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Inhibiting deactivation of iridium catalysts with bulky substituents on coordination atoms

Duo-Sheng Wang [a], Juan Zhou [b], Da-Wei Wang [a], Yin-Long Guo [b,*], Yong-Gui Zhou [a,b,*]

[a] State Key of Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China
[b] Shanghai Mass Spectrometry Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

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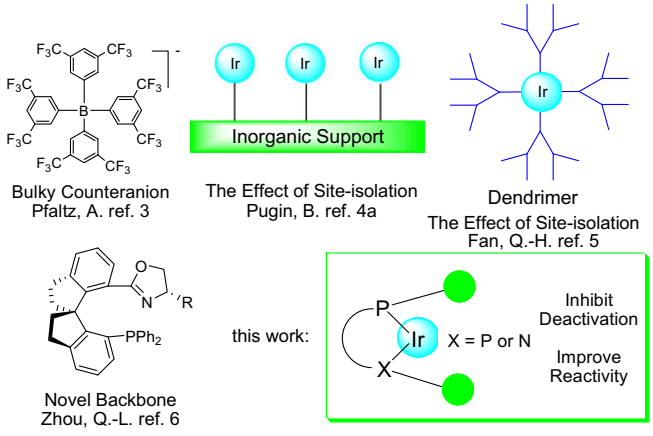
ABSTRACT

Introducing bulky groups on the coordination phosphorus atoms can effectively block the formation of inactive dimer species and improve the activity of the iridium catalysts. Results of ESI-MS analysis gave strong evidence. This strategy was successfully applied to the asymmetric hydrogenation of quinolines with up to 93% ee on S/C ratio of 25,000.

The chiral iridium catalysts with P,P or N,P ligands have been extensively investigated and successfully applied to the asymmetric hydrogenation of imines and unfunctionalized olefins.[1] However, a general drawback of these Ir/P,P and Ir/N,P catalysts is the deactivation by the irreversible formation of inactive dimers and trimers through hydrid-bridged bonds in the presence of hydrogen.[2] Recently, some successful efforts have been devoted to effectively inhibiting deactivation (as shown in Scheme 1).

Pfaltz and coworkers investigated the effect of counteranions in iridium-catalyzed enantioselectively hydrogenation of alkenes.[3] They found that the catalytic activity of the Ir/N,P catalysts increased dramatically by introducing the bulky counteranion BAr_F^- (tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate), which is a breakthrough in asymmetric hydrogenation. A straight method to prevent dimerization/trimerization is the immobilization of the chiral Ir catalysts on a solid support to achieve the site-isolation effect and inhibiting the formation of dimers/trimers.[2c,4] Pugin and Blaser et al. studied the immobilization of Ir-diphosphine catalysts on silica gel, which exhibited high turnover number in the asymmetric hydrogenation of imines.[4a] Fan and coworkers introduced BINAP-cored dendrimers to the iridium-catalyzed hydrogenation of quinolines, excellent enantioselectivities and activities were obtained.[5] With the encapsulation of the iridium complex into the dendrimer framework which reduced dimerization, therefore enhanced the productivity of the catalyst. Zhou and coworkers introduced the rigid spirobiindane scaffold to the ligand skeleton, successfully improving both reactivity and enantioselectivity of the Ir/N,P and Ir/P,P catalytic systems in the asymmetric hydrogenation of imines and quinolines.[6] Very recently, Brown and coworkers observed that by increasing the steric bulkiness of the ligand of achiral Crabtree catalyst can efficiently inhibit the formation of trimers.[7] Although great success has been obtained, searching for new strategy for inhibiting deactivation of chiral iridium catalysts is highly desirable. Encouraged by Brown's findings,[7] we envisioned that the introduction of the steric bulkiness of the substituents at the coordination phosphorus atoms should inhibit the formation of inactive dimers or trimers, and improve the catalytic activity of the chiral Ir/P,P and Ir/N,P catalysts (as shown in Scheme 1).

Keeping this in mind, some ligands bearing substituents at both 3 and 5-position of the phenyl of phosphorous atoms were investigated in the Ir-catalyzed asymmetric hydrogenation of quinolines.[5,6b,8–11] 2-Methylquinoline was chosen as a model substrate, the catalysts were prepared in situ from the ligands and $[Ir(COD)Cl]_2$ with I_2 as an additive. The hydrogenation reaction was run on a substrate-to-catalyst (S/C) molar ratio of 500. For the simple MeO-BiPhep ligand, 61% conversion and 84% ee were



Scheme 1. Some strategies for inhibiting deactivation.

* Corresponding authors. Tel./fax: +86 411 84379220 (Y.-G.Z.); Tel./fax: +86 21 54925300 (Y.-L.G.).
E-mail addresses: ygzhou@dicp.ac.cn (Y.-G. Zhou), ylguo@mail.sioc.ac.cn (Y.-L. Guo).

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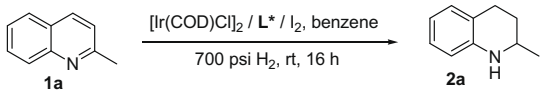
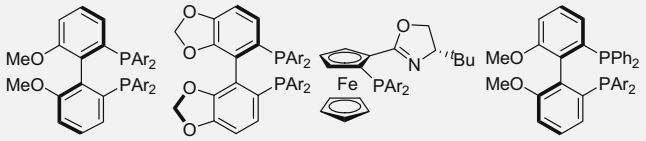
Table 1
Asymmetric hydrogenation of 2-methylquinoline[a]



Entry	Ligand	Convn.[b] (%)	Ee[c] (%)
1	**L1a**	61	84
2	**L1b**	66	73
3	**L1c**	>95	55
4	**L1d**	>95	55
5	**L2**	>95	78
6	**L3a**	76	79
7	**L3b**	90	83
8	**L4**	86	28

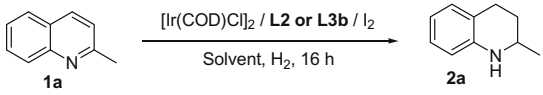


L1a: Ar = C_6H_5
L1b: Ar = 3,5-$Me_2C_6H_3$
L1c: Ar = 3,5-*t*-$Bu_2C_6H_3$
L1d: Ar = DTBM
L2: Ar = DTBM
L3a: Ar = C_6H_5
L3b: Ar = DTBM
L4: Ar = DTBM
DTBM = 4-MeO-3,5-*t*-$Bu_2C_6H_2$

[a] Conditions: 2-methylquinoline (2.5 mmol), $[Ir(COD)Cl]_2$ (0.0025 mmol), ligand (0.0055 mmol), I_2 (0.0125 mmol), 10 mL benzene.
[b] Determined by ^1H NMR.
[c] Determined by HPLC.

obtained, which were lower than that on a ratio of 100 (conversion: 61% vs >95%, ee: 84% vs 94%).[9a] Slightly higher conversion was obtained for the ligand **L1b** with 3,5-dimethyl group. Full conversions were obtained for ligands **L1c**, **L1d** and **L2** (entries 3–5), which bear bulky *tert*-butyl at 3 and 5-position of the phenyl, but lower enantioselectivities were obtained. Similar conversions were also obtained for the ferrocene derived P,N ligands **L3a** and **L3b** (conversion: 76% vs 90%, ee: 79% vs 83%), but the slightly higher enantioselectivity was obtained. Not full conversion and poor enantioselectivity were observed for the unsymmetric diphosphine ligand **L4** with a simple diphenylphosphino and bulky DTBM group (Table 1, entry 8, 86% conversion with 28% ee). It was obvious that the ligands with bulky aryl groups showed higher activity in the Ir-catalyzed asymmetric hydrogenation of quinolines.

Table 2
Asymmetric hydrogenation of 2-methylquinoline[a]



Entry	Ligand	H_2 (psi); T (°C)	Solvent	Convn.[b] (%)	Ee[c] (%)
1	**L2**	700; 25	Benzene	>95	78
2	**L2**	700; 25	Toluene	>95	74
3	**L3b**	700; 25	CH_2Cl_2	15	63
4	**L3b**	700; 25	*i*-PrOH	>95	61
5	**L3b**	700; 25	THF	>95	35
6	**L3b**	700; 25	Benzene	90	83
7	**L3b**	700; 25	Toluene	>95	89
8	**L3b**	700; 50	Toluene	94	84
9	**L3b**	300; 25	Toluene	75	78

[a] Conditions: 2-methylquinoline (2.5 mmol), $[Ir(COD)Cl]_2$ (0.0025 mmol), ligand (0.0055 mmol), I_2 (0.0125 mmol), 10 mL solvent.
[b] Determined by ^1H NMR.
[c] Determined by HPLC.

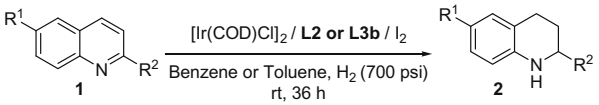
With these promising results in hand, the effect of solvents, hydrogenation pressure, and temperature on conversion and enantioselectivity was further studied using iridium complexes of **L2** and **L3b** as the catalysts, respectively (Table 2). For the ligand **L2**, both benzene and toluene gave complete conversions, and the former showed slightly higher enantioselectivity (entries 1 and 2, 78% ee vs 74% ee). For **L3b**, toluene showed better enantioselectivity and higher activity. Both by increasing the temperature or reducing pressure gave lower conversion and enantioselectivity. Thus, the optimized reaction conditions for **L2** and **L3b** were: $[Ir(COD)Cl]_2$/**L2**/benzene/700 psi H_2 and $[Ir(COD)Cl]_2$/**L3b**/toluene/700 psi H_2, respectively.

Having established the optimal conditions, the scope of substrates of these catalytic systems was explored. As summarized in Table 3, 2-alkyl-substituted quinolines were hydrogenated with moderate enantioselectivities and high yields with **L2** (entries 1–4, 61–78% ee). In contrast, moderate to excellent enantioselectivities were obtained with **L3b** (51–93% ee). For substrates with bulky 2-substituent, the hydrogenation were not fully completed. With **L3b**, the best results were obtained for 2-methylquinoline and 2,6-dimethylquinoline, the ee values were 89% and 93%, respectively (entries 5 and 8).

To further unclose the efficiency of our catalytic system, the S/C ratio increased to 5000. As shown in Table 4, for most of the substrates, **L2** displayed full conversions with moderate to good enantioselectivities. For the 2,6-dimethylquinoline, only 61% yield but 82% ee was obtained (Table 4, entry 7). As to **L3b**, for 2-methylquinoline, 94% yield and 89% ee were obtained (entry 10), for 2,6-dimethylquinoline, 93% ee and 67% yield were obtained (entry 11). Ligand **L2** exhibited very high efficiency, even when the S/C ratio increased to 25,000, the reaction could also proceed almost completely with lower ee value of 64% (entry 12). It is noteworthy that the ee values with **L2** dropped dramatically as S/C increased from 500 to 25,000 (78–64%). In contrast, for **L3b**, the S/C ratio has no effect on the enantioselectivities. These results encouraged us that an effective strategy for inhibiting deactivation of chiral iridium catalysts had been established.

Recently, ESI-MS has been used as an effective method for the characterization of catalytic species, thus providing useful information for acquisition of the existed form of the active catalyst.[2d,f,6a,12] To confirm our hypothesis and further understand the unique nature of catalytic species in our reaction system, ESI-MS analysis was performed. The spectra were collected in posi-

Table 3
Hydrogenation of **1** on S/C ratio of 500[a]



Entry	Ligand	R^1/R^2	Yield[b] (%)	Ee[c] (%)
1[d]	**L2**	H/Me	98 (**2a**)	78 (*R*)
2	**L2**	H/*n*-Bu	90 (**2c**)	68 (*R*)
3	**L2**	H/$Me_2CH(OH)CH_2$–	94 (**2e**)	62 (*S*)
4	**L2**	H/3,4-$(MeO)_2C_6H_3(CH_2)_2$–	91 (**2g**)	61 (*R*)
5[e]	**L3b**	H/Me	97 (**2a**)	89 (*R*)
6	**L3b**	H/$Me_2CH(OH)CH_2$–	96 (**2e**)	57 (*S*)
7	**L3b**	H/3,4-$(MeO)_2C_6H_3(CH_2)_2$–	89 (**2g**)	51 (*R*)
8	**L3b**	Me/Me	96 (**2h**)	93 (*R*)
9	**L3b**	MeO/Me	84 (**2i**)	79 (*R*)

[a] Conditions: quinoline (2.5 mmol), $[Ir(COD)Cl]_2$ (0.0025 mmol), ligand (0.0055 mmol), I_2 (0.0125 mmol), 10 mL solvent.
[b] Isolated yields.
[c] Determined by HPLC.
[d] Benzene for **L2**.
[e] Toluene for **L3b**.

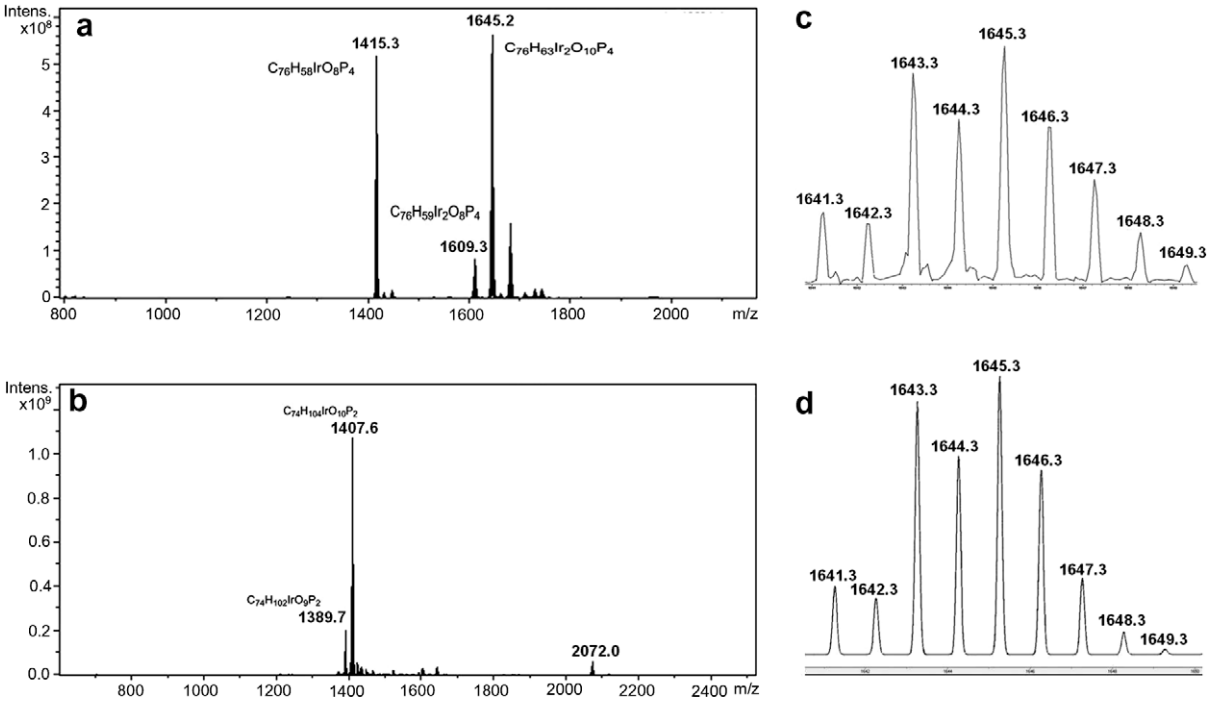
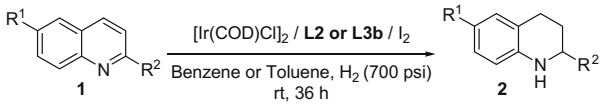


Figure 1. ESI-MS spectrum for the catalyst systems after suffering to H_2 for 16 h: (a) (*R*)-SegPhos as the ligand, (b) (*R*)-DTBM-SegPhos as ligand, (c) experimental isotopic distribution of the peak at $m/z = 1645$, (d) theoretical simulation of isotopic distribution of the peak at $m/z = 1645$.

Table 4
Hydrogenation of **1** on S/C ratio of 5000[a]



Entry	Ligand	R^1/R^2	Yield[b] (%)	Ee[c] (%)
1[d]	**L2**	H/Me	97 (**2a**)	70 (*R*)
2	**L2**	H/*n*-Pr	94 (**2b**)	49 (*R*)
3	**L2**	H/3-Butenyl	93 (**2c**)	50 (*R*)
4	**L2**	H/*n*-Pentyl	93 (**2d**)	52 (*R*)
5	**L2**	H/$Me_2CH(OH)CH_2$-	91 (**2e**)	57 (*S*)
6	**L2**	H/Phenethyl	93 (**2f**)	49 (*R*)
7	**L2**	Me/Me	61 (**2h**)	82 (*R*)
8	**L2**	MeO/Me	92 (**2i**)	79 (*R*)
9	**L2**	F/Me	95 (**2j**)	68 (*R*)
10[e]	**L3b**	H/Me	94 (**2a**)	89 (*R*)
11	**L3b**	Me/Me	67 (**2h**)	93 (*R*)
12[f]	**L2**	H/Me	94 (**2a**)	64 (*R*)

[a] Conditions: quinoline (25 mmol), $[Ir(COD)Cl]_2$ (0.0025 mmol), ligand (0.0055 mmol), I_2 (0.0125 mmol), 30 mL solvent.
[b] Isolated yields.
[c] Determined by HPLC.
[d] Benzene for **L2**.
[e] Toluene for **L3b**.
[f] S/C = 25,000/1.

tive-ion mode by diluting the toluene solutions of the catalytic system in acetonitrile after suffered to 700 psi of H_2 for 16 h. The spectra provided useful information of the catalytic systems and gave strong support to explain the results of our experiments. As shown in Figure 1a, for the simple ligand (*R*)-SegPhos, dimmers were formed in large part ($m/z = 1609$, $C_{76}H_{59}Ir_2O_8P_4^+$ and $m/z = 1645$, $C_{76}H_{63}Ir_2O_{10}P_4^+$ with the additional two H_2O molecules). Isotopic pattern simulation of the base peak at $m/z = 1645$ agreed well with the observed isotopic distribution (Fig. 1c and d), thus unambiguously establishing the elemental composition of the observed ions. For the bulky ligand (*R*)-DTBM-SegPhos (**L2**), only the monomer was formed and no dimer or trimer was found (Fig. 1b). These results were consistent with our expectation and indicated that the catalyst with more hindrance group at the coordination atoms could effectively inhibit the formation of dimers and trimers and showed higher activity. For more detailed information about the ESI-MS spectrum please see the Supplementary data.

In conclusion, a new strategy about the inhibition of deactivation of Ir catalysts, with bulky aryl groups on the coordination phosphorous atoms of P,P and N,P ligands, has been developed. This method was successfully applied to the asymmetric hydrogenation of quinolines, up to 93% ee were obtained and the S/C ratio reached 25,000. Our ongoing work is focusing on ligands design in other new catalytic system and to extend our catalytic system to other hydrogenation reactions.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.11.075.

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