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The electronic and steric effects of neutral and ionic phosphines on Ir(I)-complex catalyzed hydroaminomethylation of olefins

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ABSTRACT

The electronic and steric effects of a series of neutral and ionic (mono-/di-)phosphines on the performance of Ir(I)-complex catalysts for the hydroaminomethylation of olefins were systematically investigated by means of $^{1}J^{31}$P-^{77}Se coupling constant measurement, single-crystal X-ray diffraction, and high pressure *in situ* FTIR spectroscopy. It was found that the neutral mono-phosphines of **L1** with the moderate π-accepting nature ($^{1}J^{31}$P-^{77}Se of 753 Hz) and relatively less steric hindrance was able to spur the activities of the corresponding Ir-catalysts. In addition, the catalytic performances over the Ir(I)- and Rh(I)-precursors was compared under the same reaction conditions. The advantages of Ir(I)-catalyst over Rh(I)-catalyst for this tandem reaction were also discussed in detail.

1. Introduction

As important bulk and fine chemicals in agrochemical and pharmaceutical industries, amines are widely used for synthesizing various compounds like biologically active molecules, dyes, solvents and functional materials. Around one million tons of amine are produced annually [1,2]. Many types of reaction have been explored to produce amines up to date, such as hydroamination of alkenes or alkynes [3–5], nucleophilic substitution of alkyl halides [6–10], and cross coupling reactions [11–13], *etc.* Among the established processes, hydroaminomethylation features with high atomic economy, and therefore is one of the most effective protocols for the synthesis of valuable amines from olefins. A typical hydroaminomethylation contains three-steps (Scheme 1), *i.e.*, the hydroformylation of an olefin to an aldehyde, the subsequent condensation of the aldehyde with an amine to an imine or enamine, followed by a hydrogenation step to give the desired amine [14–16]. After the discovery of hydroaminomethylation by Reppe in 1949 [17], a number of transition-metal catalysts used for this method have been studied including Rh [18–22] and Ru [23–27] complexes. In addition, the dual metallic Rh/Ir catalysts were found to be more efficient for the hydroaminomethylation of olefins due to the individual responsibilities of the Rh-catalyst for hydroformylation and the Ir-catalyst for condensation of aldehyde with amine and the subsequent hydrogenation [28,29].

Compared to the Rh(I) ion, the Ir(I) ion presents a much weaker Lewis acidity, and thus it prefers soft phosphines over hard N-containing ligands [30–32]. Accordingly, the competitive coordination of organic amines to the Ir(I)-center and the isomerization of olefin are supposed to be suppressed over the Ir(I)-catalysts, making the hydroaminomethylation pathway becoming dominant. However, the reports about Ir-complex catalyzed hydroaminomethylation are sparse in the literature [33]. An ionic diphosphine-based Ir-catalyst for hydroaminomethylation of olefins with H_2O as the hydrogen source has been described by Liu group [33] (Scheme 2). The hydrogenation of olefins could be effectively depressed by water-gas shift reaction. Moreover, Ir-catalyzed hydroformylation with hydrogen was milder than water [34–38], and the hydrogenation of olefins can also be effectively inhibited by adjusting the syngas (CO/H_2) composition [39]. Herein, we reported Ir-catalyzed hydroaminomethylation with hydrogen by screening the suitable phosphines in milder conditions.

In order to better understand the electronic and steric effects on the performance of Ir-complex catalysts for the hydroaminomethylation of olefins, a series of neutral and ionic (mono-/di-)phosphines (**L1-L4** showed in Scheme 1) were explicitly selected (Scheme 2). Then the difference between the Ir(I)-catalysis and the Rh(I)-catalysis for hydroformylation was compared under the same reaction conditions. Since the positively charged quaternary ammoniums (such as imidazolium) are the most intensive electron-withdrawing moieties in comparison with $-CF_3$, $-NO_2$, $-COR$ *etc.*, the imidazolyl- and imidazolium-tailed phosphines with skeleton similarity (**L1** and **L2**; **L3** and **L4**) were selected in order to emphasize the different electronic effect without interference of steric hindrance. On the other hand, the pair of mono-

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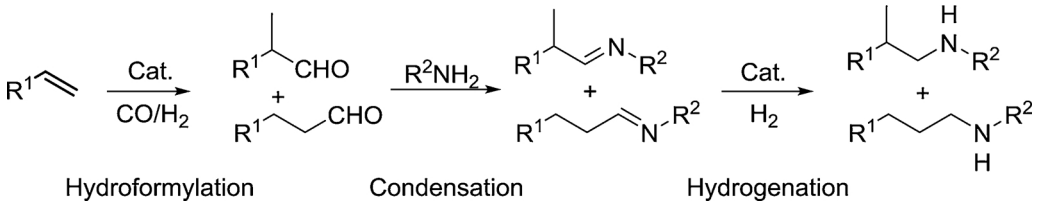
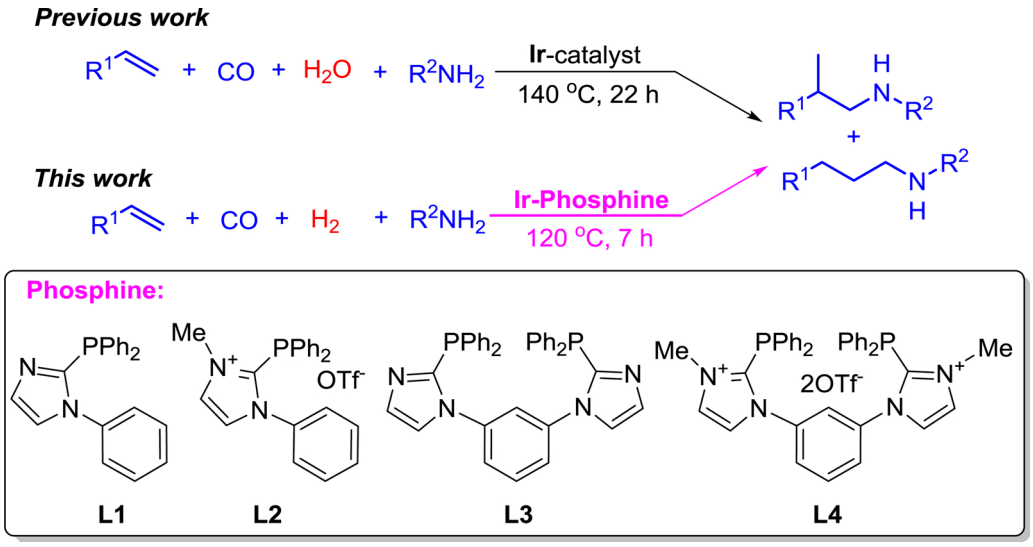


Scheme 1. Tandem hydroaminomethylation of olefins.



Scheme 2. Ir-catalyzed hydroaminomethylation of olefins.

phosphine and diphosphine (**L1** and **L3**; **L2** and **L4**) that differentiated in terms of steric effect were investigated. The means of the $^{1}J^{31}$P-^{77}Se measurement, the single-crystal X-ray diffraction (XRD) and the high pressure *in situ* Fourier transform infrared (FTIR) spectroscopy were utilized to elucidate the electronic and steric effects of the phosphine on the performance of Ir(I)-catalyst.

2. Results and discussion

The experimental sections can be found in the Supplementary information.

2.1. The electronic and steric effects of phosphines in the Ir-complexes

In order to understand the electronic effect of the selected phosphines, the values of the $^{1}J^{31}$P-^{77}Se coupling constant of the corresponding phosphines were measured by the ^{31}P NMR spectroscopy. It is well known that $^{1}J^{31}$P-^{77}Se value can be used to evaluate the π-acceptor ability of a phosphine [40,41]. An increased $^{1}J^{31}$P-^{77}Se value indicates an increase in the character of π-acceptor ability (*i.e.*, less σ-donor ability). **L1-L4** were obtained respectively *via* the replacement of one phenyl ring of PPh_3 by the imidazolyl- or imidazolium-groups.The measurement of $^{1}J^{31}$P-^{77}Se indicated that the π-accepting ability of these phosphines had the order of **L2** (780 Hz) ~ **L4** (782 Hz) > **L1** (753 Hz) ~ **L3** (751 Hz) > PPh_3 (729 Hz) [42].

Fig. 1 presents the molecular structures of the Ir-complexes (**Ir-L2**, **Ir-L3** and **Ir-L4**) [36,42] deduced from the single-crystal XRD (see Table 1 for detailed structural parameters as well). These complexes may serve as pre-catalysts for the investigated hydroaminomethylation. The structures can further help elucidate the electronic and steric effects of the involved phosphines on these complexes. As shown in Fig. 1, all these Ir(I)-complexes had a typical square-planar geometry, in which the four-coordinated Ir(I)($5d^8$)-center was bound to two phosphine fragments in *trans*-position, one CO, and one Cl- anion. Compared to the case of Ir(CO)$(PPh_3)_2$Cl [Ir-P and Ir-CO distances of 2.330(1) Å and 1.791(13), respectively, and ν_{co} 1953 cm^{-1}] [44], **Ir-L2**, **Ir-L3** and **Ir-L4** were all featured with a much shorter Ir-P [2.291 ~ 2.317 Å] and a longer Ir-CO bond distance (Ir-CO 1.815 ~ 1.845 Å), accompanied by blue-shifted CO vibrations frequency (ν_{co} of 1981 ~ 1996 cm^{-1}, Table 1). These features indicated that the enhanced π-accepting ability of **L2-L4** over that in PPh_3 facilitated the more intensive π-backdonation interaction between the Ir(I)-center and the phosphine, leading to more consolidated Ir-P linkages. To further explore the influence of the steric effect in the Ir-complexes, the topographic steric maps (Fig. 2) of these complexes was drawn with the web-page application developed by Poater et al. [45–48]. Consistently, the $\%V_{Bur}$ of **Ir-L3** was equal to **Ir-L4**, and both greater than the $\%V_{Bur}$ of **Ir-L2**. Therefore, the bi-phosphines based Ir-complexes (**Ir-L3** and **Ir-L4**) had similar steric hindrance, the regularity was also applicable to the mon-phosphines (based Ir-complexes **Ir-L1** and **Ir-L2**). In comparison to **Ir-L3** and **Ir-L4** wherein **L3** ($^{1}J^{31}$P-^{77}Se = 751 Hz) and **L4** ($^{1}J^{31}$P-^{77}Se = 782 Hz) possessed a similar steric effect, the two Ir-P distances in **Ir-L4** [2.291(1), 2.309(1) Å] were much shorter than those in **Ir-L3** [Ir-P 2.317(1), 2.310(1) Å]. In comparison to **Ir-L2** and **Ir-L4** wherein **L2** ($^{1}J^{31}$P-^{77}Se = 780 Hz) and **L4** ($^{1}J^{31}$P-^{77}Se = 782 Hz) possessed an similar electronic effect but only differ in the steric hindrance, the Ir-P distances in **Ir-L4** were also shorter than those in **Ir-L2** due to the chelating effect of the diphosphine of **L4**. As a whole, **Ir-L4** was the most stable complex due to the facilitated electronic and steric effects of **L4**. Concerning **Ir-L3** wherein **L3** possessed a moderate π-accepting nature ($^{1}J^{31}$P-^{77}Se = 751 Hz), it is noticeable that the Ir-Cl distance [2.384(1) Å] is distinctively lengthened compared to that in **Ir-L2** [2.344(2)] and in **Ir-L4** [2.374(1)], while all these complexes had a close Ir-P distance. The loose Ir-Cl linkage in **Ir-L3** could facilitate the Ir-Cl cleavage to make a vacancy on the Ir center for the accommodation of other molecules like substrate. In addition, the unimpaired Ir-P linkages in **Ir-L3** can guarantee its stability.

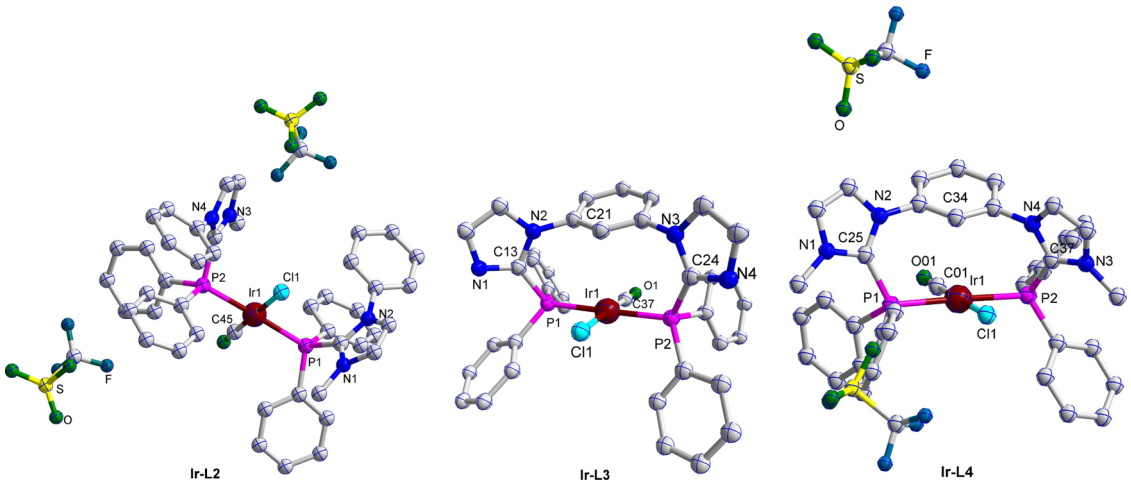


Fig. 1. The molecular models of **Ir-L2**, **Ir-L3** and **Ir-L4** deduced from the single crystal XRD results (the hydrogen atoms and the solvent molecules are omitted for clarity).

Table 1
Selected bond distances and bond angles in M-complexes studied in this work.

Ir-complex	Selected bond length/Å				ν (CO) /cm^{-1}
	M-P1	M-P2	M-Cl	M-C_{CO}	
Ir-L2 [42]	2.319(2)	2.309(2)	2.344(2)	1.845(110)	1985
Ir-L3 [42]	2.317(1)	2.310(2)	2.384(1)	1.815(57)	1981
Ir-L4 [42]	2.291(1)	2.309(1)	2.374(1)	1.825(50)	1996
Rh-L4 [43]	2.310(4)	2.299(4)	2.370(4)	1.830(50)	–
Ir(CO)(PPh_3)$_2$Cl [44]	2.330(1)	–	2.382(3)	1.791(13)	1953

2.2. Hydroaminomethylation of olefins over Ir(I)-catalyst

In the early stage of this work, different solvents, amine sources and the pressure ratios of CO/H_2 were examined under a given set of conditions with 1-octene as the model olefin (Table 2). In general, the experiments were carried out at 120 °C, under 4.0 MPa pressure of syngas, with [Ir(COD)Cl]$_2$ as the iridium precursors, catalyst to substrate ratio of 1/100, and **L1** as the ligand. This ligand was previously used for Ir-catalysed hydroformylation of olefins with high activity [36]. The solvent had a significant influence on the chemoselectivity of the reaction with the aniline as the amine sources (Entries 1–4). In particular, when *N*-methylpyrrolidone (NMP) was used as the solvent, the yield of amine for hydroaminomethylation of olefin was the highest, but the formation of a large number of imines was also observed (Entry 4). The *N*-methylaniline was found to be the best amine source in terms of chemoselectivity without the production of imines (Entry 5). When the amine source was replaced by piperidine, the tandem reaction was stopped completely (Entry 6). Since Ir-complexes were catalytically active for hydrogenation of olefins, a large number of hydrogenation products were observed in this reaction (Entries 1–5). The reduction in the partial pressure of H_2 efficiently improved the chemoselectivity of the amine product (Entries 7 and 8).

Then the electronic and steric effects of the phosphines on the performance of Ir(I)-catalyst were investigated, and the results are shown in Table 3. It can be seen that the neutral imidazolyl-tailed phosphines (**L1** and **L3**) universally corresponded to a much higher conversion of 1-octene and better selectivity to the target amines than those over the ionic imidazolium-tailed counterparts (Entries 2 *vs* 1; 4 *vs* 3). For example, over the neutral mono-phosphine of **L1**, the yield of the two kinds of amines [*N*-methyl-*N*-(2-methyloctyl)aniline and *N*-methyl-*N*-nonylaniline] reached 85 % (see GC-Mass analysis results for the product distribution in ESI) along with the low selectivity of 5% to the by-products of iso-octenes, whereas over **L2** only 39 % yield was obtained along with 10 % selectivity to iso-octenes (Entries 1 *vs* 2). Comparison between **L1** and **L3** that had a same electronic effect showed that the mono-phosphine of **L1** with less steric hindrance led to

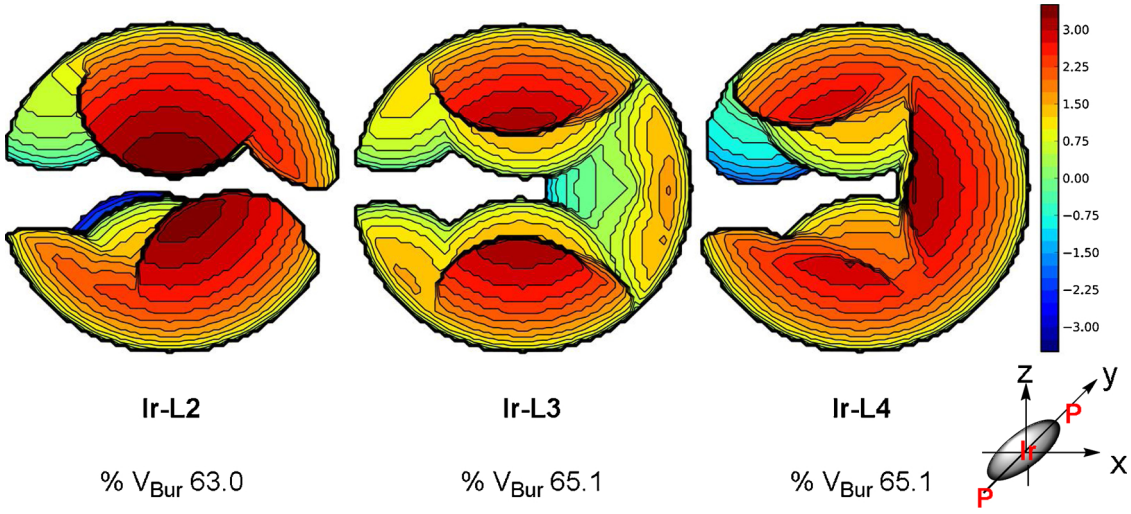
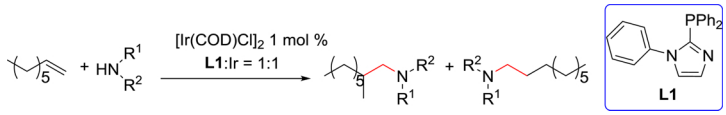


Fig. 2. Topographic steric maps of the Ir-complexes studied in this work [45–48].

Table 2
Ir-catalyzed hydroaminomethylation of 1-octene with *N*-methylaniline under different conditions[a].



Entry	Amine	Sol.	Pressure (CO/H_2)	Conv. (%)	Sel.[b] (%)					Yield (%)	L/B[b]
					Amines	Aldehydes	Isomers	Octane	Imines		
1		MeOH	1/1	97	47	–	6	30	17	46	50:50
2		Tol.	1/1	95	29	–	9	38	24	28	52:48
3		THF	1/1	97	31	–	8	33	28	30	41:59
4		NMP	1/1	96	53	–	5	15	27	51	61:38
5		NMP	1/1	95	64	–	8	28	–	61	64:36
6		NMP	1/1	10	–	–	3	7	–	–	–
7		NMP	3/1	98	80	–	7	13	–	78	72:28
8		NMP	5/1	98	87	4	5	4	–	85	72:28

[a] $[Ir(COD)Cl]_2$ 0.025 mmol (Ir 1.0 mol %), ligand **L1** 0.05 mmol, P/Ir = 1 (molar ratio), 1-octene 5.0 mmol, amine 7.5 mmol, NMP 2 mL, CO/H_2 4.0 MPa, 7 h, temperature 120 °C.
[b] Determined by GC.

a higher conversion of 1-octene and the better yield to the target amines (Entry 1 *vs* 3). A similar result was observed by the comparison between **L2** and **L4** that only differenced in their steric hindrances (Entries 2 *vs* 4). Without the involvement of any phosphine, the low yield of the amine products (35 %) was obtained over $[Ir(COD)Cl]_2$ (Entry 5). When the complexes of **Ir-L1** (or **Ir-L3**) was used to replace the mixture of $[Ir(COD)Cl]_2$ and **L1** (or **L3**) as the pre-catalyst, the very similar conversion of 1-octene and the yields of the amine products were obtained under the same conditions, indicating that the *in situ* formed **Ir-L1** (or **Ir-L3**) exhibited a same activity as the as-synthesized one (Entry 6 *vs* 1; Entry 7 *vs* 3). In contrast, the commercial PPh_3 as a typical electron-rich σ-donor ligand resulted in much lower activity towards this tandem reaction than **L1** (Entry 8 *vs* 1). Consistent to the results presented in Fig. 1 and Table 1, the enhanced π-accepting ability for **L2** and **L4** ($^1J^{31}P$-^{77}Se ~780 Hz) rendered the **Ir-L2** and **Ir-L4** complexes better stability with indication of the more consolidated Ir-P and Ir-Cl linkages due to π-backdonation interaction. Especially for **L4** with the intensive π-accepting ability as well as a favorable chelating steric effect, the corresponding **Ir-L4** was the most stable complex, which corresponded to the most inert activity due to too sluggish dissociation of the Ir-Cl bond to make a room for the activation of the olefin substrate and then the migration of CO (see Entry 4 in Table 3). As for **Ir-L3**, firstly, the exclusively loose Ir-Cl linkage facilitates the Ir-Cl cleavage to make a vacancy for the accommodation of the other molecule (like substrate).

Table 3
Ir-catalyzed hydroaminomethylation of 1-octene with *N*-methylaniline in syngas with the presence of different ligands[a].

Entry	Ligand	Conv. (%)[b]	Sel. (%)[b]					Yield (%)	L/B[b]
			Amines	Imines	Nonanals	Iso-octenes	Octane		
1	**L1**	98	87	–	4	5	4	85	72:28
2	**L2**	47	83	–	–	10	7	39	79:21
3	**L3**	80	79	–	2	11	8	63	83:17
4	**L4**	43	69	–	–	19	12	30	81:19
5	–	56	63	–	14	13	10	35	70:30
6	**Ir-L1**	99	86	–	4	6	4	85	70:30
7	**Ir-L3**	82	77	–	3	12	8	63	83:17
8	PPh_3	64	73	–	6	13	8	47	76:24
9[c]	**L1**	95	18	44	10	28	–	17	60:40
10[d]	**L1**	99	–	–	84	14	2	–	66:34
11[e]	**L1**	96	–	–	90	5	5	–	61:39
12[c]	**L4**	45	17	35	7	41	–	8	65:35

[a] $[Ir(COD)Cl]_2$ 0.025 mmol (Ir 1.0 mol%), P/Ir = 1 (molar ratio), 1-octene 5.0 mmol, *N*-methylaniline 7.5 mmol, NMP 2 mL (solvent), CO/H_2 = 5/1 (4 MPa), 7 h, temperature 120 °C.
[b] The selectivity to product and the ratio of linear product to branched one (L/B) were determined by GC and.GC–MS.
[c] $[Rh(COD)Cl]_2$ (0.025 mmol) in place of $[Ir(COD)Cl]_2$.
[d] $[Rh(COD)Cl]_2$ (0.025 mmol) in place of $[Ir(COD)Cl]_2$, but without *N*-methylaniline.
[e] $[Ir(COD)Cl]_2$ (0.025 mmol) without *N*-methylaniline.

Secondly, the solid Ir-P linkages, which was due to the π-backdonation from **L3** with the moderate π-accepting ability ($^1J^{31}$P-^{77}Se =751 Hz), can guarantee the stabilization of Ir-center against deactivation. Warranted by these two factors, **L3**-based Ir(I)-catalyst exhibited a much higher activity towards the hydroaminomethylation of 1-octene than the **L2** and **L4**-based ones (Entries 3 *vs* 2 and 4 in Table 3). Reasonably, the neutral phosphines of **L1** with a same moderate π-accepting ability as **L3** ($^1J^{31}$P-^{77}Se ~ 750 Hz) but without the chelating steric effect was responsible for the best performance for this reaction (see Entry 1 in Table 3)

However, over the **L1**-based Rh-catalyst, the low yields (17 %) of the target amines (Conv.$_{1\text{-octene}}$ 95 %, Sel.$_{\text{amines}}$ 18 %) were obtained accompanied by the formation of the imine by-products and the higher selectivity to nonanals and iso-octenes (Entry 9: Sel.$_{\text{imines}}$ 44 %, Sel.$_{\text{nonanals}}$ 10 %; Sel.$_{\text{iso-octenes}}$ 28 %) (see the results of GC-Mass analyses for the product distributions provided in ESI). Evidently, over **L1**-based Rh-catalyst, the overall yield of the hydroformylation products including the aldehydes, the imines and the target amines was only 68 % (Entry 9 in Table 3). Without the presence of *N*-methylaniline the yield of the hydroformylation products (nonanals) was increased to 83 % under the same conditions (Entry 10 in Table 3). Over **L1**-based Ir-catalyst, the total yields of the hydroformylation products including the aldehydes and the target amines was 91 % (Entry 1 in Table 3), which was quite close to the case where *N*-methylaniline was absent (Entry 11 in Table 3). Moreover, much higher selectivities to imines and nonanals were observed over the Rh(I)-catalyst compared to those over the Ir(I)-base one (Entry 9 *vs* 1 in Table 3). It is also noticeable that only two kinds of target amine (derived from 1-octene) were obtained over **L1**-based Ir-catalyst whereas four kinds of the amines (derived from 1-octene, 2-octene and 3-octene) were found in the Rh-system (see the results of GC-Mass analyses for the product distributions provided in ESI). Although the **Ir-L4** and **Rh-L4** complexes had similar structural characteristics (the Ir—P bond distances, Ir—CO bond distances and Ir—Cl bond distances can be seen in Table 1), the catalytic performance of **Ir-L4** (yield of the hydroformylation products of 30 %) was obviously better than that of **Rh-L4** (yield of the hydroformylation products of 27 %, see Entry 4 *vs* 12 in Table 3). These results revealed that **L1**-based Ir-catalyst was obviously advantageous over the corresponding Rh-catalyst for hydroaminomethylation in the following aspects. (1) The presence of *N*-methylaniline as a hard N-containing ligand deteriorated the activity of the corresponding Rh(I)-catalyst towards hydroformylation (Entry 9 *vs* 10 in Table 3), but exhibited negligible effect on the softer Ir (I)-center (Entry 1 *vs* 11 in Table 3). (2) **L1**-based Ir-catalyst gave more rise to condensation of the aldehydes with *N*-methylaniline and the subsequent hydrogenation of the imines with indication of less presence of aldehydes and no formation of the imines in the final product distributions (Entry 1 *vs* 9 in Table 3). (3) The isomerization of 1-octene was greatly depressed leading to much higher selectivities to the target amines with an L/B of 2.6 (Entry 1 *vs* 9 in Table 3), due to the relatively weaker Lewis acidity of Ir(I)-ion than Rh(I).

The evolution of **L1**-$[Ir(COD)Cl]_2$ catalyzed hydroaminomethylation of 1-octene with *N*-methylaniline in NMP was recorded under the optimized reaction conditions as shown in Fig. 3. The yields of the target amines as well as the conversion of 1-octene increased steadily with the reaction time. In the whole process, the aldehydes (nonanal and 2-methyloctanal) always had a yield of less than 6%. Evidently, the hydroformylation of 1-octene was the rate-controlling step in this tandem hydroaminomethylation.

The results in Fig. 3 suggested that all the effects that facilitated the first-step hydroformylation can give rise to the overall hydroaminomethylation. Herein, the high-pressure *in situ* FTIR spectroscopy was used to monitor the formation and stability of the active iridium-hydride (Ir-H) species responsible for the homogenous hydroformylation of olefins [49]. The continuous time-dependent highly pressure *in situ* FTIR spectra were recorded over the **L1**- and **L2**-based Ir-catalysts for hydroaminomethylation of 1-octene respectively (Fig. 4). Over the

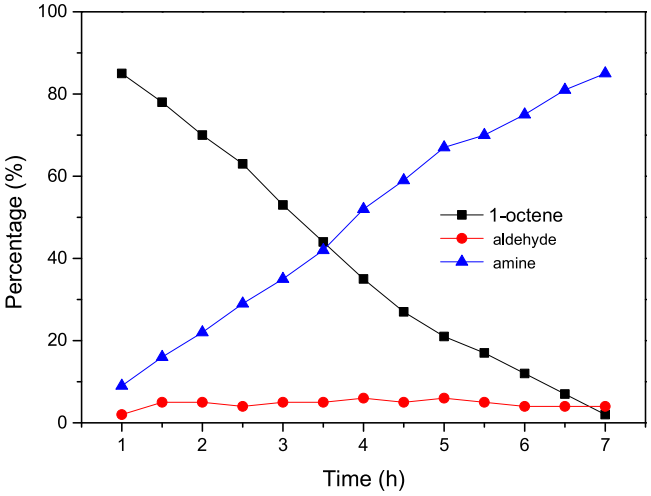


Fig. 3. The evolution profiles of the 1-octene conversion and product yield depending on the reaction time. Catalyst: **L1**-based Ir-catalyst ($[Ir(COD)Cl]_2$ of 0.025 mmol. Other conditions: **L1** of 0.025 mmol, 1-octene of 5.0 mmol, *N*-methylaniline of 8.0 mmol, NMP of 2 mL, CO/H_2 =5:1, reaction pressure of 4.0 MPa and reaction temperature at 120 °C).

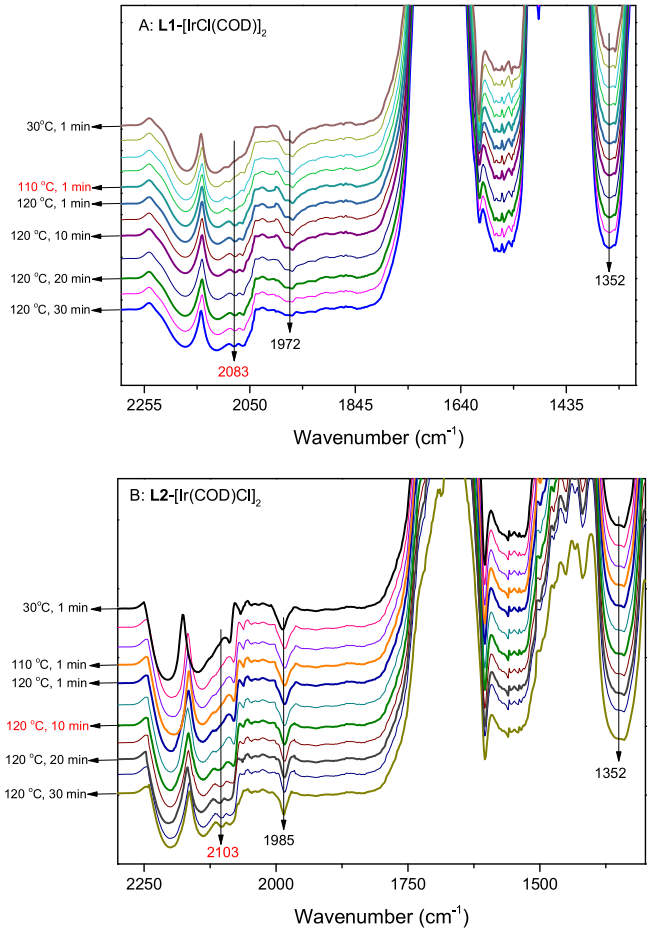


Fig. 4. The high-pressure *in situ* FTIR spectra recorded from 30 to 120 °C after mixing $[Ir(COD)Cl]_2$, **L1** (or **L2**), 1-octene, *N*-methylaniline and NMP sequentially. The mixture was pressured by 1.5 MPa syngas (CO/H_2 volume ratio = 5:1).

L1-based Ir-catalyst (Fig. 4A), the strong features at 2180 and 2115 cm^{-1} assigning to gaseous CO were always observed. In the overall monitoring process when the temperature was increased from

30 to 120 °C, an absorption peak at 2083 cm^{-1} appeared at 110 °C after holding 1 min. This peak can be identified as an active Ir-H (iridium hydride) species according to the previously reported work [33,50]. This feature presented at 120 °C for 30 min. At the same time the *ca.* 1972 cm^{-1} peak was also observed, which can be attributed to an Ir—CO intermediate. This intermediate can be accounted for the complexation of $[Ir(COD)Cl]_2$ with CO. Along with the appearance of the 2083 cm^{-1} peak (Ir-H species), the characteristic vibration of C—N bond at 1352 cm^{-1} grew stronger and stronger, which was assigned to the products of amine (see the standard FTIR spectrum of *N*-methyl-*N*-pentylaniline in S.Fig. 8 in ESI). This peak was partially overlapped with the C—N vibrations in *N*-methylaniline and NMP. In contrast, over **L2**-based Ir-catalyst, the appearance of the Ir-H vibration (see the 2103 cm^{-1} peak in Fig. 4B) occurred at 120 °C after holding 10 min, which implied that **L2**-based Ir-catalyst was relatively inert compared to over **L1**-based one.

It has been reported in Moser's pioneering work [51] that the electron-withdrawing effect of the substituents (R) in the active RhH $(CO)_3(PR_3)$ complexes could dramatically influence the Rh-H infrared vibrational frequency within the range of 2018–2050 cm^{-1}. For example, when R = $-CF_3$, $RhH(CO)_3(PR_3)$ presents a quite blue-shifted Rh-H feature of 2050 cm^{-1}. Consistent with Moser's observation, the dramatic blue-shifted Ir-H vibration of 2103 cm^{-1} was found in Fig. 3B due to the intensive electron-withdrawing effect of the positive-charged imidazolium in **L2** in comparison to the observed Ir-H species at 2083 cm^{-1} over **L1**-based system (Fig. 4A). At the same time, the CO-vibrations in the ionic phosphine based Ir-complexes/intermediates also blue-shifted to the higher frequency range (Fig. 4-B).

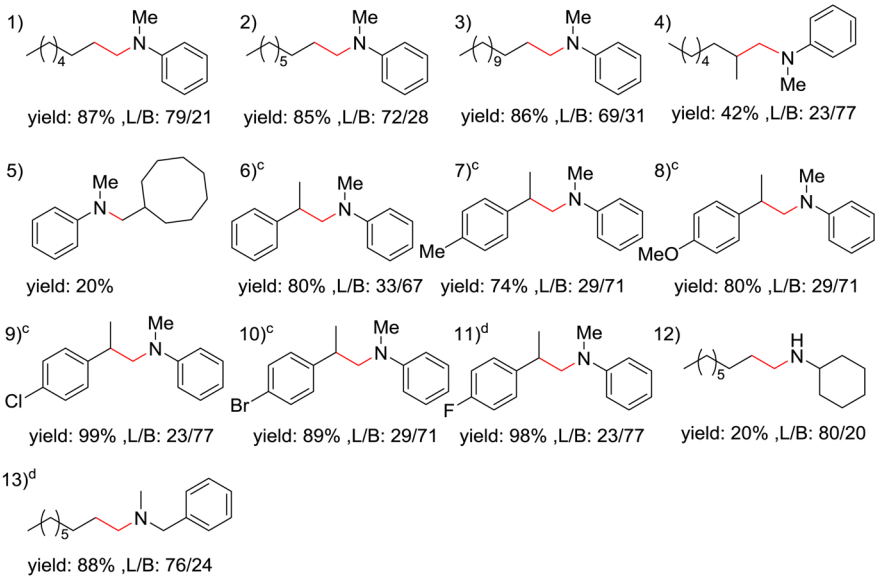
The scope of hydroaminomethylation catalyzed by **L1**-based Ir-catalyst was explored as shown in Table 4. It can be seen that good product yields (85 %～87 %) can be obtained for the linear terminal aliphatic olefins like 1-heptene, 1-octene and 1-dodecene (Entries 1–3). In contrast, the internal aliphatic olefins like 2-octene and cyclooctene, having increased steric hindrance, corresponded to much lower amine yields (Entries 4 and 5). When a series of styrene derivatives were applied to repeat the reactions at a prolonged time of 12 h, the good to excellent yields were obtained with branched amines as the major products (Entries 6–11). For example, styrene gave a 80 % yield of the target amines whereas styrene derivatives with para-positioned F-/Cl-substituents afforded 98 %～99 % yields of the products (Entries 6, 9 and 10). Unfortunately, the uses of the aliphatic primary/secondary amines instead of *N*-methylaniline universally led to dramatically reduced yields of the products (see S.Table 1 in SI). Only when the concentration of Ir-catalyst was increased to 2.0 mol %, the hydroaminomethylation of 1-octene with *N*-methyl-1-phenylmethanamine gave an improved product yield of up to 88 % (Entry 13).

3. Conclusions

The electronic and steric effects of a series of neutral and ionic (mono-/di-) phosphines (**L-1L4**) were studied in the Ir(I)-complex catalyzed hydroaminomethylation of olefins. The Ir-complex with the moderate and the less sterically hindrance ligands had the highest activity for the tandem hydroaminomethylation of olefins. It was found that **L1** with a moderate π-accepting ability ($^1J^{31}P$-^{77}Se of ～750 Hz) corresponded to the most efficient hydroaminomethylation in the four ligands examined. **L3** presented a relatively lower reaction rate than **L1** due to a larger steric hindrance and the potential chelating effect as a diphosphine, even though these two ligands had the same $^1J^{31}P$-^{77}Se of 751 Hz. The molecular structure of **Ir-L3** supported that **L3** was able to consolidate the Ir-P linkage along with a weakened Ir-Cl linkage. These structural characters led to a better performance of the **L3**-based Ir-catalyst for hydroaminomethylation than those of the **L2**- and **L4**-based ones. The *in situ* FTIR analysis proved that the presence of **L1** could

Table 4
Generality of **L1**-$[Ir(COD)Cl]_2$ catalytic system for hydroaminomethylation of olefins with amines[a].

Major Product



[a]$[Ir(COD)Cl]_2$ 0.025 mmol (Ir 1.0 mol %), **L1** 0.025 mmol, P/Ir = 1 (molar ratio), alkene 5.0 mmol, *N*-methylaniline 7.5 mmol, NMP 2 ml (solvent), CO/H_2 = 5/1 (4 MPa), 7 h, temperature 120 °C; [b] Determined by GC and GC–MS; [c] CO/H_2 = 3/1 (4.0 MPa), 12 h; [d] $[Ir(COD)Cl]_2$ 0.05 mmol (Ir 2.0 mol %), **L1** 0.05 mmol.

greatly facilitate the formation and stability of the active Ir-H species responsible for hydroformylation (as the rate-controlling step for hydroaminomethylation). Moreover, compared to the Rh(I)-complexes, the Ir(I)-complexes were more advantageous for the catalytic tandem hydroaminomethylation under the same reaction conditions, which can be due to three reasons. First, as a much softer Lewis acidic centre, Ir(I)-ion preferred phosphines over hard N-containing ligands. Hence, the available organic amines as raw materials in hydroaminomethylation had negligible influence on the performance of the Ir(I)-catalyst. Second, the isomerization of the olefins were greatly depressed over the weaker Lewis acidic Ir(I)-centre. Third, the Ir(I)-catalyst was more active for hydrogenation of the imines than the corresponding Rh(I)-catalyst.

CRediT authorship contribution statement

Huan Liu: Conceptualization, Investigation, Formal analysis, Data curation, Writing - original draft. **Da Yang:** Investigation, Formal analysis, Data curation, Writing - original draft. **Yixuan Yao:** Investigation, Formal analysis, Data curation. **Yongqiang Xu:** Formal analysis, Resources. **Hongyan Shang:** Supervision, Funding acquisition, Project administration. **Xufeng Lin:** Supervision, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.110843.

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