEt_3)_3$ (10a). A solution of 10 mg of the complex in 540 μL of C_6D_6 and 10 μL of CD_3OH was prepared. The decomposition was performed and analyzed in a manner similar to the decomposition of **1c** and repeated three times. Unlike results obtained for the decompositions of **1b,c**, **11a,b** were generated in a practically 1:1 ratio.

(102) $^{31}P\{^1H\}$ NMR is reported: Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 704.

Stability of *cis*-$[HIr(OMe)(PMe_3)_4]PF_6$ (12).[7n] A 15 mg sample was dissolved in THF and left in a pressure vessel at 70 °C. No change was observed in the reaction mixture. **12** was also found to be stable for 1 week in a solution of 50 μL of methanol and 500 μL of benzene at room temperature.

Attempted Reaction of 3 with $P(CD_3)_3$. A 150 μL C_6D_6 solution containing 22.7 μL of PMe_3 (10 mol equiv) was added to a solution of 10 mg of **3** in 350 μL of C_6D_6 and 50 μL of methanol. After 1 week at room temperature, no change was observed. The solvent and phosphine were stripped off under high vacuum, and the residue was redissolved in toluene. No incorporation of $P(CD_3)_3$ into **3** was observed by ^2H NMR.

Attempted Reaction of 11 with $P(n\text{-}Bu)_3$. A 150 μL C_6D_6 solution containing 25 μL of $P(n\text{-}Bu)_3$ (10 mol equiv) was added to a solution of 10 mg of **11** in 390 μL of C_6D_6 and 10 μL of methanol. No change was observed after 1 month at room temperature.

Reaction of 10 with $P(n\text{-}Bu)_3$. The procedure above was repeated using **10**. After a few hours, **10** completely disappeared, giving rise to an untractable mixture. It is most likely that mono-, di-, and triphosphine substitution products were generated and that more than a single isomer was present for the mono- and disubstituted products.

Acknowledgment. We thank the U.S.-Israel Binational Science Foundation (BSF), Jerusalem, Israel (Grant No. 89-00374), for financial support.

JA942301C