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Iridium Complexes in Olefination Reactions

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Summary: Iridium complexes were found to catalyze the olefination of aldehydes in the presence of triphenylphosphine with both ethyl diazoacetate and trimethylsilyldiazomethane. Conjugated esters were obtained under mild reaction conditions at room temperature using $[IrCl(cod)]_2$*, whereas Vaska's complex was used to synthesize terminal alkenes from trimethylsilyldiazomethane.*

Introduction

Various late transition metal complexes derived from Mo,[1] Re,[2] Fe,[3] Ru,[4] and Co[5] catalyzed the olefination of aldehydes with diazo carbonyl reagents and triphenylphosphine.[6] These nonbasic reaction conditions allowed the synthesis of conjugated esters and ketones in high yields and excellent *E*-selectivity. Other catalytic systems based on ruthenium,[7] rhodium,[8] and copper[9] complexes have been developed for the methylenation of aldehydes and ketones with trimethylsilyldiazomethane, 2-propanol, and triphenylphosphine. Terminal alkenes were produced in high yield and high chemoselectivities under these mild reaction conditions, which are compatible with a variety of functional groups. In contrast to the other complexes of the group 9 metals, such as cobalt and rhodium, the catalytic activity of iridium complexes with diazo compounds remained largely unexploited.[10,11] To the best of our knowledge, these complexes have never been used as catalysts for the olefination of carbonyl compounds with diazo compounds. Iridium complexes may not only lead to novel improved olefination reaction conditions but also serve eventullay as a tool for mechanistic studies. Herein, we describe the use of $[IrCl(cod)]_2$ and Vaska's complex[12] as catalysts in the olefination of aldehydes with both ethyl diazoacetate and trimethylsilyldiazomethane.

Results and Discussion

Iridium-Catalyzed Olefination of Aldehydes with Diazo Compounds. Ethyl diazoacetate and trimethylsilyldiazomethane were selected as readily available diazo reagents to test iridium complexes as catalysts for the olefination of 3-phenylpropanal in the presence of triphenylphosphine and various additives (Table 1). $[IrCl(cod)]_2$ was found to be a very efficient catalyst for the olefination with ethyl diazoacetate at room temperature, whereas no reaction was observed with Vaska's complex (entry 4 vs 9). $[IrCl(cod)]_2$ is known to react with triphenylphosphine to form $Ph_3PIr(cod)Cl$,[13] which is the active species in the olefination process.[14] The more labile cyclooctadiene ligand may liberate a coordination site, thus explaining the difference of catalytic activity between this complex and Vaska's complex. Although the reaction proceeded without an additive, the use of 1.1 equiv of 2-propanol or 0.1 equiv of benzoic acid was found to accelerate considerably the reaction (entry 1 vs 2 and

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(14) An X-ray crystal structure of $Ph_3PIr(cod)Cl$, prepared from $[IrCl(cod)_2]_2$ and triphenylphosphine, has been obtained; see Supporting Information for details. This species showed catalytic behavior similar to that of a mixture of $[IrCl(cod)_2]_2$ and triphenylphosphine for the olefination of aldehydes with ethyl diazoacetate.

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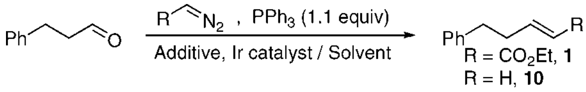
Table 1. Optimization of the Iridium-Catalyzed Olefination of 3-Phenylpropanal



entry	diazo (equiv)	additive (equiv)	Ir catalyst (mol %)	solvent	temp (° C)	time (h)	Conv. (%)[a,b]
1	EtO_2CCHN_2 (1.4)	---	$[IrCl(cod)]_2$ (1.2)	THF	23	3	65 (**1**)
2	EtO_2CCHN_2 (1.4)	$PhCO_2H$ (0.1)	$[IrCl(cod)]_2$ (1)	THF	23	2	≥98 (**1**)
3	EtO_2CCHN_2 (1.2)	*i*-PrOH (1.1)	$[IrCl(cod)]_2$ (1.2)	THF	23	3	88 (**1**)
4	EtO_2CCHN_2 (1.4)	*i*-PrOH (1.1)	$[IrCl(cod)]_2$ (1.2)	THF	23	3	≥98 (**1**)
5	EtO_2CCHN_2 (1.4)	*i*-PrOH (1.1)	$[IrCl(cod)]_2$ (1.2)	DCM	23	3	95 (**1**)
6	EtO_2CCHN_2 (1.4)	*i*-PrOH (1.1)	$[IrCl(cod)]_2$ (1.2)	Dioxane	23	3	92 (**1**)
7	EtO_2CCHN_2 (1.4)	*i*-PrOH (1.1)	$[IrCl(cod)]_2$ (1.2)	Ether	23	3	≥98 (**1**)
8	EtO_2CCHN_2 (1.4)	*i*-PrOH (1.1)	$[IrCl(cod)]_2$ (1.2)	Toluene	23	3	95 (**1**)
9	EtO_2CCHN_2 (1.4)	*i*-PrOH (1.1)	$IrClCO(PPh_3)_2$ (2.5)	THF	23	18	0
10	EtO_2CCHN_2 (1.4)	*i*-PrOH (1.1)	$IrClCO(PPh_3)_2$ (2.5)	THF	reflux	18	≥98 (**1**)
11	$TMSCHN_2$ (1.8)	*i*-PrOH (1.1)	$[IrCl(cod)]_2$ (1.2)	THF	23	4	0
12	$TMSCHN_2$ (1.8)	*i*-PrOH (1.1)	$[IrCl(cod)]_2$ (1.2)	THF	reflux	4	≥98 (**10**)
13	$TMSCHN_2$ (1.4)	*i*-PrOH (1.1)	$IrClCO(PPh_3)_2$ (2.5)	THF	23	8	0
14	$TMSCHN_2$ (1.4)	*i*-PrOH (1.1)	$IrClCO(PPh_3)_2$ (2.5)	THF	reflux	2	75 (**10**)
15	$TMSCHN_2$ (1.8)	*i*-PrOH (1.1)	$IrClCO(PPh_3)_2$ (2.5)	THF	reflux	2	≥98 (**10**)

[a] Determined by GC-MS. [b] E:Z ratios for alkene 1 are 98:2 in all cases.

4).[15] Furthermore, the reaction with $[IrCl(cod)]_2$ catalyst proceeded equally well in various solvents at room temperature. These reaction conditions are extremely mild and advantageous compared to a number of other catalytic systems. Whereas $[IrCl(cod)]_2$ catalyst produced the desired alkene in complete conversion at room temperature, a temperature higher than 50 °C (typically 80 °C) is required to achieve the same transformation with ruthenium[4] and cobalt complexes.[5] It is only when using the not commercially available iron(II) porphyrin as catalyst that the olefination of aldehydes with ethyl diazoacetate proceeded at room temperature.[6]

Surprisingly, there was very little difference between the catalytic activity of $[IrCl(cod)]_2$ versus Vaska's complex for the methylenation of 3-phenylpropanal with trimethylsilyldiazomethane and triphenylphosphine. Both complexes did not catalyze the reaction at room temperature (Table 1, entries 11 and 13). Conversely, total conversion for the terminal alkene was observed when the reaction was refluxed in THF (entries 12 and 15).

The reaction conditions for the formation of conjugated esters from ethyl diazoacetate and triphenylphosphine in the presence of 1 mol % of $[IrCl(cod)]_2$ allowed the transformation of a variety of aliphatic and aromatic aldehydes (Table 2). Either a full equivalent of 2-propanol or a catalytic amount of benzoic acid was used as additive to promote the reaction. In all cases, the *E:Z* ratio was greater than 95:5. The reaction was compatible with various functional groups including carbamate, alkene, and ketone. Furthermore, not only did an electron-rich aromatic group provide the desired alkene in high yields, but also electron-poor aromatic and heteroaromatic groups were compatible with the reaction conditions, leading to alkenes **8** and **9** in good yields.

We have also tested the methylenation of aldehydes using 2.5 mol % of Vaska's complex and trimethylsilyldiazomethane

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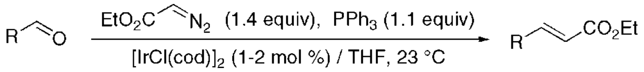
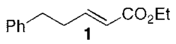
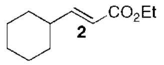
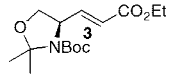
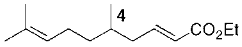
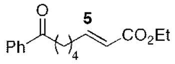
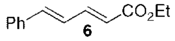
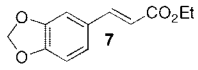
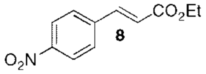
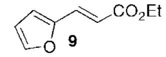
[15] For a discussion regarding the effect of a Bronsted acid in olefination reactions, see ref 4e.

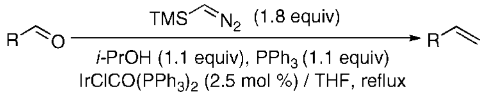
Table 2. Iridium-Catalyzed Olefination of Aldehydes with Ethyldiazoacetate

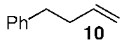
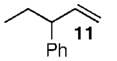
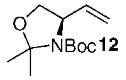
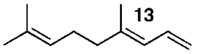
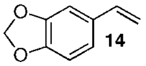


entry	product	*i*-PrOH (1.1 equiv) yield (%)[a] (*E*:*Z* ratio)[b]	$PhCO_2H$ (1.1 equiv) yield (%)[a] (*E*:*Z* ratio)[b]
1	 **1**	75 (98 : 2)	67 (98 : 2)
2	 **2**	59 (95 : 5)	80 (95 : 5)
3	 **3**	81 (99 : 1)	79 (99 : 1)
4	 **4**	88 (96 : 4)	53 (96 : 4)
5	 **5**	54 (97 : 3)	58 (97 : 3)
6	 **6**	72 (99 : 1)	69 (99 : 1)
7	 **7**	63 (99 : 1)	86 (99 : 1)
8	 **8**	81 (99 : 1)	83 (99 : 1)
9	 **9**	71 (99 : 1)	75 (99 : 1)

[a] Isolated yields. [b] Determined by GC-MS.

Table 3. Iridium-Catalyzed Methylenation of Aldehydes with Trimethylsilyldiazomethane



entry	product	yield (%)[a]
1	 **10**	69
2	 **11**	62
3	 **12**	72
4	 **13**	67
5	 **14**	71

[a] Isolated yields.

with a few substrates (Table 3). Moderate yields were obtained for aliphatic, aromatic, and conjugated aldehydes when running the reaction in refluxing THF.

Conclusion

In conclusion, we have demonstrated the use of iridium complexes as catalysts for the olefination of aldehydes with diazo compounds and triphenylphosphine. The olefination reaction with ethyl diazoacetate and $[IrCl(cod)]_2$ as catalyst proceeded at room temperature to lead to conjugated esters with selectivities greater than 95:5 favoring the *E* isomer.

Experimental Section

Iridium-Catalyzed Olefination of Aldehydes using 2-Propanol (Procedure A). To a solution of chloro-1,5-cyclooctadieneiridium (0.013 g, 0.020 mmol) in THF (10 mL) was added triphenylphosphine (0.288 g, 1.10 mmol) and 2-propanol (0.084 mL, 1.1 mmol), followed by the aldehyde (1.00 mmol). To the resulting red mixture was added ethyl diazoacetate (0.141 mL, 1.40 mmol). Gas evolution was observed, and the resulting mixture was stirred at room temperature. When the olefination reaction was complete by TLC analysis, the product was purified by flash chromatography.

Iridium-Catalyzed Olefination of Aldehydes Using Benzoic Acid (Procedure B). To a solution of chloro-1,5-cyclooctadieneiridium (0.013 g, 0.020 mmol) in THF (20 mL) were added triphenylphosphine (0.577 g, 2.20 mmol) and benzoic acid (0.024 g, 0.20 mmol) followed by the aldehyde (2.00 mmol). To the resulting red mixture was added ethyl diazoacetate (0.282 mL, 2.80 mmol). Gas evolution was observed, and the resulting mixture was stirred at room temperature. When the olefination reaction was complete by TLC analysis, the product was purified by flash chromatography.

Iridium-Catalyzed Methylenation of Aldehydes (Procedure C). To a solution of chlorocarbonylbis(triphenylphosphine)iridium (0.019 g, 0.025 mmol) in THF (10 mL) were added triphenylphosphine (0.288 g, 1.10 mmol) and 2-propanol (0.084 mL, 1.1 mmol) followed by the aldehyde (1.00 mmol). To the resulting yellow mixture was added trimethylsilyldiazomethane (0.026 mL, 1.80 mmol, 6.8 M). Gas evolution was observed, and the resulting mixture was stirred at reflux temperature. When the methylenation reaction was complete by TLC analysis, the product was purified by flash chromatography.

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Note Added after ASAP Publication. The version published May 9, 2008 contained errors in the last column of Table 1. The corrected version was published May 27, 2008.

Supporting Information Available: Characterization data and spectra (^1H and ^{13}C NMR) for new compounds and details of the X-ray diffraction study. This material is available free of charge via the Internet at http://pubs.acs.org.

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