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Hydrogen elimination in the thermal decomposition of iridium-*n*-alkyl complexes

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Abstract

Iridium complexes $L_2Ir(CO)X$ (L = PPh_3, $P(p\text{-}FC_6H_5)_3$, CO; X = Cl, I) and $L_2Ir(CO)X_3$ (L = PPh_3, $P(p\text{-}FC_6H_5)_3$; X = Cl, I) were allowed to react with $CH_3(CH_2)_6CD_2Li$ and $CH_3(CH_2)_5CD_2CH_2Li$ to form the respective n-octyliridium complexes. Thermal decomposition of these complexes yielded solely $D_2C{=}CH(CH_2)_5CH_3$ and $CHD_2(CH_2)_6CH_3$ from the 1,1-dideuteriooctyliridium complexes and $H_2C{=}CD(CH_2)_5CH_3$ and $CDH_2CD_2(CH_2)_5CH_3$ from the 2,2-dideuteriooctyliridium complexes. Thus, productive decomposition of the *n*-alkyliridium complexes occurred exclusively by a β-hydrogen elimination mechanism. This is in accord with the previously reported reaction of $(PPh_3)_2Ir(CO)Cl$ with $CH_3(CH_2)_5CD_2CH_2Li$ [1] and demonstrates that changing the steric and electronic nature of the donor ligands on the iridium is insufficient to induce productive decomposition by α-hydrogen elimination.

Keywords: Iridium; Alkyls; Elimination reactions

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1. Introduction

Late transition metal–alkyl complexes bearing both α and β-hydrogens frequently undergo hydrogen elimination reactions to form olefinic products. This decomposition is generally believed to occur directly via β-hydrogen elimination, although reports of α-hydrogen elimination followed by a 1,2-hydrogen shift have also appeared [2]. The products from α- and β-elimination are readily distinguishable in appropriately labeled complexes, however, in unlabeled complexes the products are identical (Scheme 1). This potential for misidentification of the decomposition mechanism in unlabeled reactions has prompted us to reexamine the thermal decomposition pathways occurring in a number of late transition metal–alkyl complexes.

α-Hydrogen elimination has been reported in the rearrangement and decomposition of several iridium complexes. Iridium-methyl complexes have been observed to undergo α-hydrogen elimination during both thermal and photolytic decomposition [3] and an iridacyclohexadiene bearing only a vinylic hydrogen in the β position was reported to undergo an α-hydrogen elimination during rearrangement [4]. Rapid α-hydrogen elimination and readdition followed by β-hydrogen elimination was also suggested to account for deuterium incorporation into olefins produced from the reaction of alkenes with $\{IrD_2(\eta^2\text{-}O_2CCF_3)[P(p\text{-}FC_6H_4]\}$ [5]. It should be noted, however, that the same product can be rationalized on the basis of α-hydrogen elimination followed by a 1,2-hydride shift. This report of α-hydrogen elimination in competition with β-hydrogen elimination prompted us to further explore iridium–alkyl complexes in which both α- and β-eliminations are possible.

Iridium-alkyl complexes bearing both α- and β-hydrogens are generally reported to decompose by the β-hydrogen elimination pathway [6]. However, few of these studies actually included deuterium labeling [7] to determine the origin of the eliminated hydrogen. One such labeling study was reported by Schwartz and Cannon [1], in which the decomposition of the octyliridium complex, $(CH_3(CH_2)_5CD_2CH_2)Ir(CO)(PPh_3)_2$, was clearly shown to proceed by β-hydrogen elimination. We have expanded on this original study by modifying the steric and electronic properties of the non-alkyl ligands in an attempt to induce α-elimina-

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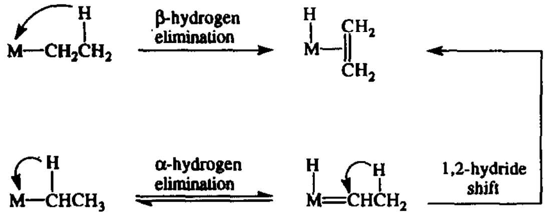
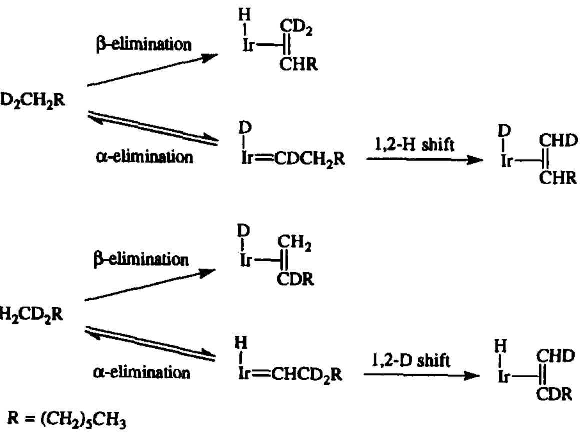


Scheme 1.



Scheme 2.

tion. The original complex was also included as a baseline for comparison to the modified complexes. Both α- and β-labeled octyl ligands were examined.

2. Results and discussion

2.1. Preparation and thermolysis of iridium–octyl complexes

The deuterated starting materials, 1-bromo-1,1-dideuteriooctane and 1-bromo-2,2-dideuteriooctane, were synthesized with 91–96% and 82–90% label incorporation (two deuteriums), respectively [8,9]. The octyllithium which was prepared from the bromide by standard procedures [10] was contaminated with 1-octene, 2-octene and octane as a result of Wurtz-type elimination reactions [11]. The presence of these byproducts necessitated isolation of the octyllithium prior to reaction with the iridium complexes. This purified octyllithium did not further decompose to olefinic products after 12 h in dry diethylether at either 0°C or 25°C. Reaction of the octyllithium with atmospheric water did produce octane but no octenes.

A series of related octyliridium complexes were examined in which the donor ligands, halide ligands, and iridium oxidation states were varied. Iridium(I) complexes were of the type $L_2Ir(CO)X$, where $L = PPh_3$, $X = Cl$, I; and $L = P(p\text{-}FC_6H_4)$, CO, $X = Cl$. Iridium(III) complexes $L_2Ir(CO)X_3$ ($L = PPh_3$, $P(p\text{-}FC_6H_4)$, $X = Cl$; and $L = PPh_3$, $X = I$) were also examined. Replacing the chloride ligands with iodide had no discernible effect on the reaction products. Synthesis of $(CO)_3IrCl_3$ was attempted both from the reaction of carbon monoxide with $IrCl_3$ and by chlorination of $(CO)_3IrCl$, but was unsuccessful [12].

Freshly prepared diethylether solutions of 1,1-dideuteriooctyllithium or 2,2-dideuteriooctyllithium were added to the appropriate iridium chloride complex suspended in diethylether. The resulting octyliridium complexes were soluble in diethylether and were decomposed by warming the solution. Following decomposition, which was accompanied by a color change, the volatile products were collected by vacuum transfer and analyzed by GCMS and ^1H and ^2H NMR spectroscopy. The 1,1-dideuteriooctyl ligand produced 1,1-dideuterio-1-octene and 1,1-dideuteriooctane, while the 2,2-dideuteriooctyl ligand formed 2-deuterio-1-octene and 1,2,2-trideuteriooctane (Table 1). These labeled products indicate that decomposition occurred via the β-hydrogen elimination pathway (Scheme 2). No products were observed to result from α-hydrogen elimination followed by a 1,2-hydrogen shift. (Nonproductive α-hydrogen elimination equilibria were not detectable by the labeling scheme used in these studies.) Neither 2-octene nor hexadecane was observed from these reactions [13].

Table 1
Volatile products isolated from the reaction of iridium complexes with dideuterium-labeled octyllithium

Complex	$CH_2(CH_2)_6CD_2Li$		$CH_3(CH_2)_5CD_2CH_2Li$	
	$CH_3(CH_2)_5CH{=}CD_2$ (%)	$CH_3(CH_2)_6CHD_2$ (%)	$CH_3(CH_2)_5CD{=}CH_2$ (%)	$CH_3(CH_2)_5CD_2CH_2D$ (%)
$(PPh_3)_2Ir(CO)Cl$	51	49	44	56
$(PPh_3)_2Ir(CO)I$	32	68		
$[P(p\text{-}FC_6H_4)]_2Ir(CO)Cl$	55	45	34	66
$Ir(CO)_3Cl$	46	54		
$(PPh_3)_2Ir(CO)Cl_3$	36	64	42	58
$(PPh_3)_2Ir(CO)I_3$	44	56	39	61
$[P(p\text{-}FC_6H_4)]_2Ir(CO)Cl_3$	38	66	43	57

2.2. *Effect of varying the donor ligands*

The donor ligands were varied on the iridium(I) complexes to determine whether the decomposition pathway adopted by the alkyl ligand would be influenced by their steric and electronic properties. On a simplistic level, the ability of a ligand to stabilize electron density build up on the iridium should favor the transient carbene species formed by α-hydrogen elimination [14,15]. The ligands' steric bulk should affect the general ease of decomposition, and could also influence the conformation adopted by the octyl ligand, thereby dictating which hydrogens are accessible to the metal center. Of the three ligands examined, (PPh_3, $P(p\text{-}FC_6H_5)_3$ and CO), triphenylphosphine and its *para*-fluorophenyl derivative have essentially the same steric profile, while the fluorine-containing ligand is less electron donating. Carbon monoxide, in contrast, is a much smaller ligand and is also a strong π-acid.

These differing properties of the donor ligands did affect the rate of formation and decomposition of the octyliridium complexes. However, the labeling patterns observed in the products consistently supported β-hydrogen elimination as the only productive decomposition pathway. Thus, altering the steric and electronic profiles of the donor ligands in this manner was insufficient to induce α-hydrogen elimination as the productive decomposition course.

2.3. *Effect of the iridium oxidation state*

Iridium(III) complexes, $L_2Ir(CO)Cl_3$, containing the donor ligands PPh_3 and $P(p\text{-}FPh)_3$ (L) were synthesized to compare the effect of oxidation state on the decomposition pathway of the alkyl complexes. The previously reported example of α-elimination occurred in an iridium(III) complex containing $P(p\text{-}FC_6H_5)$ and (η^2-O_2CCF_3) ligands [5]. Thus it was thought that the higher metal oxidation state, coupled with the fluorinated ligands, may have stabilized the carbene intermediate formed via α-hydrogen elimination as already discussed. Once again, no discernible effect on the fate of the deuterium label in the products was observed, indicating that β-hydrogen elimination occurred regardless of the iridium oxidation state. The coordinatively saturated iridium(III) complexes reacted more slowly than the iridium(I) complexes and no evidence for reduction of the iridium(III) to iridium(I) was observed prior to decomposition.

2.4. *Conclusions*

Products arising exclusively from β-hydrogen elimination were obtained from the thermal decomposition of a series of deuterium labeled *n*-octyliridium complexes. The non-alkyl ligands on the iridium were varied to provide complexes with a range of steric and electronic properties, however, these changes had no apparent effect on the identity of the decomposition products. All the labeled products obtained indicated that decomposition proceeded via a β-hydrogen elimination pathway, although the presence of non-productive α-hydrogen elimination equilibria can not be ruled out. These results are in accord with the β-hydrogen elimination observed by Schwartz for the parent compound $(CH_3(CH_2)_5CD_2CH_2)Ir(CO)(PPh_3)_2$; changing the donor ligands on the iridium did not alter the course of the decomposition. It has been suggested that substituents attached directly to the alkyl ligand have a greater impact on the nature and stabilization of the desired carbene complexes [16], therefore subsequent studies will focus on modifications of this type.

3. Experimental section

Tris(*p*-fluorophenyl)phosphine, $(PPh_3)_2IrCl(CO)$, $(PPh_3)_2IrI(CO)$, $IrCl_3 \cdot nH_2O$, $[IrCl(CO)_3]n$, and $[(cod)IrCl]_2$ [17] were obtained from Strem Chemicals. $IrCl_4 \cdot 2H_2O$ was purchased from Aldrich. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium-benzophenone ketyl. 1-Bromo-1,1-dideuteriooctane [8], 1-bromo-2,2-dideuteriooctane [9], $(PPh_3)_2IrCl_3(CO)$ [18], $(PPh_3)_2IrI_3(CO)$ [19], $(P(p\text{-}FC_6H_5)_3)_2IrCl(CO)$ [20], and $(P(p\text{-}FC_6H_5)_3)_2IrCl_3(CO)$ [21], were synthesized by literature methods. Other reagents and solvents were purchased from commercial sources and used as received. All reactions were carried out under argon.

Mass spectral analyses were performed on a Hewlett Packard MSD GC/MS with a 30 m × 0.25 mm SE 30 capillary column. NMR spectra were obtained in $CDCl_3$ or CCl_4 at 25°C on a Bruker AC300 spectrometer.

3.1. *Preparation of 1,1-Dideuteriooctyllithium [10]*

A solution containing 123 μl 1-bromo-1,1-dideuteriooctane (0.70 mmol) and 25 mg lithium (3.6 mmol) in 1 ml diethyl ether was stirred under Ar at 0°C for 2 h. The resulting solution was cannulated away from any unreacted lithium and the octyllithium was dried under vacuum to remove octane and octene byproducts. Readdition of 1 ml diethyl ether resulted in a clear solution which was kept at 0°C and used immediately without further purification. Sample octyllithium solutions were monitored over the course of 24 h, but no further formation of olefinic byproducts was observed. Introduction of atmospheric water to the octyllithium resulted only in octane formation.

3.2. General procedure for the synthesis and decomposition of octyliridium complexes [1]

Freshly prepared 1,1-dideuteriooctyllithium in diethyl ether was cannulated into a suspension of the iridium complex (0.035 mmol) in 1.0 ml diethyl ether at 0°C. A solution formed immediately. The resulting octyliridium complex was warmed to room temperature and allowed to decompose. After 0.1–2 h the volatile products were collected under vacuum and were analyzed by GC/MS and ^{1}H and ^{2}H NMR spectroscopy.

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