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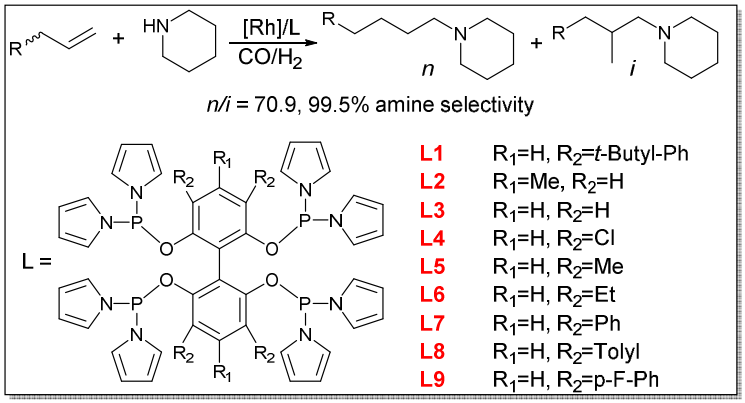
Abstract

A concise and elegant protocol was developed to prepare linear amines by the regioselective hydroaminomethylation of terminal olefins with pyrrole-based tetraphosphorus ligands. It was documented that the reactivity of ligand was modulated by the substituent of the biphenylphosphane moiety. Ligand **L5** containing electron-donating group exhibited the highest reactivity, which provided up to 70.9 *n/i* ratio and 99.5% amine selectivity for 1-pentene and 31.3 *n/i* ratio and 97.9% amine selectivity for 1-hexene.



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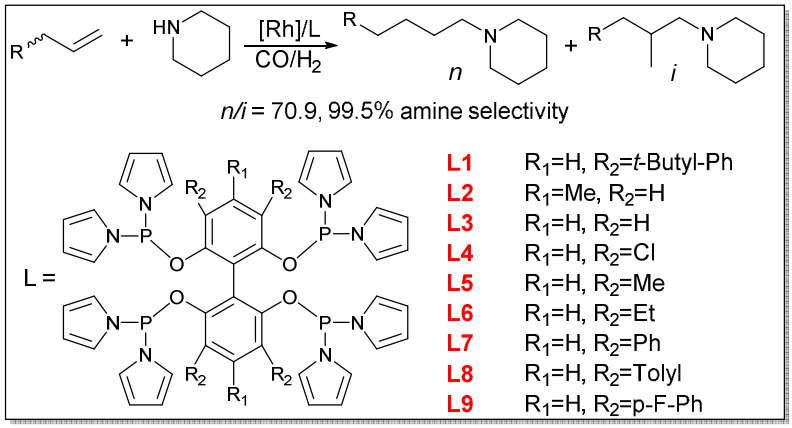

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COMMUNICATION

Rhodium-catalyzed regioselective hydroaminomethylation of terminal olefins with pyrrole-based tetraphosphorus ligands

Guodu Liu [a, b, c], Zhao Li [a], Huiling Geng*[a, b, d], and Xumu Zhang*[b]

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A concise and elegant protocol was developed to prepare linear amines by the regioselective hydroaminomethylation of terminal olefins with pyrrole-based tetraphosphorus ligands. It was documented that the reactivity of ligand was modulated by the substituent of the biphenylphosphane moiety. Ligand L5 containing electron-donating group exhibited the highest reactivity, which provided up to 70.9 n/i ratio and 99.5% amine selectivity for 1-pentene and 31.3 n/i ratio and 97.9% amine selectivity for 1-hexene.

Hydroaminomethylation represents one of the most important catalytic protocols for the synthesis of amines as it is an environmentally benign and atom-efficient method using ubiquitous readily available olefins as starting material.[1-2] These amine products are versatile intermediates and building blocks for many valuable pharmaceuticals, bioactive natural products, dyes, agrochemicals and fine chemicals.[3] Most commonly in hydroaminomethylation bisphosphorus ligands along with rhodium metal precursors were used.[4] The representative ligands include Iphos with 9 *n/i* ratio and 97% amine selectivity for 2-butene, Naphos with 99 *n/i* ratio and 6% amine selectivity for 2-butene,[5] Xantphos with 48 *n/i* ratio and 97% amine selectivity for 1-pentene,[6] and Xantphenoxaphos with 24 *n/i* ratio and 98% amine selectivity for 2-hexene.[7]

The pioneering work on hydroaminomethylation reaction was first reported by Reppe in 1949.[8] More than sixty years later, the efficiency and comprehensive applications of this reaction were documented by Eilbracht's group, in which they prepared a series of highly functionalized diamines and triamines with potential biological activities utilizing Rh-catalyzed hydroaminomethylation of hetero-functionalized olefins.[9] A series of rhodium catalysts based on modified Naphos- and Xantphos-ligands were developed for *n*-selective hydroaminomethylation of terminal and internal olefins by Beller and coworkers. Furthermore, they also ingeniously designed and synthesized a series of other rhodium complexes to realize the preparation of various bioactive compounds.[10] And many other excellent catalysts based on rhodium and novel synthetic applications were reported by the groups of Vogt,[11] Alper,[12] Kalck,[13] Ding[14] and others.[15] Meanwhile, methodology improvements on biphasic systems[16] and microwave-assisted hydroaminomethylation were presented as well.[17]

Recently, we have reported the synthesis and application of pyrrole-based tetraphosphorus ligand TPPB (2,2′,6,6′-tetrakis (dipyrrolyl phosphoramidite)-1,1′-diphenyl) and a series of its derivatives, which showed high regioselectivity for the isomerization-hydroformylation of internal olefins, styrene derivatives and other functionalized olefins.[18] To explore the reactivity of this catalytic system, we designed and synthesized two new pyrrole-based ligands: 3,3′,5,5′-tetra *t*-butyl phenyl substituted diphenyl pyrrole-based tetraphosphorus ligand **L1**, and 4,4′-dimethyl substituted diphenyl pyrrole-based tetraphosphorus ligand **L2** (Figure 1). These two new ligands and other seven known pyrrole-based tetraphosphorus ligands were then chelated with rhodium to catalyze the hydroaminomethylation of terminal olefins. To our delight, most complexes could efficiently transform terminal olefins to the corresponding linear amines with up to > 99% conversion and high linear amine selectivity. Herein, we present our recent results on the hydroaminomethylation of terminal olefins with these ligands.

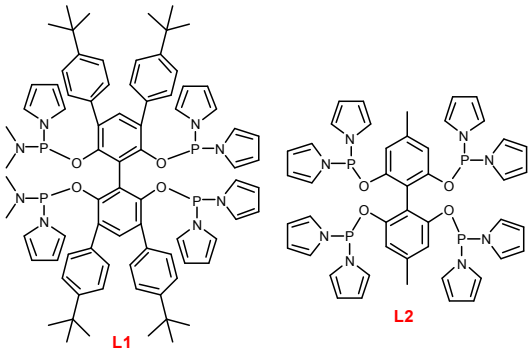
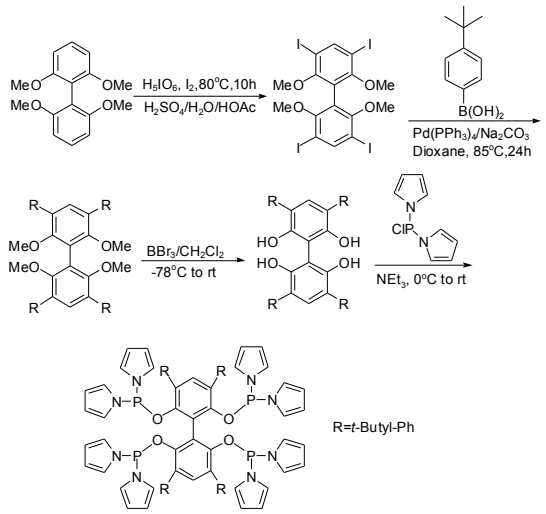
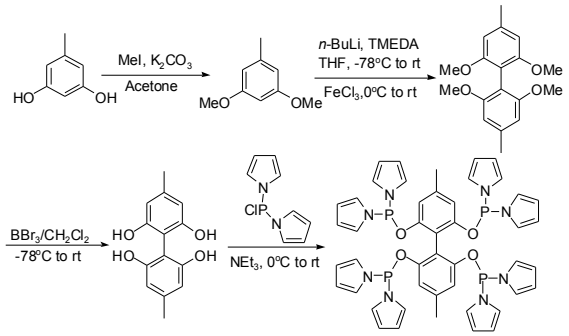


Figure 1. The structure of new pyrrole-based tetraphosphorus ligands.

Firstly, two new pyrrole-based ligands (**L1** and **L2**) were synthesized according to the following procedures. Diphenyl with 3,3′,5,5′-tetra *t*-butylphenyl could be prepared in good yield from iodo-substituted derivative with its boronic acid *via* Suzuki coupling. Treatment of the substituted 2,2′,6,6′-tetramethoxy-biphenyl with boron tribromide gave the parent tetraol, followed by reaction with chlorodipyrrolylphosphine to furnish ligand **L1** in the presence of NEt_3 at room temperature (Scheme 1).[18b] Ligand **L2** was synthesized from 5-methylbenzene-1,3-diol in four steps. This diol was firstly protected with iodomethane to form 1,3-dimethoxy-5-methyl benzene. Then following the known procedures,[18a] compound tetraol could be afforded in two simple steps.[19] In the presence of NEt_3, tetraol smoothly reacted



Scheme 1. Synthesis of ligand **L1**.

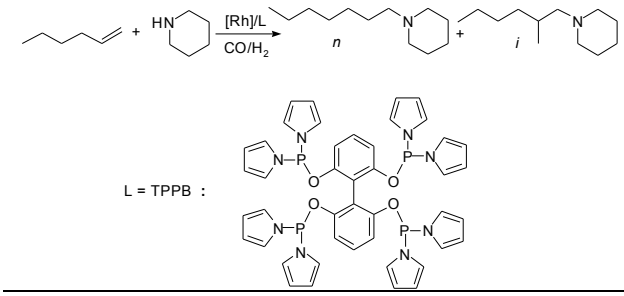


Scheme 2. Synthesis of ligand **L2**.

with freshly made chlorodipyrrolylphosphine to yield the desired pyrrole-based tetraphosphorus ligand **L2** successfully. These two new ligands were air-stable solid. The unoptimized yields for them were around 25~30%.

TPPB (**L3**) was picked as the standard ligand for the hydroaminomethylation of 1-hexene and piperidine. Reaction conditions were optimized based on the previous study of this reaction.[20-21] $Rh(acac)(CO)_2$ gave the best *n/i* ratio of 19.2 in the 1:1 mixed solvent of methanol and toluene at 125°C (Table 1, entries 1-3), thus, it was used as standard precursor for the further optimization. Various solvents and pressures were tested for better amine selectivity and higher *n/i* ratio. Although the *n/i* ratio was 27.8 in the 2:1 mixture of 2-propanol and ethanol, the amine selectivity was not ideal (entry 5). We could conclude that polar solvents are beneficial for full conversion of 1-hexene and higher amine selectivity, though under these conditions the regioselectivity was a little lower than other circumstances (entries 6-8). Using 2-propanol as solvent, higher regioselectivity (*n/i* =29.3), higher amine selectivity (91.6%) and full conversion were observed for 1-hexene (entry 9). Consequently, with 2-propanol as the solvent, different pressures were set out to search for the optimal CO/H_2 pressure. When the pressure of CO/H_2 was 5/5 bar, the highest *n/i* ratio of amine was achieved as 45.2, but amine selectivity was somewhat lower as the intermediates, enamines, couldn't be fully hydrogenated in 8 hours (entry 12). When the pressure of H_2 was gradually increased, to our surprise, 30.1 *n/i* ratio and 92.4% amine selectivity were achieved with

Table 1. Hydroaminomethylation of 1-hexene and piperidine with TPPB under different reaction conditions [a]



Entry	Cata.	Solvent	CO/H_2 (bar)	Temp. (°C)	Con. (%)	Amine sel. [b]	Linear sel. [b]	
							n/i	*n*-Amine (%) [c]
1	A	Me/To=1:1	7/35	125	99	81.7	19.2	95.0
2	B	Me/To=1:1	7/35	125	99	84.7	11.8	92.2
3	C	Me/To=1:1	7/35	125	99	91.1	7.6	88.4
4	A	Et/To=2:1	7/35	125	80	65.8	25.3	96.2
5	A	Pr/Et=2:1	7/35	125	99	83.2	27.8	96.4
6	A	Pr/Me=2:1	7/35	125	99	91.6	13.1	92.9
7	A	Pr/Me=1:1	7/35	125	99	94.0	9.6	90.6
8	A	Pr/Me=1:2	7/35	125	99	96.1	6.6	86.8
9	A	2-PrOH	7/35	125	99	91.6	29.3	96.7
10	A	2-PrOH	10/50	125	99	83.5	14.8	93.2
11	A	2-PrOH	7/7	125	99	83.6	18.3	94.8
12	A	2-PrOH	5/5	125	99	75.8	45.2	97.8
13	A	2-PrOH	5/10	125	99	87.5	27.1	96.4
14	A	2-PrOH	5/30	125	99	90.6	32.0	96.9
15	A	2-PrOH	5/35	125	99	92.4	30.1	96.8
16	A	2-PrOH	5/40	125	99	92.1	17.2	94.5
17	A	2-PrOH	5/35	130	99	92.0	16.9	94.4

[a] Reaction conditions: S/Rh = 1000, 1 μmol Rh precursor, 4 μmol TPPB (**L3**), 1 mmol 1-hexene, 1mmol piperidine, 125 °C, 8 h, 3 mL solvent. A = $Rh(acac)(CO)_2$, B = $[Rh(cod)_2]BF_4$, C = $[Rh(cod)Cl]_2$, Me = methanol, Et = ethanol, Pr = 2-propanol, To = toluene. [b] Selectivity and *n/i* ratio were determined by GC analysis using 2-methoxyethyl ether (0.1 mL) as an internal standard. [c] Percentage of linear amine in all amines.

5/35 bar CO/H_2 in 8 hours (entry 15). However, further increasing the pressure of H_2 to 40 bar resulted in the decrease of amine selectivity and *n/i* ratio (entry 16). We also heightened the temperature to 130 °C, unfortunately, the *n/i* ratio and amine selectivity was descended simultaneously (entry 17). The preliminary optimal conditions were as follows: $Rh(acac)(CO)_2$, S/L/Rh = 1000/4/1, 2-propanol, 125℃, 5/35 bar CO/H_2, which were applied in the next ligands screening.

Under optimized reaction conditions, a series of pyrrole-based tetraphosphorus ligands (**L1-L9**, Figure 2) were subjected to the regioselective hydroaminomethylation of 1-hexene. In all cases,

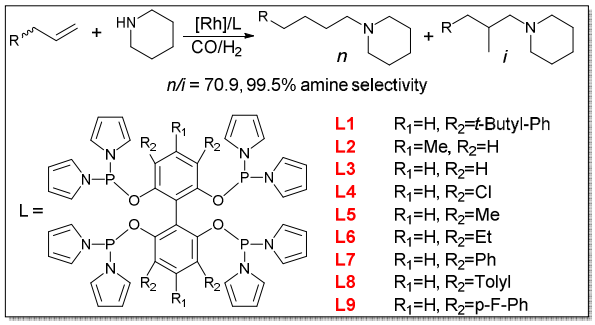
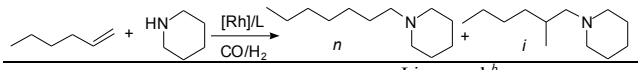


Figure 2. The structure of pyrrole-based tetraphosphorus ligands for the hydroaminomethylation of terminal olefins.

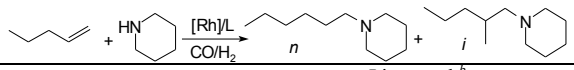
Table 2. Hydroaminomethylation of 1-hexene and piperidine with pyrrole-based ligands [a]



Entry	Ligand	Con. (%)	Amine sel.[b]	Linear sel.[b]		TON [d]
				n/i	*n*-Amine (%)[c]	
1	**L3**	99	93.2	30.1	96.8	938
2	**L4**	99	92.6	13.5	93.1	853
3	**L5**	99	97.9	31.3	96.9	940
4	**L6**	99	99.2	14.5	93.5	919
5	**L7**	99	99.6	10.8	91.5	902
6	**L8**	99	97.1	11.9	92.2	886
7	**L9**	99	98.2	11.3	91.9	893
8	**L1**	99	98.6	12.4	92.5	903
9	**L2**	99	99.8	5.22	83.9	830

[a] Reaction condition: S/Rh = 1000, 1 μmol $Rh(acac)(CO)_2$, 4 μmol ligand, 1 mmol 1-hexene, 1 mmol piperidine, 125 °C, 8 h, 3 mL 2-propanol. Selectivity and *n/i* ratio were determined by GC analysis using 2-methoxyethyl ether (0.1 mL) as an internal standard. [c] Percentage of linear amine in all amines. [d] Turnover number of linear amine.

Table 3. Hydroaminomethylation of 1-pentene and piperidine with pyrrole-based ligands [a]



Entry	Ligand	Con. (%)	Amine sel.[b]	Linear sel.[b]		TON [d]
				n/i	*n*-Amine (%)[c]	
1	**L3**	99	95.1	14.1	93.4	878
2	**L4**	99	93.8	14.6	93.6	869
3	**L5**	99	99.5	70.9	98.6	971
4	**L6**	99	98.7	32.2	97.0	947
5	**L7**	99	99.4	17.3	94.5	929
6	**L8**	99	99.6	16.9	94.4	931
7	**L9**	99	99.2	23.5	95.9	941
8	**L1**	99	99.2	22.7	95.8	941
9	**L2**	99	99.9	27.7	96.5	954

[a] Reaction conditions: S/Rh = 1000, 1 μmol $Rh(acac)(CO)_2$, 4 μmol ligand, 1 mmol 1-pentene, 1 mmol piperidine, 125 °C, 8 h, 3 mL 2-propanol. [b] Selectivity and *n/i* ratio were determined by GC analysis using 2-methoxyethyl ether (0.1 mL) as an internal standard. [c] Percentage of linear amine in all amines. [d] Turnover number of linear amine.

no N-formylpiperidine was detected and the conversion of 1-hexene was more than 99%. However, the fluctuations of *n/i* ratio and amine selectivity were totally different. The introduction of substituent to the diphenylphosphane moiety of TPPB dramatically affected both the regioselectivity of amines and the activity of Rh catalytic system. For ligand **L5**, the methyl groups at 3,3′,5,5′-position of the diphenylphosphane moiety exerted the electronic impact on the regioselectivity of the amine products. The electron-donating alkyl-substituted ligands (**L2**, **L5** and **L6**) showed higher reactivities than chloric substituted ligand **L4** and aromatic substituted ones (**L1** and **L7**-**L9**) (entries 3-4, 9 *vs.* 2, 5-8). Those ligands with electron-withdrawing groups, especially **L4** gave the lowest amine selectivity with moderate regioselectivity (entry 2). Other electron-donating aromatic substituted ligands showed good amine selectivity while the regioselectivity was relatively low (entries 6 and 8). The 4,4′–dimethyl substituted ligand **L2** gave the highest amine selectivity (up to 99.8%), but the linear regioselectivity decreased (entry 9). Therefore, as far as the total catalytic reactivity was concerned, **L5** was the best ligand with 97.9% amine selectivity, 31.3 *n/i* ratio and 940 turnover number for the regioselective hydroaminomethylation of 1-hexene (entry 3).

These pyrrole-based ligands were also applied in the regioselective hydroaminomethylation of 1-pentene and piperidine under the same reaction conditions. Given the amine selectivity and regioselectivity, all ligands revealed better reactivity for 1-pentene than that of 1-hexene, and the influence of the substituents was consistent with that of 1-hexene. Most of the amine selectivity was up to 99%. The highest *n/i* ratio was 70.9 with 99.5% amine selectivity, which was offered by ligand **L5**, the best ligand for 1-hexene (Table 3, entry 3). A surprising result was achieved with **L2**, the 4,4′–dimethyl substituted ligand. Its amine selectivity was up to 99.9% (almost 100%), the *n/i* ratio was 27.2, and the total amine product was 96.5% (entry 9). Thus, two ligands, **L5** (TON of 971) and **L2** (TON of 954) worked excellently for the hydroaminomethylation of 1-pentene.

Conclusions

In conclusion, a concise and green method was developed to synthesize linear amines using the rhodium-catalyzed regioselective hydroaminomethylation of 1-hexene and 1-pentene with pyrrole-based tetraphosphorus ligands. The substituents of the diphenylphosphane moiety of the ligands greatly affected the amine selectivity and regioselectivity. The 3,3′,5,5′-tetramethyl substituted pyrrole-based tetraphosphorus ligand **L5** was found to be the best ligand at hand, with up to 70.9 *n/i* ratio and 99.5% amine selectivity for 1-pentene and 31.3 *n/i* ratio and 97.9% amine selectivity for 1-hexene. Moreover, the 4,4′–dimethyl substituted ligand **L2** also showed excellent reactivity, 99.9% amine selectivity and 27.7 *n/i* ratio, for the regioselective hydroaminomethylation of 1-pentene. The mechanism of the effect of the substituent on the ligands' stereoselectivity is not very clear, which will be disclosed in our further study.

Experimental Section

General Procedure for Hydroaminomethylation of 1-Hexene with Piperidine.[20] All hydroaminomethylation experiments were performed in a nitrogen-filled glove box. In a typical experiment, a 10-mL long neck vial with a magnetic stirring bar was charged with TPPB (4 μmol, 3.5 mg) and $Rh(acac)(CO)_2$ (1 μmol, 0.1 mL of 10 mmol solution in toluene). After the mixture was stirred for 10 min, 1-hexene (1 mmol, 0.125 mL) and piperidine (1 mmol, 0.098 mL) was added, then followed by adding 2-propanol (3 mL) and 2-methoxyethyl ether (0.1 mL, internal standard). The reaction mixture was transferred to an autoclave, all vials were covered with a simple lid. The autoclave was purged with H_2 three times and subsequently charged with CO (5 bar) and H_2 (35 bar). After the reaction was carried out at 125 ℃ for 8 h, the autoclave was then cooled to room temperature and depressurized carefully in a well-ventilated hood. The reaction mixture was immediately analyzed by GC to determine the conversion and regioselectivity.

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Notes and references

[a] *College of Science, Northwest A&F University, Yangling, Shaanxi 712100, China. E-mail: genghuiling5@163.com*
[b] *Department of Chemistry and Chemical Biology and Department of Medicinal Chemistry, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854, United States. Fax: (+1) 732-445-6312. E-mail: xumu@rci.rutgers.edu*
[c] *Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China.*
[d] *Key Laboratory of Production and Utilization of Biological Resources in Tarim Basin, Xinjiang Production & Corps, Alar, Xinjiang 843300, China.*

† Electronic Supplementary Information (ESI) available: Synthetic prodecures, the NMR characterization and enantioselectivity analysis of the products. See DOI: 10.1039/b000000x/

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