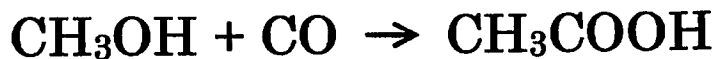
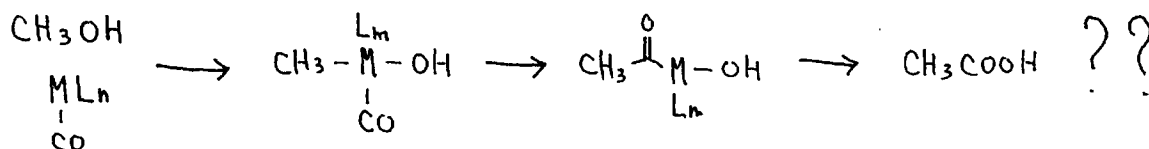


Iridium/iodide-Catalyzed Methanol Carbonylation

Mechanistic Studies of the Cativa Process



At a glance, this reaction is very simple and easy.



But is it true?? This seminar introduces the Concept which overcomes problems of this reaction.

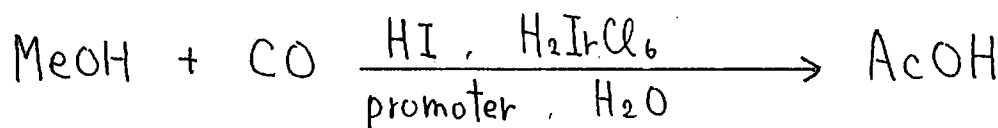
① Introduction

Acetic acid is used primarily as a raw material for vinyl acetate and acetic anhydride synthesis, and as a solvent for purified terephthalic acid. It is also used as a raw material for dyes, drugs, and so on.

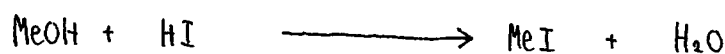
At present, industrial processes for the production of acetic acid are dominated by methanol carbonylation and the oxidation of acetaldehyde or of hydrocarbons. Nowadays, approximately 60% of the total world acetic acid manufacturing capacity is covered by the carbonylation of methanol catalyzed by Rh and Ir.

Rh-catalyzed process is called "Monsanto process". And Ir-catalyzed process is "Cativa Process". Cativa process has the advantage of no precipitation of IrI₃. By contrast, the precipitation of RhI₃ at low pCO can be problematic in the product purification stage.

• Overall reaction of Cativa Process



- H₂IrCl₆ is added as a catalyst precursor and is converted into catalyst in the rxn solution.
- promoter = [Ru(CO)₄I₂], [Os(CO)₄I₂], ZnI₂, InI₃ ... etc.
- HI is added in order to convert MeOH into MeI.



© Mechanistic studies

J|A|C|S

ARTICLES

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Promotion of Iridium-Catalyzed Methanol Carbonylation: Mechanistic Studies of the Cativa Process

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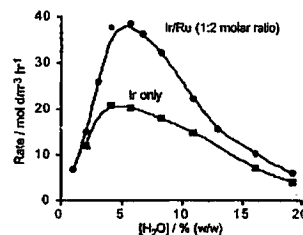


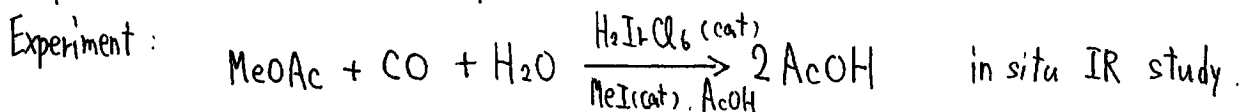
Figure 1. Batch autoclave data* for iridium and iridium/ruthenium catalytic effect of water concentration on carbonylation rate at ca. 30% (w/w) MeOAc, 8.4% (w/w) MeI, 1950 ppm Ir, 28 barg total pressure, and 190 °C. The data plotted are listed in the Supporting Information (Table S1).

Experimental results previously reported

- ① Dependence on a range of process variables such as pCO, [MeI], [MeOAc] and [H₂O]
 - ✓ strong positive dependence on [MeOAc]
 - ✓ zero order in [MeI] above a threshold.
 - ✓ independence of pCO above ca. 10 bar
 - ✓ maximum activity is achieved at ca. 5% w/w H₂O
- ② (i) carbonyl or halocarbonyl complexes of W, Re, Ru and Os
(ii) iodide of Zn, Cd, Hg, Ga and In
enhance the activity of the catalyst.
- ③ By contrast, LiI and Bu₄NI are Catalytic poisons.
- ④ Rate determining step involves the dissociative Substitution of I⁰ by CO from Ir catalyst followed by migratory CO insertion.

Additive	Additive:Ir mole ratio	Carbonylation rate / mol dm⁻³ h⁻¹ / 22 barg
None	-	8.2
[Ru(CO)₂I₂]	5:1	21.6
IbI₃	5:1	14.8
[Os(CO)₂I₂]	5:1	18.6
[Re(CO)₃I]	5:1	9.7
[W(CO)₆]	5:1	9.0
ZnI₂	5:1	11.5
CdI₂	5:1	14.7
HgI₂	5:1	11.8
GaI₃	5:1	12.7
LiI	2:1	2.5
LiI	5:1	very slow
Bu₄NI	1:1	2.7

o Purpose: What is the active catalyst?



Results:

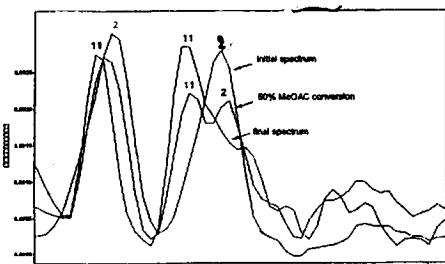
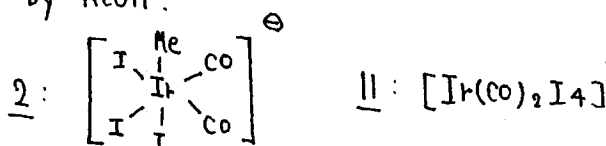
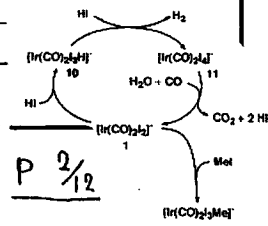


Figure S1 In situ FTIR spectra from a batch carbonylation run with an Ir-only catalyst. Assignments of bands to complex 2 ([Ir(CO)₂I₂Me]) and 11 ([Ir(CO)₂I₄]) are indicated.

* MeOAc was used as a substrate because standing concentration of MeOH is low due to esterification by AcOH.



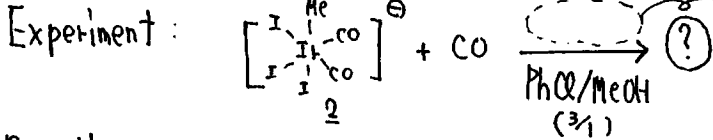
Complex	$\nu(\text{CO})$ / cm⁻¹	NMR Solvent	$\delta^1\text{H}$, J/Hz	$\delta^1\text{H}$, J/Hz
2a (reactant)	2093	CD₂Cl₂	2.14 (d, CH₃), $^1\text{J}_{\text{H-C}}$ 138.9	-16.1 (s, CH₃)
	2040			156.2 (s, CO)
		CD₃OD	2.09 (d, CH₃), $^1\text{J}_{\text{H-C}}$ 139.1	-16.0 (s, CH₃)
		CD₂Cl₂		156.1 (s, CO)



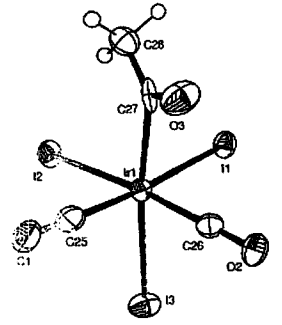
P 2/2

Conclusion: 2 seems to be "active" catalyst?

• Purpose: What is 2 converted into?



in the absence of promoter.



Results:

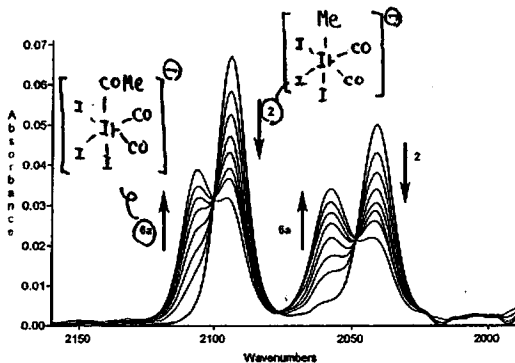
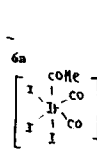


Fig. 4 Series of IR spectra recorded in situ during the reaction of 2 with CO (5.5 barg) in PhCl-MeOH (1:1 v/v) at 33 °C.



$\nu(\text{CO})$, cm^{-1}	solvent	$\delta^1\text{H}$, J/Hz
2105	CD ₂ Cl ₂	3.06 (d, COCH ₃)
2057		$J_{\text{H-C}}$ 130.1, $J_{\text{H-Fe}}$ 5.9
1670b	CD ₂ OD	3.03 (d, COCH ₃)
		$J_{\text{H-C}}$ 130.4, $J_{\text{H-Fe}}$ 5.9

6a $\delta^{13}\text{C}$, J/Hz

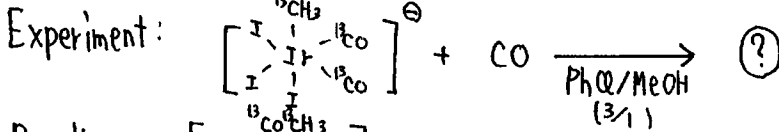
50.0 (d, COCH ₃)
198.7 (d, COCH ₃), $J_{\text{C-Fe}}$ 34.7
152.1 (s, CO)
49.9 (d, COCH ₃)
198.1 (d, COCH ₃), $J_{\text{C-Fe}}$ 33.6
151.9 (s, CO)

6a was isolated and analysed by X-ray diffraction.

Conclusion:

2 is converted into 6a on the condition above.

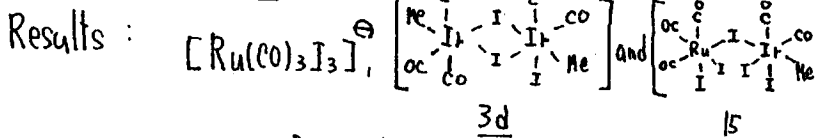
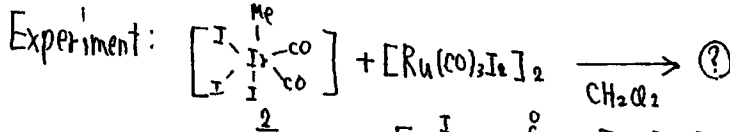
• Purpose: What is the mechanism of conversion from 2 into 6a?



Results:
$$\left[\begin{array}{c} \text{I} \\ | \\ \text{I} - \text{Ir} - \text{CO} \\ | \quad | \\ \text{I} \quad \text{I} \\ \text{CO} \end{array} \right]^-$$
; $^1\text{J}_{\text{C-C}}$ doublets in the ^{13}C NMR spectra were observed.

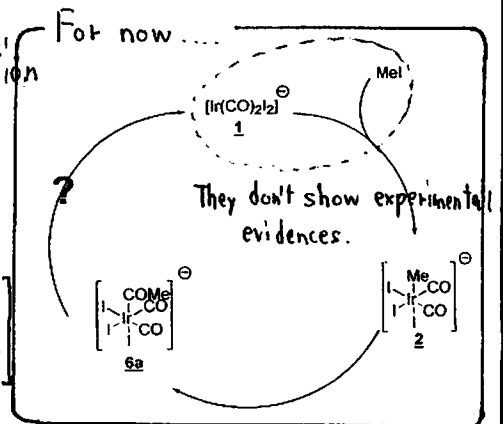
Conclusion: the methyl group migrates to a CO ligand already coordinated to Ir in 2.

• Purpose: What does promoter do in the carbonylation of 2?



were formed.

$\nu(\text{CO})$, cm^{-1}	solvent	$\delta^1\text{H}$, J/Hz	$\delta^{13}\text{C}$, J/Hz
2116	CD ₂ Cl ₂	1.94 (d, CH ₃) major.	-5.2 (s, CH ₃) major
2072		$J_{\text{H-C}}$ 138.9	152.4, 150.3, 150.0 (s, CO)
		1.88 (d, CH ₃) minor.	-8.8 (s, CH ₃) minor
		$J_{\text{H-C}}$ 138.9	



15

^{13}C (ppm)	$J(\text{C-H})$ and $J(\text{C-C})$ /Hz
187.1, s; 186.2, d; 155.3, s; -141, s	3.39 (1/2)

J. Chem. Soc., Dalton Trans. 2002, 711

3d was analysed by X-ray diffraction. (next page)

15 wasn't observed when polar solvent (MeCN or MeNO₂) was used, and probably isn't a significant intermediate.

Results: methyl migration in 4 had a substantially lower activation barrier (between 35 and 47 kJ/mol⁻¹).

— Explanation of this result —

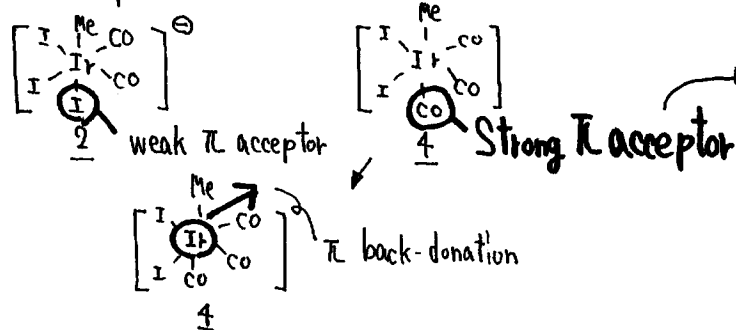


Table 3. Calculated Activation Energies (ΔE^\ddagger) and Reaction Energies (ΔE_{rel}) for Migratory CO Insertion in 2 and 4 and Calculated Reaction Energies (ΔE_{CO}) for Carbonylation of 2 and 4 to Give 6a and 7, Respectively (values in kJ mol⁻¹)

reactant	method	ΔE^\ddagger	ΔE_{rel}	ΔE_{CO}
[Ir(CO) ₂ Me] ⁻ , <u>2</u>	MP2 2DZ*	149.0	46.2	-64.7*
	ADF ⁴⁶	124.7	14.8	
	B3LYP ⁵⁰	117.6	-10.9	
[Ir(CO) ₂ I, Me], <u>4</u>	MP2 2DZ*	102.1	16.4	-58.8*
	ADF ⁴⁶	78.2	-12.2	
	B3LYP ⁵⁰	82.8	-29.3	

* Single-point 2DZ* calculation on 2DZ optimized structures.

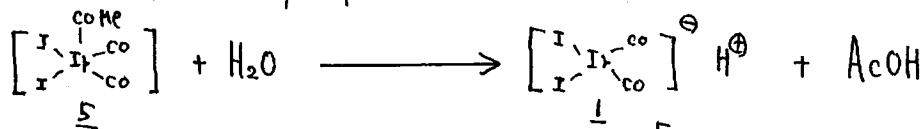
decrease electron density of Ir
 ↓
 make π back-donation weak
 ↓
 raise the electrophilicity of CO ligand
 ↓
 promote methyl migration RR

Conclusion: The pathway that 2 is converted into 7 via 3d, 4 and 5 is faster than the one that 2 is converted into 6a.

◦ Purpose: How does the product (AcOH) form?
 How is the catalytic turnover completed?

Experiment: but they don't show any experimental data and they proposed the mechanism of catalytic turnover without any evidence.

Proposed mechanism: Hydrolysis of 5

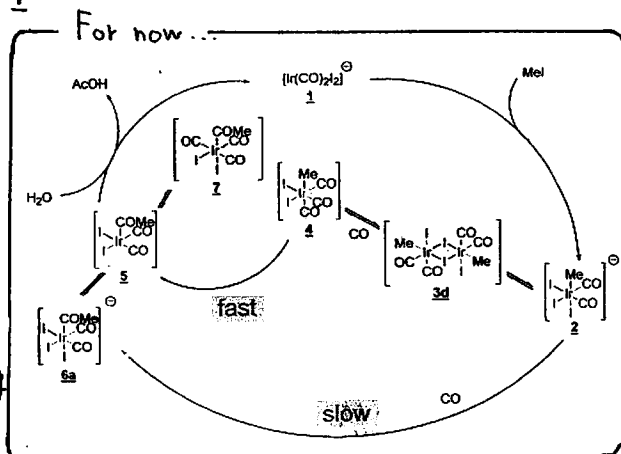
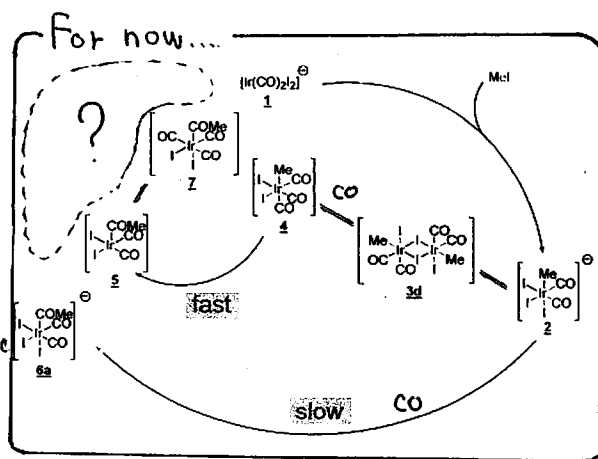


◦ Purpose: What is the role of promoter?

Experiment: MeOAc + CO + H₂O

$\frac{[\text{Ru}(\text{CO})_2\text{I}_2]}{\text{MeI}(\text{cat}), \text{AcOH}} \xrightarrow{\text{IR study}} \frac{\text{H}_2\text{I}_2(\text{cat})}{\text{IR study}}$

* MeOAc was used as a substrate because standing concentration of MeOH would be low due to esterification by AcOH. (page 2)



Results :

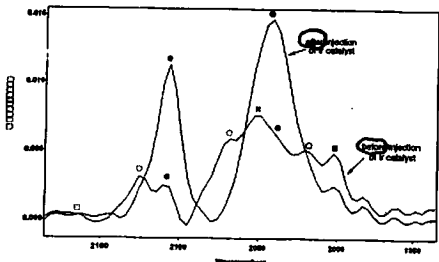
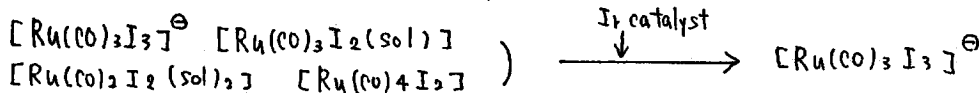


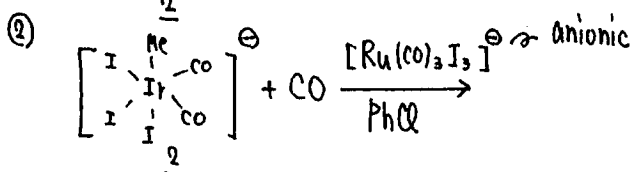
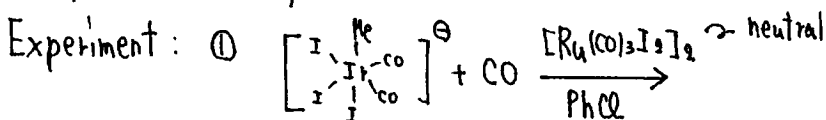
Figure S3 In situ HP-IR spectra from a batch carbonylation run (2:1 Ru: Ir). Assignments of bands are as follows: ● [Ru(CO)₃I₃]⁻; ■ [Ru(CO)₃I₂(sol)]; ○ [Ru(CO)₃I₂(sol)₂]; □ [Ru(CO)₃I₂].

- the bands of Ir species were hindered by strong bands of Ru species (Tot)
- but, it was demonstrated that before the injection of Ir catalyst, Ru promoter was present as a mixture of Ru(II) iodocarbonyl species, and after the injection of Ir catalyst, $[Ru(CO)_3I_3]^-$ became dominant.



Is there any difference between neutral Ru species and anionic Ru species?

• Purpose: Clarify the difference between **neutral** Ru species and **anionic** ones.



Additive	[Ru]/[Ir]	% MeOH v/v	pressure /bar/g	$10^3 k_{app} / h^{-1}$				
				33 °C	80 °C	85 °C	93 °C	108 °C
None			5.5		0.41	1.2	3.6	20
[Ru(CO) ₃ I ₂] ⁻	0.008		5.5			3.8		
[Ru(CO) ₃ I ₂] ⁻	0.027		5.5			12.2		
[Ru(CO) ₃ I ₂] ⁻	0.044		5.5			17.8		
[Ru(CO) ₃ I ₂] ⁻	0.062		5.5			24.3		
[Ru(CO) ₃ I ₂] ⁻	0.078		5.5		20.1	35.4	73.1	215
[Ru(CO) ₃ I ₂] ⁻	0.119		5.5			42.2		
[Ru(CO) ₃ I ₂] ⁻	0.156		5.5			44.1		

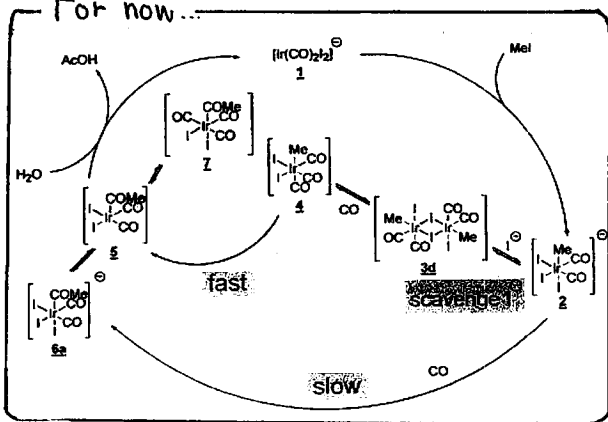
Additive	[Ru]/[Ir]	% MeOH v/v	pressure /bar/g	$10^3 k_{app} / h^{-1}$				
				33 °C	80 °C	85 °C	93 °C	108 °C
None			5.5		0.41	1.2	3.6	20
[Ru(CO) ₃ I ₂] ⁻	0.078		5.5				4	
[Ru(CO) ₃ I ₂] ⁻	0.078		5.5				4	

Results: ① Addition of the **neutral** Ru complex gave substantial rate **enhancement**.

② Addition of the **anionic** Ru complex didn't lead to any appreciable promotion or inhibition.

Conclusion: The ability of **accept an iodide ligand** is a key property of promoter

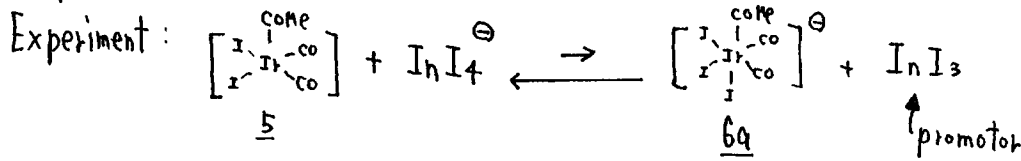
For now...



→ By scavenging I^- from 2, reaction system leads to fast migratory CO insertion pathway (4 → 5).

Where does scavenged I^- go?
 I^- is transferred back to Ir?

• Purpose: Demonstrate that I^\ominus is **not** transferred back to Ir.



(* InI_3 was used as a promoter probably because if Ru complex was used, strong CO bands of Ru complex hindered the bands of 5 or 6a.)

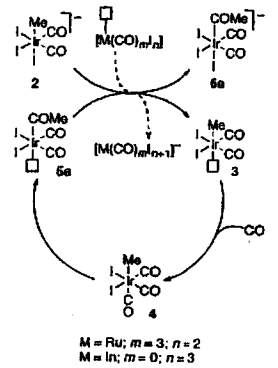
Results: only 5's bands were observed by IR study.

Conclusion: I^\ominus is not transferred back to Ir.

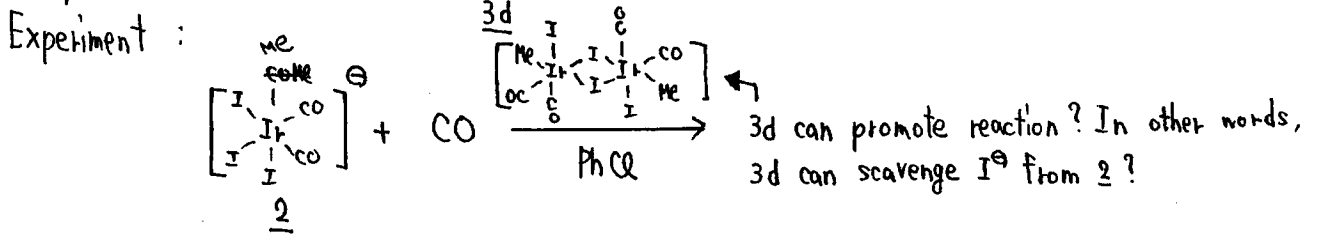


They proposed that I^\ominus could be transferred between Ir centers as shown Scheme 6.

Scheme 6. Mechanism for Promotion of Carbonylation of 2 by Iodide Abstractors



• Purpose: Demonstrate the reasonableness of Scheme 6.



Results:

Table S6 Observed rate constants k_{obs} for carbonylation of 2 in the presence of additives in PhCl.

Promoter	[promoter]/[Ir]	pressure/barg	$10^3 k_{obs}/s^{-1}$								
			80 °C	85 °C	93 °C	108 °C	122 °C				
None	-	5.5	0.41	1.2	3.6	20	140				
<u>InI₃</u>	0.05	5.5			<u>48.9</u>						
<u>InI₃</u>	0.10	5.5	24.4		<u>112</u>	361	688				
<u>InI₃</u>	0.15	5.5			<u>155</u>						
<u>InI₃</u>	0.20	5.5			<u>179</u>						

Promoter	[promoter]/[Ir]	pressure/barg	$10^3 k_{obs}/s^{-1}$							
			80 °C	85 °C	93 °C	108 °C	122 °C			
<u>3d</u>	0.05	5.5			<u>56</u>					
<u>3d</u>	0.10	5.5	26.5	37.4	<u>108</u>	396				
<u>3d</u>	0.15	5.5			<u>185</u>					
<u>3d</u>	0.20	5.5			<u>221</u>					

Conclusion: I^\ominus is transferred between Ir centers. In this scenario, the additives (InI_3 or $[\text{Ru}(\text{CO})_3\text{I}_2]_2$) behave more like an initiator.



Then, where I^\ominus scavenged by additives is transferred?

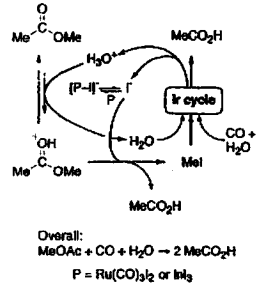


Considering of the content of reaction mixture, counteraction of the additives would be $\text{H}_3\text{O}^\oplus$. ex. $[\text{Ru}(\text{CO})_3\text{I}_3]^\ominus \text{H}_3\text{O}^\oplus$, $\text{InI}_4^\ominus \text{H}_3\text{O}^\oplus$



They proposed that these species can act as Brønsted acid catalysts for the reaction of HI with MeOAc. (Scheme 8)

Scheme 8. Catalytic Cycle for Ionic Iodide, Showing Acid-Catalyzed Mechanism for Activation of Methyl Acetate*



They couldn't show the direct evidence of this proposal, but they show an observation which backs up it.

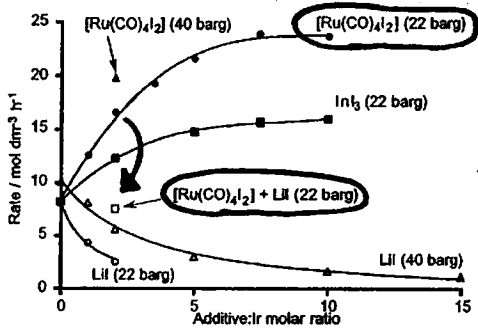
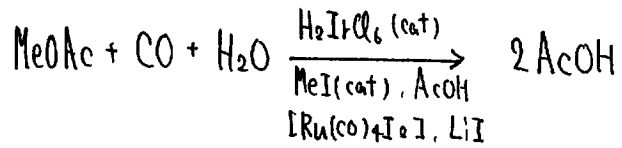


Figure 2. Batch autoclave data: effect of $[\text{Ru}(\text{CO})_4\text{I}_2]$, IrI_3 , and LiI on carbonylation rate (190°C , 1500 rpm). Total pressures 22 and 40 barg correspond to CO partial pressures 7.5 and 25.5 bar, respectively. Autoclave charge: MeOAc (648 mmol), H_2O (943 mmol), AcOH (1258 mmol), MeI (62 mmol), H_2IrCl_6 (1.56 mmol) plus additive if required. Carbonylation rate measured at 50% conversion of MeOAc .

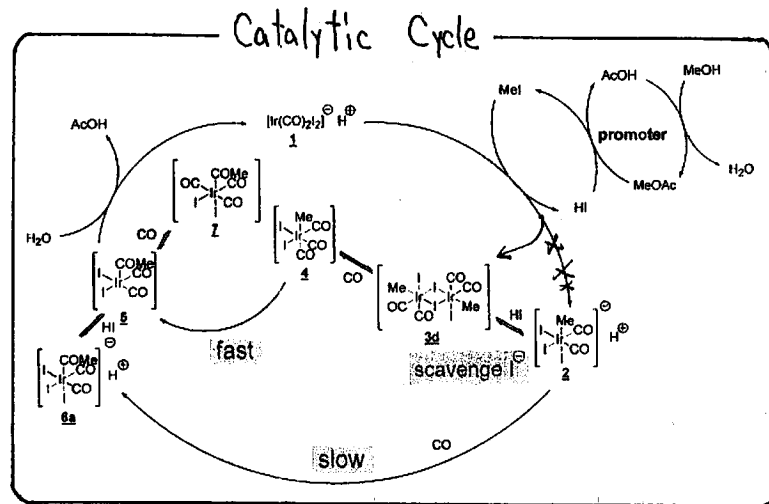
Experiment:



Results: promotional effect of $[\text{Ru}(\text{CO})_4\text{I}_2]$ was negated by an equimolar quantity of LiI . (← equivalent to addition of $[\text{Ru}(\text{CO})_3\text{I}_3] \text{Li}^+$)

Conclusion: H_3O^+ as a counteraction of promoter species appears to be crucial to obtain above normal carbonylation rates.

At last, catalytic cycle was completed.



~ key concept ~

- ① Scavenge I^- with metal complexes.
- ② Metal complexes can act as Brønsted acids.

Halocarbon as a ligand of Ir complex
Iridium Complexes of Some Halocarbons and the Crystal and Molecular Structure of *cis,trans*-[IrH₂(o-C₆H₄I₂)(PPh₃)₂]BF₄

Robert H. Crabtree,* J. W. Faller,* Michelle F. Mellea, and Jennifer M. Quirk
 Department of Chemistry, Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06511

organometallics 1982, 1, 1361

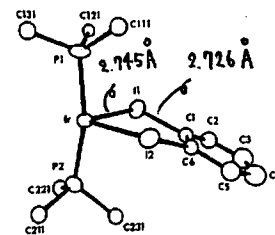
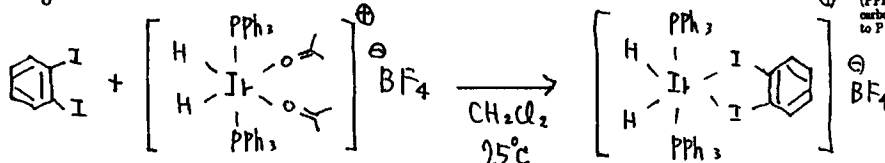


Figure 1. An ORTEP diagram of the core of the [IrH₂(o-C₆H₄I₂)(PPh₃)₂]⁺ cation. The hydrogen ligands were not located, and carbon atoms of the C₆H₄ groups other than the one directly bound to P have been omitted for clarity.

cf. [Ir(p-OMeC₆H₄)₂(PPh₃)₂]⁺ [Ir(PPh₃)₂]⁺
 2.786 Å
 [Ir(CO)(Me)₂]⁺ [Ir-I] I]₂
 Ir-I = 2.694 Å, Ir-(μ-I) = 2.710 Å

- The bond distances are in the same range as the corresponding bonds to iodide in other Ir complexes.
- But ligand is bound **relatively weakly**. For example, they can all be displaced by MeCN.

Unusually Mild and Selective Hydrocarbon C-H Bond Activation with Positively Charged Iridium(III) Complexes

Bruce A. Arndtsen and Robert G. Bergman*

Science 1995, 270, 1970

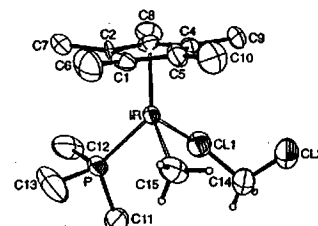
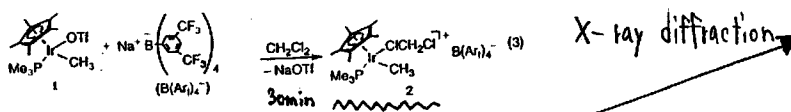
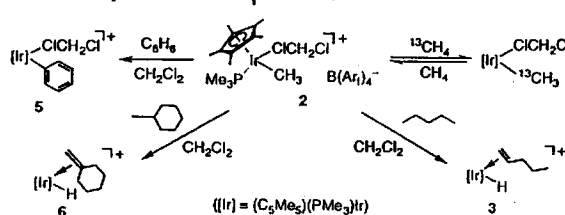


Fig. 1. An ORTEP diagram of complex 2 (borane counterion removed for clarity). Selected bond lengths and angles: Ir-P: 2.276 (3) Å; Ir-Cp: 1.857 Å; Ir-C(15): 2.105 (12) Å; Ir-C(1): 2.462 (3) Å; C(1)-C(14): 1.820 (15) Å; C(14)-C(2): 1.730 (15) Å; P(1)-Ir-C(15): 85.4 (3)°; P(1)-Ir-C(1): 88.97 (13)°; C(15)-Ir-C(1): 92.2 (4)°; C(1)-C(14)-C(2): 110.7 (8)°.

reactivity of complex 2



The high activity of 2 is due to the **lability of the CH₂Cl₂ ligand**, whose dissociation allows access to the 16-electron Ir cation.

Fig. 2. Alkane and arene C-H bond activation by 2.

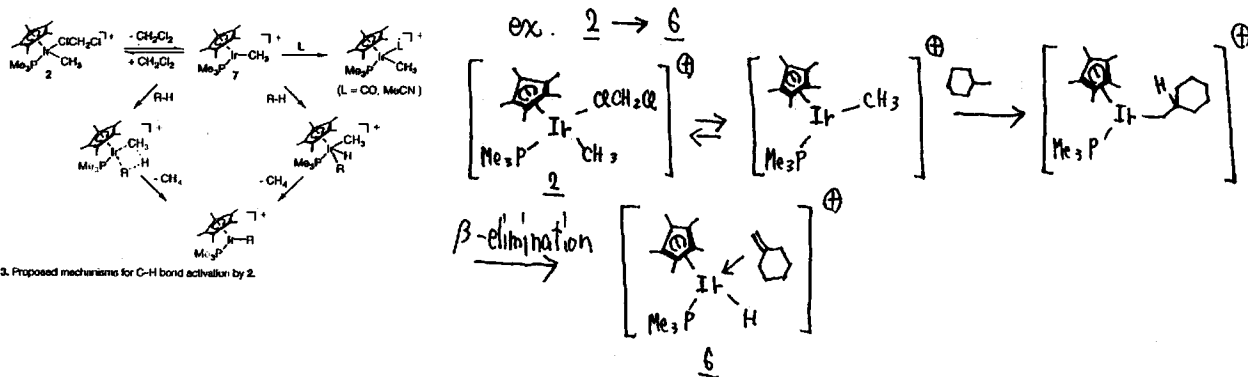
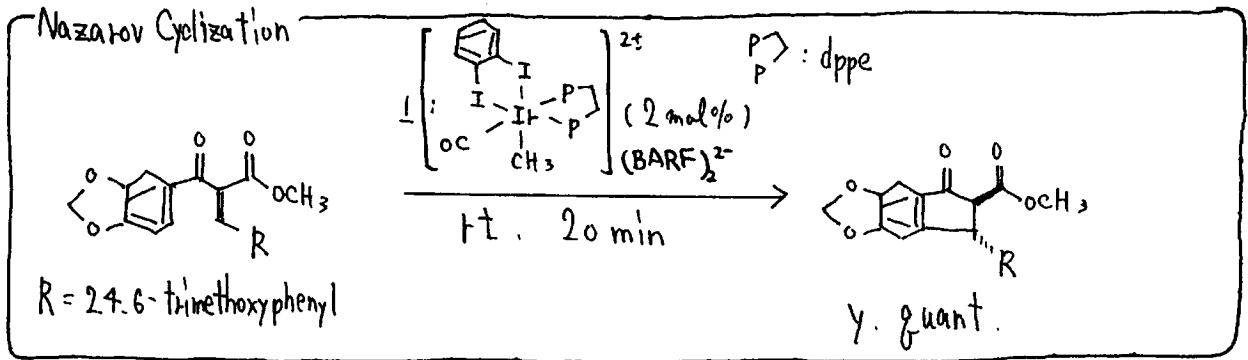


Fig. 3. Proposed mechanisms for C-H bond activation by 2.

Efficient Catalysis of Nazarov Cyclization Using a Cationic Iridium Complex Possessing Adjacent Labile Coordination Sites

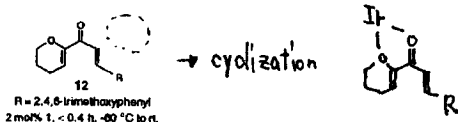
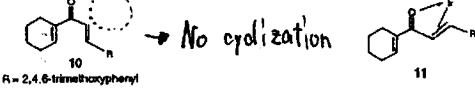
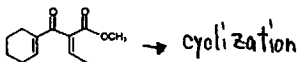
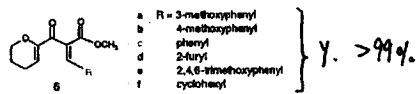
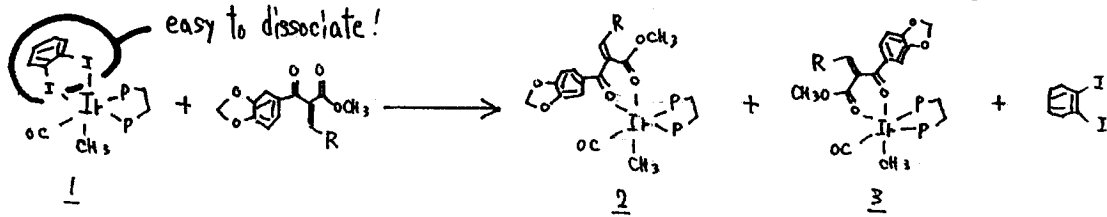
Mesfin Janka, Wei He, Alison J. Frontier,* and Richard Eisenberg*
Department of Chemistry, University of Rochester, Rochester, New York 14627

- Nazarov Cyclization -
protic or Lewis acid-promoted 4π-electrocyclization
that can convert divinyl ketones into cyclopentenones.

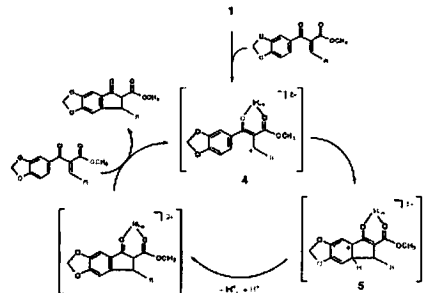


• Cationic Ir(III) complex possesses **electrophilic** character. But its configuration in a **d⁶ hexacoordinate** environment confers **inertness** on its cationic complexes.

Weak coordinating ability of the provides adjacent labile sites



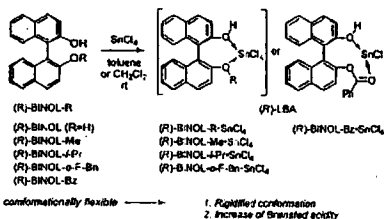
proposed mechanism



© Metal Complex as Brønsted Acid

Chiral Proton Donor Reagents: Tin Tetrachloride—Coordinated Optically Active Binaphthol Derivatives

HIDEAKI ISHIBASHI, KAZUAKI ISHIHARA, HISASHI YAMAMOTO
Graduate School of Engineering, Niigata University, SORST, Japan Science and Technology Corporation (JST), Furo-cho, Chikusa, Niigata 464-8603, Japan.

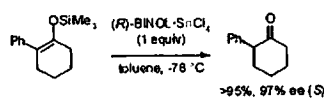


Scheme 1.

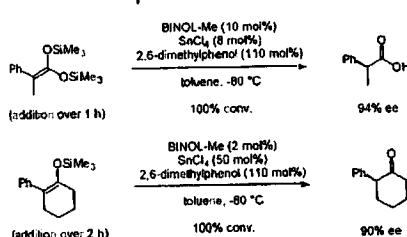
← Lewis acid-assisted chiral Brønsted acids (chiral LBAs)
The coordination of a Lewis acid to Brønsted acid would restrict the direction of the proton and increase its acidity.

① Enantioselective protonation of silyl enol ethers and ketene disilyl acetals.

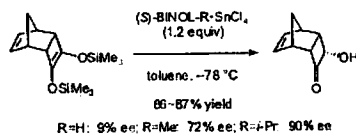
• stoichiometric version



• catalytic version

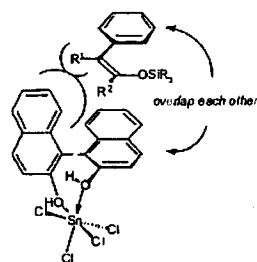


← Catalytic version was achieved by using 2,6-dimethylphenol as a proton source.

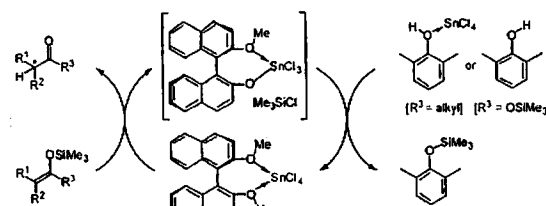


Scheme 3.

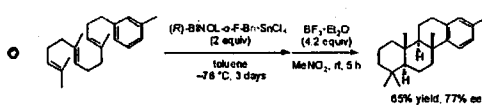
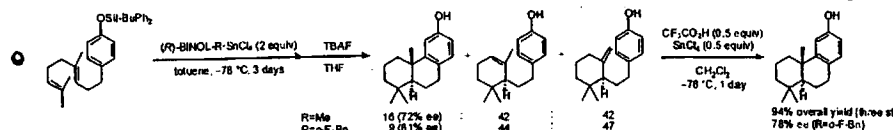
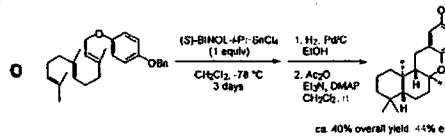
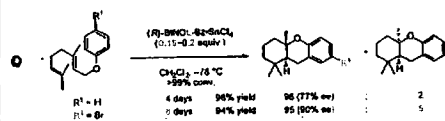
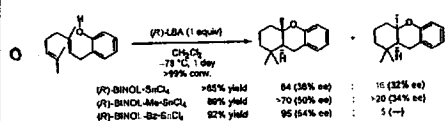
↓ transition state assembly



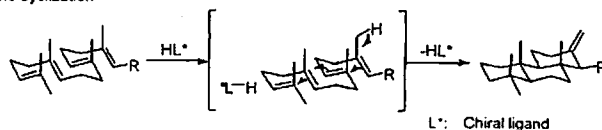
↓ catalytic cycle



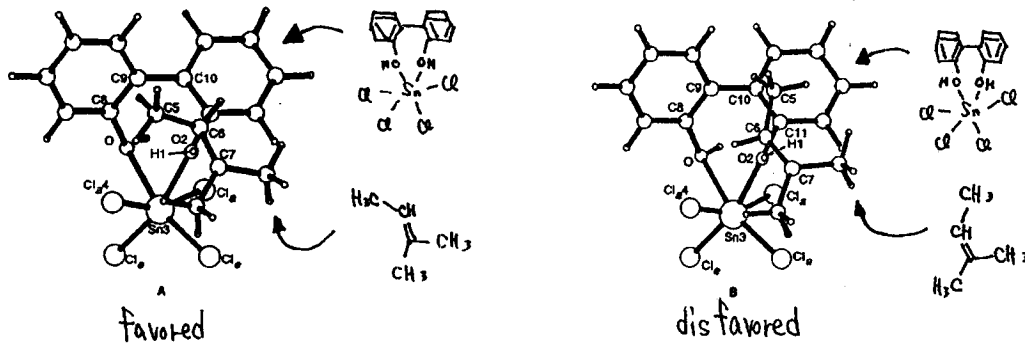
② Enantioselective polyene cyclization



Stork-Eschenmoser hypothesis - Ene Cyclization



• computational optimized structure of biphenol-SnCl₄ complex with 2-methyl-2-butene



③ Recent works

The Crystallographic Structure of a Lewis Acid-Assisted Chiral Brønsted Acid as an Enantioselective Protonation Reagent for Silyl Enol Ethers

Kazuaki Ishihara, Daisuke Nakashima,[†] Yukihiko Hiraiwa,[†] and Hisashi Yamamoto^{*,†}

Graduate School of Engineering, Nagoya University, SORST, Japan Science and Technology Corporation (JST), Furo-cho, Chikusa, Nagoya 464-8603, Japan

J. Am. Chem. Soc. 2003, 125, 24

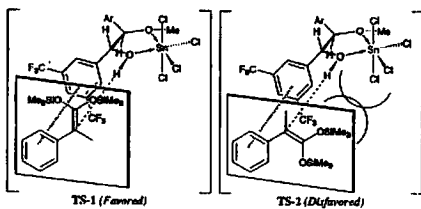
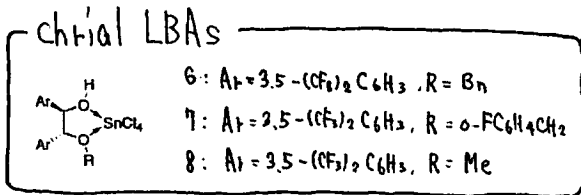


Figure 2. Proposed transition-state assemblies.

Table 2. Enantioselective Protonation of Silyl Enol Ethers or Ketene Disilyl Acetals with (R,R)-LBAs

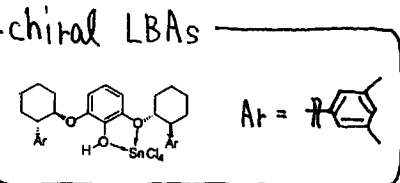
entry	LBA	solvent	product	ee (%) [config.] ^a
1	(R,R)-6-SnCl ₄	CH ₂ Cl ₂	11	83 [S] of 37 [S] ^b
2	(R,R)-7-SnCl ₄	toluene	12	86 [S] → 98 [S] ^c
3	(R,R)-7-SnCl ₄	toluene	13	90 [S]
4	(R,R)-8-SnCl ₄	toluene	14	90 [S]
5	(R,R)-7-SnCl ₄	toluene	15	83 [S]
6	(R,R)-7-SnCl ₄	toluene	16	85 [S]
7	(R,R)-6-SnCl ₄	toluene	17	76 [S] of 37 [R] ^d

^a The ee values were determined by HPLC or GC analysis of ketones or methyl esters derived from carboxylic acids (cat. HCl, (THF)₂ in MeOH).
^b The ee values are indicated when (R)-BINOL derivatives-SnCl₄ were used in toluene.
^c The ee value after recrystallization from a CH₂Cl₂-hexane bilayer system.

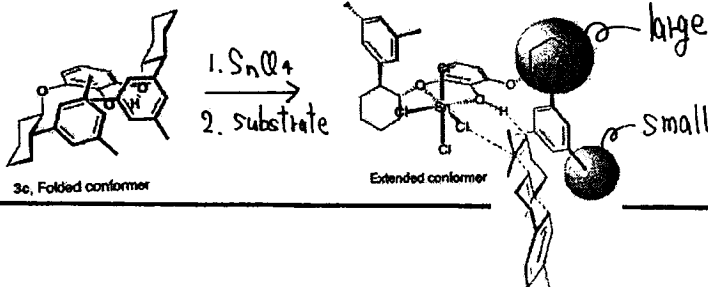
- π-π electronic attractive interaction between a Ph group of the substrate and a 3,5-(CF₃)₂C₆H₃ group closer to the HaCt.
- steric repulsion between Me₃SiO groups and an SnCl₄ or CF₃ group.

Tin(IV) Chloride-Chiral Pyrogallol Derivatives as New Lewis Acid-Assisted Chiral Brønsted Acids for Enantioselective Polyene Cyclization

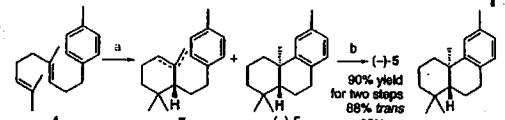
Keiko Kumazawa,[†] Kazuaki Ishihara,^{*,†} and Hisashi Yamamoto^{*,†}



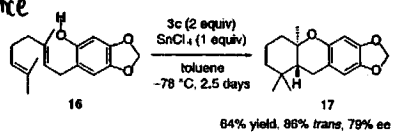
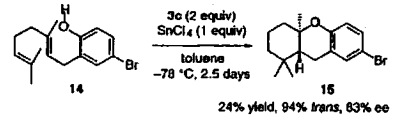
observed absolute stereopreference is due to steric hindrance.



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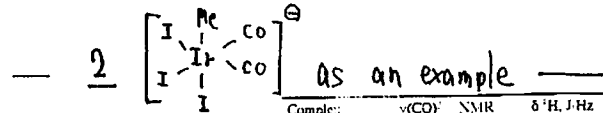


^a Conditions: (a) 3c (2 equiv), SnCl₄ (1 equiv), toluene, -78 °C, 1 day; (b) CF₃CO₂H (10 equiv), SnCl₄ (2 equiv), i-PrNO₂, -78 °C, 1 day.



Appendix

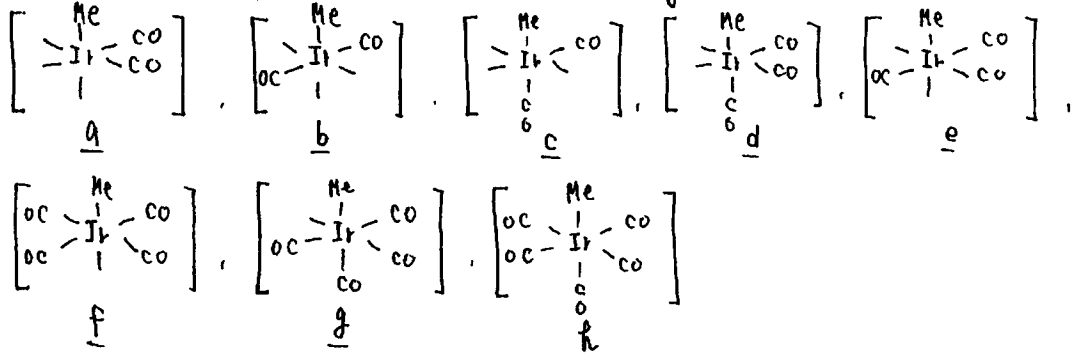
Assignment of intermediates



2

^{13}C NMR -16.1 (s) \rightarrow Me $\left[\begin{array}{c} \text{Me} \\ | \\ \text{I} - \text{Ir} \\ | \\ \text{I} \end{array} \right]$

IR two $\nu(\text{CO})$ bands \rightarrow at least, two CO ligands exist.



^{13}C NMR 156.2 (s) \rightarrow all CO are equivalent because of only one peak is observed.

a, b, f are OK.

IR two $\nu(\text{CO})$ bands \rightarrow a is the right structure.

表 1. CO 伸縮による赤外線吸収バンドの本数と構造との関係 933

錯体	異性体	構造 ¹⁾	点群	吸収バンドの数 ¹²⁾
$\text{M}(\text{CO})_4$			T_d	1
$\text{M}(\text{CO})_4$			C_{4v}	3 ¹³⁾
$\text{M}(\text{CO})_4\text{L}$	trig		D_{3h}	1
$\text{M}(\text{CO})_4\text{L}$	trig		C_{2v}	4 ¹⁴⁾
$\text{M}(\text{CO})_4\text{L}$	mer		C_{2v}	3 ¹⁴⁾
$\text{M}(\text{CO})_4\text{L}$	fac		C_{2v}	2
$\text{M}(\text{CO})_5$			D_{3h}	2
$\text{M}(\text{CO})_5$	アキシャル		C_{4v}	3 ¹⁵⁾
$\text{M}(\text{CO})_5$	エクვაトリアル		C_{2v}	4

表 1-5 (つづき)

錯体	異性体	構造 ¹⁾	点群	吸収バンドの数 ¹²⁾
$\text{M}(\text{CO})_5\text{L}$			D_{3h}	1
$\text{M}(\text{CO})_5\text{L}$			C_{2v}	3
$\text{M}(\text{CO})_5\text{L}$			T_d	1

1) L と結合していない結合を表す位置の空欄には CO が結合している。
 12) CO 伸縮振動数で予測される赤外線吸収バンドの本数は形式的な遷移状態に基づいている。ある場合には、脚注で説明するように、観測される吸収バンドの本数は予想より少なくなる。
 13) 4 個の CO 配位子が金属原子と同一平面上にあれば、吸収バンド数は 2 となる。
 14) トランス位の CO 配位子がほとんど同一平面上にあれば、吸収バンド数は 1 本減る。
 15) 3 個の CO 配位子がほとんど同一平面上にあれば、吸収バンド数は 2 となる。

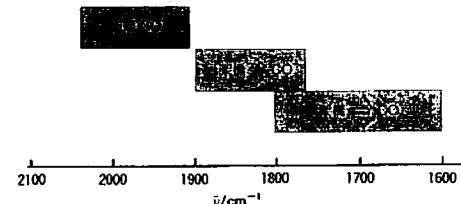


図 16-2 中性の金属カルボニル化合物における CO 伸縮のおよその波数範囲。一般に赤外分光計がスペクトルを表示するやり方に合わせて、高波数(すなわち高振動数)を左側に表示していることに注意せよ。