IRIDIUM COMPLEXES AS HYDROSILYLATION CATALYSTS

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Summary:

Iridium complexes have been found to be active as catalysts for hydrosilylation reactions, especially for those involving 1,3-dienes and 1-alkynes. For ketones, iridium complexes show maximum activity if one molar equivalent (relative to iridium) of triphenylphosphine is added to the reaction mixture. Iridium complexes are also active catalysts for the hydrosilylation of α,β-unsaturated ketones, although the regioselectivity differs from that obtained with rhodium complexes. Attempts at asymmetric hydrosilylation of keto compounds using iridium complexes resulted in extremely low enantiomeric excesses.

Article:

Introduction

In contrast to rhodium compounds, the corresponding iridium complexes have been little studied as hydrosilylation catalysts [1]. This is, undoubtedly, due to the fact that ligand-free complexes of iridium are easily reduced to the metal [2], and that tertiary phosphine supported iridium complexes can undergo oxidative addition with silanes to yield catalytically inactive adducts such as $[IrHCl(SiX_3)(PPh_3)_2]$, I, [3]. The catalytic inactivity of $[IrHCl(SiX_3)(PPh_3)_2]$ is in contrast to the proposed catalytic intermediacy of the corresponding rhodium compound [41].

We have attempted to explore the catalytic activity of iridium complexes using two basic approaches to overcome the difficulties outlined above. Firstly, organic compounds capable of complexing with iridium, such as 1,3-dienes which yield isolable $[IrCl(diene)]_2$ complexes [5], would be expected to be less easily reduced to the metal, and hence hydrosilylated more readily. Secondly, for substrates such as mono-olefins or ketones, which would not be expected to form stable complexes, it would be predicted that addition of an appropriate amount of a stabilizing ligand such as a phosphine would yield an active catalyst, since such ligands are known to stabilize metals in the low oxidation states believed to be present during hydrosilylation reactions [6]. The ratio of P:Ir would, however, have to be below 2:1 to prevent formation of I. In addition to verifying these two concepts, we have investigated the hydrosilylation of α,β-unsaturated ketones and asymmetric hydrosilylation using iridium complexes.

Experimental

General procedures

All reactions were carried out under pure nitrogen, using freshly distilled, dry liquids. Proton NMR spectra were recorded on a Varian Associates T60 spectrometer; infrared spectra were taken with a Perkin-Elmer 457 grating spectrophotometer as thin films.

The GLC analyses of reaction products were carried out on a Varian Aerograph A-700 Autoprep Gas Chromatograph, using a 6 ft column of 10% SE30 on Chromosorb G, with the exception of the 2-cyclohexenone hydrosilylation products where a 20 ft column of 15% SE30 on Chromosorb G was used, employing appropriate internal standards. Preparative GLC separations were carried out on the same machine, using the 20 ft column of 15% SE30 on Chromosorb G. The silanes were purchased or prepared according to

literature methods. The chiral phosphines (+)-DIOP and neomenthyldiphenylphosphine, NMDPP were purchased from Strem Chemicals Inc., and (+)-1-[dimethylaminomethyl]-2-(diphenylphosphino)ferrocene, [(+)-FcNP] was a gift from Dr. W. R. Cullen. Optical rotations were taken on a Perkin-Elmer 241 polarimeter.

Hydrosilylation of cyclohex-2-enone and related systems

Cyclohex-2-enone (4.0 ml, 4.0 g, 41 mmol) was added to $[IrCl(C_8\text{-}H_{14})_2]_2$ (40 mg, 4.5×10^{-2} mmol) in a two-necked flask equipped with a condenser and magnetic stirring bar. The flask was cooled in ice and phenyl-methylsilane (5.8 ml, 5.2 g, 42 mmol) added via a syringe. The mixture was allowed to warm to room temperature and stirred for a further 2 h. A solution of potassium carbonate (20 mg) in 20 ml methanol was added carefully to the reaction mixture, which was then stirred for 1 h. The methanol was distilled off, and GLC analysis of the residue indicated the presence of cyclohex-2-en-1-ol, which was identified by comparison of its GLC retention time with an authentic sample. For systems that produced a mixture of cyclohexanone and cyclohex-2-en-1-ol, the same procedure was followed, and the products were identified by comparison of their GLC retention times with authentic samples, on several different columns. The yields were calculated using internal standards, such as decane or dodecane, based on quantitative standardizations using pure cyclohex-2-en-1-ol and cyclohexanone.

Quantitative reactions

These were carried out as above, but reduced to half the scale. After the hydrolysis with methanol, a GLC standard was added and the yields of cyclohexanone and cyclohex-2-en-1-ol determined by comparison with standardizations obtained using authentic samples.

Attempted asymmetric hydrosilylations

These were all carried out using the same procedure, which will be illustrated for the hydrosilylation of acetophenone by diphenylsilane, using neomenthyldiphenylphosphine, NMDPP.

Neomenthyldiphenylphosphine (32 mg, 9.9×10^{-2} mmol) was dissolved in 1 ml of benzene and $[Ir(1,5\text{-}COD)Cl]_2$ (33 mg, 4.9×10^{-2} mmol) added. The solution was stirred at room temperature for 30 min, and then cooled in ice while a solution of diphenylsilane (3.0 ml, 3.0 g, 16 mmol) and acetophenone (2.0 ml, 2.1 g, 17 mmol) in 5 ml benzene was added. The ice bath was removed and the solution stirred at room temperature overnight. A solution of hydrochloric acid (4 ml 2 M HCl in 20 ml acetone) was added to the reaction mixture to hydrolyze the silyl ether. The layers were separated, the organic layer was dried with calcium sulfate and the solvent removed by vacuum. Distillation of the residue gave 1-phenylethanol (1.5 g, 77%), b.p. 50 °C/1 mmHg, identified by its ^{1}H NMR spectrum. The optical rotation was determined in dichloromethane (*c* 2.27) and was found to be zero. Other phosphines used in an analogous fashion were (+)-DIOP (molar ratio of DIOP:Ir 1:2) (0% enantiomeric excess) and (+)-1-[dimethylaminomethyl]-2-(diphenylphosphino)ferrocene ((+)-FcNP) (1% enantiomeric excess of *S*-alcohol). The asymmetric hydrosilylation of ethyl pyruvate was attempted, using a similar method, with the catalyst systems $[IrCl(COD)]_2$— 2NMDPP and $[IrCl(COD)]_2$-2(+)-FcNP with enantiomeric excesses of 0% and 7% of the (+)-alcohol, respectively.

Other hydrosilylations

These were carried out using standard procedures outlined in the literature [7, 8]. Identification was by isolation and comparison of ^{1}H NMR and IR spectra with those of authentic samples, or by comparison of GLC retention times with those of authentic samples. Quantitative reactions were carried out as outlined, and yields were calculated using an appropriate internal standard.

Results and discussion

1,3-Dienes and 1-alkynes

Organic substrates that are capable of forming stable complexes with iridium and thus preventing its reduction, such as 1-pentyne and 2,3-dimethylbuta-1,3-diene, DMBD, are readily hydrosilylated, especially with triethylsilane, when an essentially ligand-free iridium complex $[IrCl(COE)_2]_2$ (COE = *cis*-cyclooctene), II, is used (Tables 1 and 2). With DMBD the reaction is very regioselective, giving essentially only the 1,4-adduct,

$(CH_3)_2C=C(CH_3)CH_2SiEt_3$, with triethylsilane. This is in contrast to the results reported for some rhodium complexes [7], where a mixture of 1,4-addition and 1,2-addition is reported. This may be rationalized in terms of the accepted mechanism for the hydrosilylation of 1,3-dienes (Scheme 1). The π-a1lyl complex, III, is formed by addition of the oxidative adduct [$HMSiR_3$] (M = metal plus all other ligands) to DMBD. This π-allyl complex may rearrange to the σ-alkenyls IV and V, which will lead to the 1,4-adduct and 1,2-adduct respectively. The formation of the tertiary σ-alkenyl, V, is less likely to be expected with the larger iridium atom, due to steric effects, than with rhodium. This should lead to a relatively larger amount of 1,4-adduct for iridium, in agreement with experimental results, Although the size difference between iridium and rhodium is small, due to the Lanthanide Contraction, the results can best be rationalized by assuming that this difference may be a factor in determining the isomer ratio. The results with alkoxysilanes are poor, and less well-defined. The decrease of catalytic activity on going from alkylsilanes to alkoxysilanes parallels results obtained with rhodium complexes [4]. The greater stability, and hence decreased catalytic activity, of the oxidative adducts of electron-withdrawing silanes, such as alkoxysilanes, with rhodium compounds has been proposed to account for this phenomenon [4]. A similar explanation can be used to rationalize the results with iridium. Addition of triphenylphosphine at a ratio of P:Ir of 1:1 causes the yield to decrease, perhaps due to the steric hindrance of the bulky phosphine. The isomer ratio does not vary, as the isomer favored by a bulky metal center is essentially the only adduct formed.

TABLE 1

Hydrosilylation of 2,3-dimethylbuta-1,3-diene[a]

Catalyst	Silane	Yield of 1:1 adducts[b]	Ratio 1,4:1,2 isomers[c]
$[(COE)_2IrCl]_2$	$HSiEt_3$	95	93:7
$[(COE)_2IrCl]_2 + 2\ PPh_3$	$HSiEt_3$	65	93:7
$[(COE)_2IrCl]_2$	$HSi(OEt)_3$	16	56:44
$[(COE)_2IrCl]_2 + 2\ PPh_3$	$HSi(OEt)_3$	12	53:47
$[(COE)_2IrCl]_2 + 2\ PPh_3$	$HSi(OEt)_2Me$	0	—

[a]COE = cyclooctene; 0.01 g, 1.1×10^{-3} mmol $[(COE)_2IrCl]_2$; 6.3 mmol $HSiEt_3$, or 5.4 mmol $HSi(OEt)_3$, or 6.2 mmol $HSi(OEt)_2Me$; 8.8 mmol DMBD; 60 °C/6 h.
[b]Based on silane, calculated by quantitative GLC.
[c]Isomer ratio estimated by GLC.

TABLE 2

Hydrosilylation of pent-1-yne by $[(COE)_2IrCl]_2$[a]

$PrC{\equiv}CH + HSiEt_3 \xrightarrow{60°C/6\ h}$ *cis*- and *trans*-$PrCH{=}CHSiEt_3$

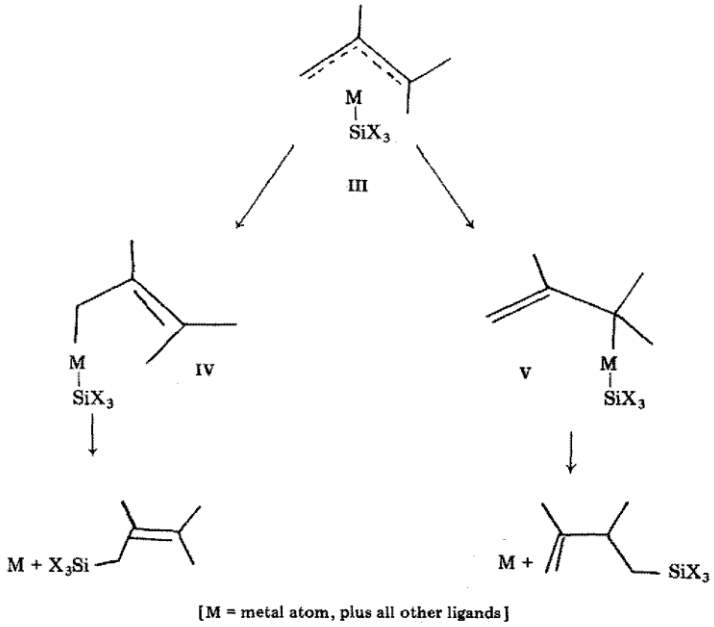
Catalyst	Yield of pent-1-enylsilanes[b]	Isomer ratio[c]		
		trans	*cis*	other
$[(COE)_2IrCl]_2$	76	16	83	1
$[(COE)_2IrCl]_2 + 2\ PPh_3$	100	30	70	0
$[(COE)_2IrCl]_2 + P(o\text{-}C_6H_4OMe)_3$	62	17	77	6

[a]COE = cyclooctene; 0.01 g, 1.1×10^{-3} mmol $[(COE)_2IrCl]_2$; 6.3 mmol $HSiEt_3$; 10 mmol $C_3H_7C{\equiv}CH$.
[b]Based on silane; calculated by GLC.
[c]Isomer ratio estimated by GLC.

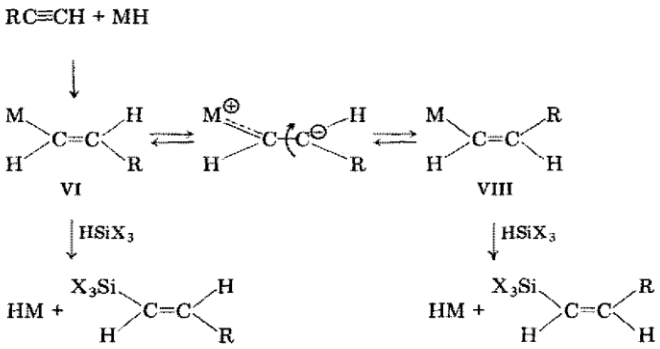
Iridium complexes yield a mixture of *cis*- and *trans*-1-triethylsilylpent-1-enes from the hydrosilylation of pent-1-yne by triethylsilane. Like $[RhCl(COE)_2]_2$, which also gives a mixture of the two pentenes with a *cis:trans* ratio of 61:29 [8], $[IrCl(COE)_2]_2$ gives a similar *cis:trans* ratio of 84:16 under the same conditions. This may be rationalized in terms of the mechanism proposed for rhodium catalysts [8] (Scheme 2). The small size differences between rhodium and iridium would not be expected to be so important for σ-alk-1-enyls such as *cis*- and *trans*-M—CH=CHR, (Scheme 2), as for the σ-alkenyls proposed as intermediates for the hydrosilylation of DMBD. Use of a catalyst system involving the good donor ligand, $P(o\text{-}C_6H_4OMe)_3$, does not alter the isomer ratio, in contrast to the rhodium systems where an increase in *cis*-pent-1-enes was observed. The origins of this effect are obscure. In all the iridium-catalyzed reactions, small amounts (2-5%) of a third isomer were formed and, as in the rhodium case, this was tentatively assigned as 1-triethylsilylpent-2-ene, based on comparison of its GLC retention time with an authentic sample. This third isomer could be formed by isomerization of the initially-formed internal adducts [8].

Ketones and olefins

The effect of addition of a ligand such as triphenylphosphine to the a weakly coordinating substrate such as cyclohexanone (Table 3). With no added ligand, a modest yield of the 1:1 adduct is formed; this yield may be increased by addition of triphenylphosphine at a P:Ir ratio of 1:1. Presumably, as outlined in the introduction, the triphenylphosphine is able to stabilize the catalyst system and allows more efficient hydrosilylation. However, if a P:Ir ratio of 2:1 is used, the system ceases to be a catalyst for this reaction, due to the formation of the catalytically inert adduct $[IrHCl(SiEt_3)(PPh_3)_2]$.



Scheme 1. Proposed mechanism for the hydrosilylation of 2,3-dimethylbuta-1,3-diene (DMBD) [12].



Scheme 2. Proposed mechanism for the hydrosilylation of 1-alkynes [8].

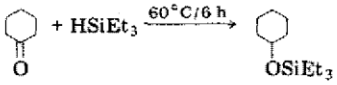
The utility of iridium-based catalysts for the hydrosilylation of 1-olefins is poor. Even the addition of phosphines does not increase the activity noticeably (Table 4).

α, β-Unsaturated ketones

Ojima *et al.* [9] have reported the hydrosilylation of α, β-unsaturated carbonyl compounds catalyzed by Wilkinson's compound. Hydrosilylation can occur in a 1,2- or 1,4-mode, illustrated below for cyclohex-2-enone, eqn. (1). Methanolysis of the silyl ethers leads to an allylic alcohol from 1,2-addition, and to the ketone via the enol from 1,4-addition. This reduction can be extremely regioselective; for example, the hydrosilylation of mesityl oxide by $HSiEt_3$ yields exclusively the 1,4-adduct, whereas $PhSiH_3$ yields exclusively the 1,2-adduct [9].

TABLE 3

Hydrosilylation of cyclohexanone catalyzed by $[(COE)_2IrCl]_2$ [a]



Catalyst	Yield[b] (%)
$[(COE)_2IrCl]_2$	64
$[(COE)_2IrCl]_2 + 2\ PPh_3$	76
$[(COE)_2IrCl]_2 + 4\ PPh_3$	2

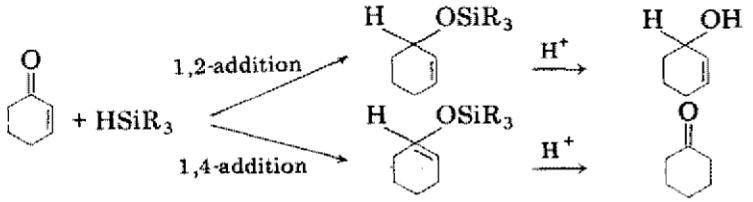
[a] COE = cyclooctene; 0.010 g, 1.1×10^{-3} mmol $[(COE)_2IrCl]_2$; 6.3 mmol $HSiEt_3$; 9.7 mmol cyclohexanone.
[b] Based on silane; calculated by GLC

TABLE 4

Hydrosilylation of oct-1-ene using $[(COE)_2IrCl]_2$ [a]

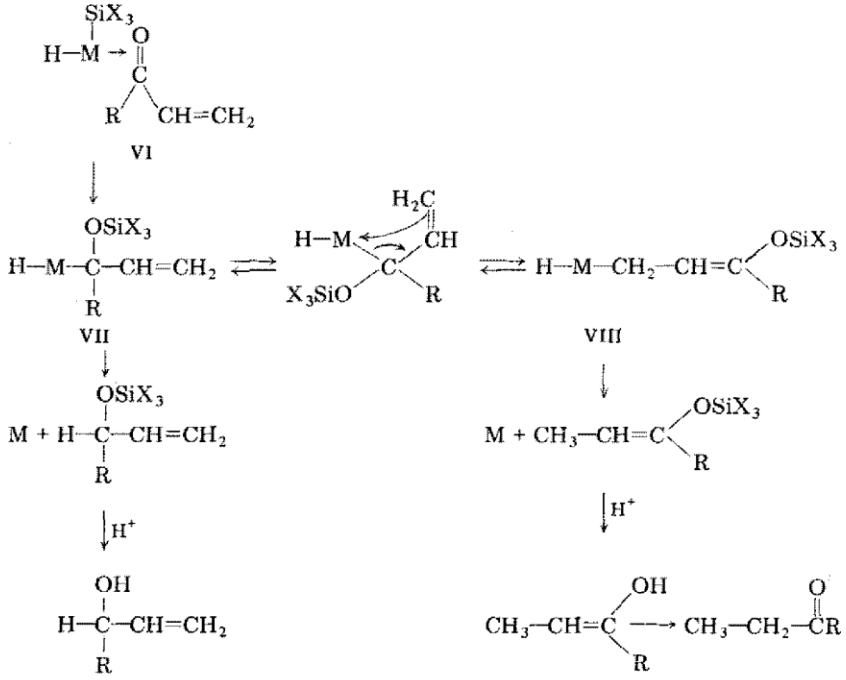
Catalyst	Silane	Temp/Time (°C) (h)	Yield of 1-octylsilane[b] (%)
$[(COE)_2IrCl]_2 + 2\ PPh_3$	$HSiEt_3$	60/6	30
$[(COE)_2IrCl]_2 + 2\ PPh_3$	$HSiEt_3$	100/6	23
$[(COE)_2IrCl]_2 + 2\ P(o\text{-}C_6H_4OMe)_3$	$HSiEt_3$	100/6	25
$[(COE)_2IrCl]_2 + 2\ PPh_3$	$HSi(OEt)_3$	100/6	4
$[(COE)_2IrCl]_2$	$HSiMe_2Ph$	60/6	18
$[(COE)_2IrCl]_2 + 2\ PPh_3$	$HSiMe_2Ph$	60/6	0

[a] COE = cyclooctene; 0.010 g, 1.0×10^{-3} mmol $[(COE)_2IrCl]_2$; 6.3 mmol $HSiEt_3$, or 5.4 mmol $HSi(OEt)_3$, or 6.5 mmol $HSiMe_2Ph$; 6.4 mmol 1-octene.
[b] Based on silane; calculated by quantitative GLC.



(1)

The mechanism proposed to explain this regioselectivity [9] is outlined in Scheme 3. The intermediate, VI, formed by coordination of the α,β-unsaturated ketone to the adduct formed by oxidative addition of the silane, undergoes a silicon migration from the metal to the carbonyl oxygen of the unsaturated ketone to give the a-siloxyalkenylmetal hydride, VII. This is a logical extension of the mechanism proposed for the hydrosilylation of saturated ketones [10], which has been supported by spin-trapping experiments [11]. The adduct VII can rearrange to the adduct VIII. VII will yield the 1,2-adduct (allylic alcohol, after methanolysis), whereas VIII will yield the 1,4-adduct (ketone, after methanolysis). The rate of isomerization of VII to VIII will be determined by the steric bulk of the silane. A large silane will destabilize the adduct VII due to steric hindrance with the metal center, and increase the rate of formation of VIII and hence the amount of 1,4-adduct. Thus, the results with Wilkinson's compound can be explained. The more bulky triethylsilane causes rapid isomerization of VII to VIII and formation of the 1,4-adduct (ketone), whereas with the less bulky phenylsilane, VII does not rearrange and the sole product is the 1,2-adduct (allylic alcohol).



[M = metal atom, plus all other ligands]

Scheme 3. Proposed mechanism for the hydrosilylation of α,β-unsaturated ketones [9].

$[Ir(COE)_2Cl]_2$ and $[Ir(COD)Cl]_2$ (COE = *cis*-cyclooctene; COD = *cis, cis*-cycloocta-1,5-diene) are also excellent catalysts for this type of reaction, and our results are summarized in Table 5. The results may be easily accommodated by Scheme 3. For example, with $C_6H_5(CH_3)SiH_2$ and cyclohex-2-enone the reaction is quantitative and selective, giving only the 1,2-adduct (allylic alcohol). According to the proposed mechanism, the iridium complex, which does not have the bulky PPh_3 ligands present in Wilkinson's compound, should exhibit reduced steric repulsion *between* the coordinated ligands (in VII), effectively preventing the isomerization to VIII. Therefore, only the 1,2-adduct would be expected. In the reaction of Et_3SiH and cyclohex-2-enone catalyzed by $[Ir(COE)_2Cl]_2$, the yield is quantitative but the selectivity is lower, and different, from that reported for catalysis by Wilkinson's compound. Wilkinson's compound gives only 1,4-adduct in similar reactions; however, with the ligand-free iridium complex the rate of isomerization of VII to VIII would also be lessened for the bulkier Et_3SiH, and hence a larger amount of 1,2-adduct would be expected, as is found. In accord with this rationale, the use of $[Ir(COE)_2Cl]_2$-$2PPh_3$, (more sterically crowded about the iridium) yields more of the ketone (1,4-adduct).

TABLE 5

Hydrosilylation of α, β-unsaturated ketones[a]

Catalyst[b]	Ketone	Silane	Temperature (°C)	Yield[c] (%)	Ratio of alcohol: ketone[c]
$[Ir(COE)_2Cl]_2$	cyclohex-2-enone	$HSiEt_3$	25	100	76:24
$[Ir(COE)_2Cl]_2$	cyclohex-2-enone	$HSiEt_3$	60	42	69:31
$[Ir(COE)_2Cl]_2$ + 2 PPh_3	cyclohex-2-enone	$HSiEt_3$	60	77	39:61
$[Ir(COD)Cl]_2$	cyclohex-2-enone	$HSiEt_3$	25	40	73:27
$[Ir(COE)_2Cl]_2$	cyclohex-2-enone	$H_2SiMePh$	25	90	100:0
$[Ir(COE)_2Cl]_2$ + 2 PPh_3	cyclohex-2-enone	$H_2SiMePh$	25	94	59:41
$[Ir(COD)Cl]_2$	cyclohex-2-enone	$H_2SiMePh$	25	56	100:0
$[Ir(COE)_2Cl]_2$	mesityl oxide	$HSiEt_3$	25	100	75:25

[a] 2.0 g, 2.1×10^{-2} mol cyclohexenone added to 20 mg, 2×10^{-5} mol catalyst, followed by 2.1×10^{-2} mol of silane. Reacted for 2 h, then a solution of 10 mg K_2CO_3 in 5 ml methanol added and allowed to react for 1 h.
[b] COE = cyclooctene; COD = cycloocta-1,5-diene.
[c] Calculated by quantitative GLC.

Asymmetric hydrosilylation

The asymmetric hydrosilylation of keto compounds such as acetophenone or ethyl pyruvate was also attempted using a $[Ir(COD)Cl]_2$-2L catalyst system (L = chiral phosphine such as neomenthyldiphenylphosphine, (+)-DIOP, or (+)-1-(dimethylaminomethyl)-2-(diphenylphosphino)-ferrocene, (+)-FcNP). The chemical yields were satisfactory, but the optical yields were extremely low, reaching a maximum of 7% enantiomeric excess (see Experimental Section). These are much lower than those obtained with rhodium, perhaps due to the fact that with iridium we were limited to a P:Ir ratio of 1:1 (as we have shown that catalytic activity ceases at ratios of P:Ir of 2:1), whereas the high optical yields obtained with rhodium involved ratios of P:Rh of 2:1 and greater.

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