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Highly Regioselective Hydroaminomethylation of Terminal Olefins to Linear Amines Using Rh Complexes with a Tetrabi Phosphorus Ligand**

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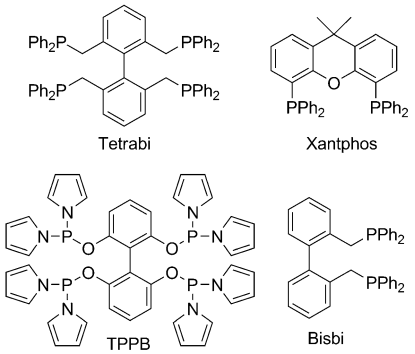
Abstract: A highly regioselective hydroaminomethylation of terminal olefins catalyzed by Rh complexes with 2, 2′, 6, 6′-tetrakis ((diphenylphosphino)-methyl)-1, 1′-biphenyl (Tetrabi) ligand has been developed. Up to 99% amine selectivity, 168 linear/branched amine product ratio (*n/i*), and 97.4% linear amine yield has been obtained at a substrate/rhodium precursor ratio (S/Rh) of 1000 with this methodology. The turnover number was achieved 6930 at 10000 S/Rh ratio, and the *n/i* can reach up to >525. Several different olefins and secondary amines have been applied successfully with high chemoselectivity (99%), yield (>98%), and regioselectivity (>120).

Keywords: hydroaminomethylation · linear amines · olefins · regioselectivity · rhodium · Tetrabi ligand

Introduction

Linear aliphatic amines are of significant importance in the chemical and pharmaceutical industries. Million-ton scale of linear amines is produced per year. They are used as solvents, fine chemicals, agrochemicals, pharmaceutical intermediates, and vulcanization accelerators.[1] Hydroaminomethylation,[2] an environmentally benign, one-pot, atom-efficient synthesis of amines from inexpensive ubiquitous olefins, consists of an initial regioselective hydroformylation followed by a reductive amination. Since the discovery of this reaction at BASF AG by Reppe,[3] notable advances have been especially reported by Eilbracht and co-workers in the 2000 s.[4] During this time, Beller and co-workers have made a great contribution to regioselective hydroaminomethylation.[5] One of their successes is the first general efficient regioselective (linear to branched amine product ratio (*n/i*) > 98:2) hydroaminomethylation of terminal olefins by using a practical rhodium catalyst and modified Naphos and Xantphos derivatives as the controlling ligands (Scheme 1).[6]



Scheme 1. Structures of applied ligands.

Recently, we have developed two systems of tetraphosphorous ligands,[7] which are based on a biphenyl backbone and can be successfully applied in the highly regioselective hydroformylation of terminal olefins and internal olefins. Now we have a great interest to test our ligands for hydroaminomethylation reactions. Under the optimized reaction conditions we obtained 99% amine selectivity, 168 *n/i* ratio and 97.4% linear amine yield with full conversion, by using Tetrabi[7b,d] and [Rh(acac)(CO)$_2$] at 1000 S/Rh (S/R = substrate to rhodium precursor ratio). The turnover number, which refers to the number of moles of substrate that one mole of catalyst can convert before becoming inactivated, of Tetrabi was 6930 with excellent amine selectivity at 10000 S/Rh ratio, and the *n/i* ratio of amine can reach to >525 at 5000 to 10000 S/Rh ratio. Several different olefins and secondary amines have been applied successfully with high chemoselectivity (99%) and regioselectivity (>120) for the compatibility of this method.

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[**] Tetrabi = 2, 2′, 6, 6′-tetrakis ((diphenylphosphino)methyl)-1, 1′-biphenyl.

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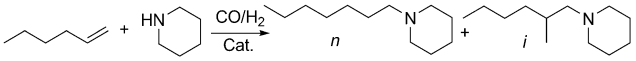
Results and Discussion

Two of our tetraphosphorous ligands: Tetrabi and TPPB,[7c] have been tested for their potential in this reaction, and three different Rh precursors have been applied at the same time for the hydroaminomethylation of 1-hexene and piperidine. 4, 5-Bis (diphenylphosphino)-9, 9-dimethylxanthene (Xantphos)[8] and 2, 2′-bis [diphenylphosphino]-methyl)-1, 1′-biphenyl (Bisbi)[9] have been used as the "standard ligand" because Xantphos is the most well-known ligand in hydroaminomethylation for its high regioselectivity, whereas Bisbi has also been studied for a long time for its hydroaminomethylation activities (Scheme 1).

As shown in Table 1, all the entries have 99% conversion, but the amine selectivities and *n/i* ratios are very different. Tetrabi can afford a *n/i* ratio of up to 198 by using $[Rh(acac)(CO)_2]$ as the precursor (Table 1, entry 1), whereas 2, 2′, 6, 6′-tetraki (dipyrrolylphosphoramidite)-1, 1′-biphenyl (TPPB) unfortunately does not achieve good selectivity; only an *n/i* ratio of 19 was achieved with $[Rh(acac)(CO)_2]$ (Table 1, entry 4). Xantphos achieved a *n/i* ratio of 100 and a linear amine yield of 95.3% with $[Rh(cod)_2]BF_4$ (cod = 1,5-cyclooctadiene; Table 1, entry 8), which shows an excellent activity of regioselective hydroaminomethylation and is consistent with the published result.[6] With regards to linear amine selectivity and yield, Bisbi does not perform well compared with Tetrabi; the best result is 146 *n/i* ratio with only 78.6% linear amine yield (Table 1, entry 10). Depending on the applied ligands and rhodium precursors, TPPB, which is an excellent ligand for the regioselective hydroformylation of 2-hexene, does not work for the regioselective hydroaminomethylation of 1-hexene. It is implied that the hydroaminomethylation reaction conditions may have a negative influence on the regioselectivity of the hydroformylation step, and there is no inevitable connection between these two reactions, especially under different reaction conditions. The reason for the significant differences between Bisbi and Tetrabi is that Tetrabi has a higher concentration of the selective catalytic species due to the presence of multiple chelating modes: a rhodium metal center can form four possible equivalent bidentate complexes[10] (Scheme 2). Compared with Xantphos, the best and highly reproducible result of the *n/i* ratio was obtained by using Tetrabi and $[Rh(acac)(CO)_2]$, whereas the formation of *N*-formylpiperidine was little higher because of its high formylation activity. Hence, a combination of Tetrabi and $[Rh(acac)(CO)_2]$ was chosen as the catalyst system for further studies.

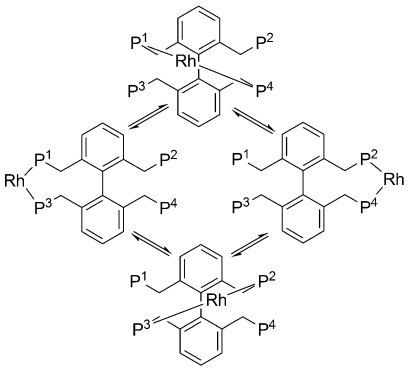
Different single solvents were introduced for the suppression of *N*-formylpiperidine (Table 2, entries 1–7). The study showed that full conversion of 1-hexene can be obtained in ethanol with a 61 *n/i* ratio and 4% of *N*-formylpiperidine (Table 2, entry 2), and the formation of *N*-formylpiperidine can be suppressed to 0.5% with 65% conversion in toluene

Table 1. Hydroaminomethylation of 1-hexene with piperidine by using different Rh precursors and ligands.[a]



Entry	Ligand [1 μmol]	Rh precursor [4 μmol]	Conv. [%]	yield [%][b]	Amine selectivity [%][c]	*N*-formyl-piperidine [%][d]	*n/i*
1	Tetrabi	$[Rh(acac)(CO)_2]$	99	90.8	92.2	7.8	198
2	Tetrabi	$[Rh(cod)_2]BF_4$	99	90.8	92.4	7.6	126
3	Tetrabi	$[Rh(cod)Cl]_2$	99	81.4	84.1	7.1	45
4	BTPP	$[Rh(acac)(CO)_2]$	99	77.6	81.7	–	19
5	BTPP	$[Rh(cod)_2]BF_4$	99	78.2	84.7	–	12
6	BTPP	$[Rh(cod)Cl]_2$	99	81.0	91.1	–	8
7	Xantphos	$[Rh(acac)(CO)_2]$	99	88.8	90.6	4.3	99
8	Xantphos	$[Rh(cod)_2]BF_4$	99	95.3	97.2	2.8	100
9	Xantphos	$[Rh(cod)Cl]_2$	99	90.3	95.8	2.2	20
10	Bisbi	$[Rh(acac)(CO)_2]$	99	78.6	79.9	6.9	146
11	Bisbi	$[Rh(cod)_2]BF_4$	99	87.7	90.1	6.4	60
12	Bisbi	$[Rh(cod)Cl]_2$	99	76.8	82.8	5.3	15

[a] Reaction condition: S/Rh = 1000, L/Rh = 4:1, [Rh] (1 μmol), 1-hexene (1 mmol), piperidine (1 mmol), in methanol/toluene (3 mL 1:1) at $CO:H_2 = 7/35$ bar, 125 °C for 4 h. [b] Yield of *n*-amine. [c] Selectivity and yield was determined by GC analysis using 2-methoxyethyl ether (0.1 mL) as an internal standard, the average value of three repeated runs and two injections per run. [d] Other by-products were the corresponding aldol product and *N*-methylpiperidine.



Scheme 2. Enhanced chelating ability of Tetrabi ligand.

(Table 2, entry 7). The best *n/i* ratio was 150, which was obtained in 2-propanol with 85% conversion and 0.5% of *N*-formylpiperidine, however the hydrogenation activity of enamine is not good enough (Table 2, entry 3). It is suggested to use a combination of ethanol and toluene or 2-propanol for the full conversion, excellent amine selectivity, *n/i* ratio, and the suppression of *N*-formylpiperidine. As shown in Table 2 (entries 9–15), ethanol mixed with toluene or ethanol mixed with 2-propanol have been tested in different ratios. A regioselectivity of 215 with 92.7% linear amine yield was achieved in 2:1 mixture of ethanol and toluene (Table 2, entry 10), and 96.8% linear amine yield was obtained applying a 2:1 mixture of 2-propanol and ethanol with the ratio of 134 (Table 2, entry 14). We chose a 2:1 mixture of 2-propanol and ethanol as the standard solvent for further optimization. As the time increased, the conversion extends to more than 99% at 6 h with 168 *n/i* ratio (Table 2,

Table 2. Optimization of the reaction conditions for the hydroaminomethylation of 1-hexene with piperidine using [Rh(acac)(CO)$_2$] and the Tetrabi ligand.[a]

Entry	Solvent	P (CO/H$_2$) [bar]	T [°C]	t [h]	L/Rh	Conversion [%]	n-Amine yield [%]	Selectivity [%][b] Amine	Enamine	N-formyl-piperidine	Aldol product	n/i
1	MeOH	7/35	125	8	4	>99	86.5	89.3	–	9.4	1.3	46
2	EtOH	7/35	125	8	4	>99	91.2	93.6	–	4	2.4	61
3	2-PrOH	7/35	125	8	4	85	77.5	91.8	2.8	0.5	4.9	150
4	EtOAc	7/35	125	8	4	65	4.6	7.1	56.2	1.2	35.5	–
5	dioxane	7/35	125	8	4	75	3.5	4.7	80.5	0.9	13.9	–
6	THF	7/35	125	8	4	70	7.4	10.5	73.3	1.3	14.9	–
7	toluene	7/35	125	8	4	65	3.3	5.1	60.2	0.5	34.2[c]	–
8	MeOH/toluene = 1:1	7/35	125	8	4	>99	90.8	92.2	–	6.4	1.4	198
9	EtOH/toluene = 1:1	7/35	125	8	4	>99	42.1	42.6	53.2	0.9	3.3	355
10	EtOH/toluene = 2:1	7/35	125	8	4	>99	92.7	94.1	1.5	2.0	2.4	215
11	EtOH/toluene = 5:1	7/35	125	8	4	>99	94.2	96.0	–	2.6	1.4	110
12	2-PrOH/EtOH = 11:1	7/35	125	8	4	>99	91.8	93.3	1.4	0.5	4.8	152
13	2-PrOH/EtOH = 5:1	7/35	125	8	4	>99	94.2	95.8	1.1	0.5	2.6	140
14	2-PrOH/EtOH = 2:1	7/35	125	8	4	>99	96.8	98.5	–	0.8	0.7	134
15	2-PrOH/EtOH = 1:1	7/35	125	8	4	>99	96.2	98.2	–	1.0	0.8	60
16	2-PrOH/EtOH = 2:1	7/35	125	4	4	90	73.5	81.7	–	0.8	17.5[c]	192
17	2-PrOH/EtOH = 2:1	7/35	125	6	4	>99	97.4	99.0	–	0.5	0.5	168
18	2-PrOH/EtOH = 2:1	7/35	125	12	4	>99	95.1	97.3	–	1.5	1.2	78
19	2-PrOH/EtOH = 2:1	7/35	125	6	2	95	92.8	98.4	–	0.9	0.7	135
20	2-PrOH/EtOH = 2:1	7/35	125	6	1	90	88.0	98.8	–	0.8	0.5	94
21	2-PrOH/EtOH = 2:1	5/25	125	6	4	95	90.5	95.9	–	0.8	3.3	145
22	2-PrOH/EtOH = 2:1	10/50	125	6	4	>99	94.1	96.4	–	3.2	0.4	71
23	2-PrOH/EtOH = 2:1	7/35	115	6	4	80	76.9	97.2	–	0.7	2.1	93
24	2-PrOH/EtOH = 2:1	7/35	120	6	4	90	86.3	96.6	–	1.6	1.8	143
25	2-PrOH/EtOH = 2:1	7/35	130	6	4	>99	94.7	96.4	–	2.1	1.5	121
26	2-PrOH/EtOH = 2:1	7/35	135	6	4	>99	94.0	96.1	–	2.7	1.2	85

[a] Reaction conditions: [Rh(acac)(CO)$_2$] (1 μmol), ligand = Tetrabi, 1-hexene (1 mmol), piperidine (1 mmol), solvent (3 mL). [b] Selectivity and yield was determined by GC analysis using 2-methoxyethyl ether (0.1 mL) as an internal standard, the average value of three repeated runs and two injections per run. [c] Major other by-products were aldehydes.

entry 17), and the *n/i* ratio drops from 192 to 78 (Table 2, entries 14 and 16–18). The ratio of ligand to rhodium precursor (L/Rh) varies from 4 to 1, and the best result was achieved using a L/Rh ratio of 4 (Table 2, entry 17). With a 1:5 ratio of CO/H$_2$, variation of the pressure showed that 7/35 bar is optimum; 5/25 bar leads to lower conversion and 10/50 bar results in a lower *n/i* ratio (Table 2, entries 21 and 22). A temperature of 125 °C is favorable because a lower temperature slows down the reaction speed and a higher temperature decreases the *n/i* ratio (Table 2, entries 23–26). Hence, under the optimized reaction conditions (1-hexene/Tetrabi/[Rh(acac)(CO)$_2$] = 1000:4:1, 1-hexene/piperidine (1:1) in a mixture of 2-propanol and ethanol (2:1, 3 mL), at CO:H$_2$ = 7/35 bar and 125 °C for 6 h) the product is generated with 99% amine selectivity, 168 *n/i* ratio, and 97.4% linear amine yield with full conversion.

Next, we studied the turnover number (the number of moles of substrate that one mole of catalyst can convert before becoming inactivated; TON) of Tetrabi to explore its activity. The S/Rh ratio was increased from 1000 to 10000, with a longer time required for the complete conversion of 1-hexene. The TON of the linear amine can reach 6930 according to the reaction with [Rh(acac)(CO)$_2$], to give 99% amine selectivity and 100% linear amine at 10000 S/Rh ratio, in which the only by-product is the branched enamine. At a ratio of 2500, 0.2% of branched enamine was produced, and the *n/i* ratio of amine was 525 with full conversion of 1-hexene (Table 3, entry 2). At the ratio of 5000, 8000, and 10000, the linear amine is actually quantitative (100% of amine product as enamine was the only by-product), whereas the conversion of 1-hexene drops from 99 to 70% (Table 3, entries 3–5). The reason for the existence of the branched enamine should be the lower hydrogenation activity of Tetrabi catalyst system for the branched enamine at such a low concentration. Thus, the *n/i* ratio of amine must be >525 at 5000 to 10000 S/Rh ratio with less than 1% branched enamine (for details, see the Supporting Information). To the best of our knowledge, such a clean linear amine has never been achieved before.

Finally, several different terminal olefins and secondary amines were introduced to demonstrate the compatibility of our method. In all cases, the reaction proceeds with an extremely high degree of chemoselectivity (99%) and amine yield (>98%) towards the linear amines. We were pleased to find that not only lower but also higher aliphatic olefins react well with piperidine to give the linear amine products with excellent selectivity (up to 208), whereas higher 1-octene needs a longer time to get full conversion (121 *n/i* ratio) (Table 4, entries 1–3). *N*-methylbenzylamine and other aliphatic secondary amines (such as morpholine or di-

Table 3. Turnover number test of Tetrabi with [Rh(acac)(CO)$_2$] for hydroaminomethylation.[a]

Entry	S/Rh	t [h]	Conv. [%]	yield [%][c]	Selectivity [%][b] Amine	Isoenamine	By-product[d]	TON[e]	n/i[f]
1	1000	6	99	97.5	99.1	–	0.9	981	156
2	2500	12	99	97.4	99.0	0.2	0.8	2450	525
3	5000	24	95	94.6	99.6	0.4	–	4731	>525[f]
4	8000	30	85	84.7	99.7	0.3	–	6780	>525[f]
5	10000	36	70	69.3	99.0	1.0	–	6930	>525[f]

[a] Reaction conditions: Tetrabi/[Rh(acac)(CO)$_2$]=4:1, 1-hexene (1 mmol), piperidine (1 mmol), 125 °C, CO/H$_2$=7/35 bar, 2-propanol/ethanol (2:1, 3 mL). [b] Selectivity and yield was determined by GC analysis using 2-methoxyethyl ether (0.1 mL) as an internal standard, the average value of three repeated runs and two injections per run. [c] Yield of *n*-amine. [d] The major by-product is *N*-formylpiperidine. [e] Turnover number was determined on the basis of GC, error is estimated at <200. [f] No branched amine observed by GC.

hexylamine) also react well with 1-hexene to give the corresponding amines in high yield and selectivity; the highest n/i ratio of 250 was obtained with dihexylamine (Table 4, entries 4–6). We have also tested the internal olefins and other functional olefins with different functional amines at the same time, and have already achieved good results; these results are beyond the scope of this article and will therefore be published in due course.

Conclusion

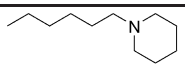
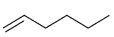
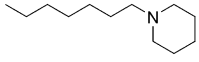
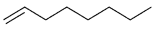
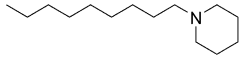
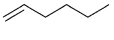
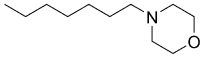
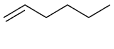
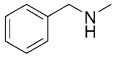
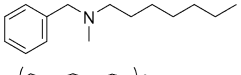
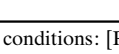
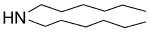
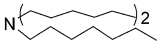
Our Tetrabi ligand was first successfully applied in the direct synthesis of amines from terminal olefins with secondary amines by hydroaminomethylation. The key to the success is the use of a Tetrabi ligand together with [Rh(acac)(CO)$_2$]. Remarkably, the highest regioselectivity (> 525) was achieved with 99% amine selectivity by using 1-hexene and piperidine as the basic reactants, whereas the TON can reach to 6930 at 10000 S/Rh ratio. A variety of terminal olefins and secondary amines have been applied successfully for the compatibility of this method. In general, aliphatic olefins and secondary amines give the corresponding linear amines with a high degree of chemoselectivity (99%), regioselectivity (>120), and amine yield (>98%).

Furthermore, we have already produced amounts of Tetrabi (100 g) and a ligand system of Tetrabi derivatives, which will probably give solid prospective support for the further application of other functional olefins and amines, such as internal olefins, styrene derivatives, and primary amines. Therefore, this atom-economic and environmentally friendly synthesis of amines with Tetrabi will be valuable to the chemical and pharmaceutical industries.

Experimental Section

General methods: All reactions and manipulations were performed in a nitrogen-filled glove box or using standard Schlenk techniques, unless otherwise noted. Anhydrous solvents were purchased from EMD chemicals Inc. [Rh(acac)(CO)$_2$] was purchased from Strem chemicals. All reagents were purchased from either Aldrich or VWR and were used without further purification. All olefins, amines, and catalysts were stored in the nitrogen filled glove box before use. Tetrabi was prepared according to the literature procedure.[7d] ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz FT-NMR spectrometer. All chemical shifts are reported in ppm. A positive ion mass spectrum of sample was acquired on a Thermo LTQ-FT mass spectrometer with an electrospray ionization source. Gas chromatography (GC) was performed on a HP 7890 series system using a β-Dex 225 column from Supelco, (30 m x 0.25 mm ID). The products were isolated from the reaction mixture by solvent evaporation and further purified by column chromatography on 200–400 mesh silica gel supplied by Sorbent technologies. All yields reported refer to GC using 2-methoxyethyl ether as an internal standard. The purity of isolated compounds was confirmed to be >98% pure by GC, NMR. The linear to branched ratios were determined by GC analysis of the crude reaction mixtures prior to flash chromatography. Compounds known in the literature were characterized by comparing their ^{1}H

Table 4. Hydroaminomethylation of various olefins and amines.[a]

Entry	Olefin	Amine	Major product	Conv. [%]	Amine[b] selectivity [%]	Amine yield[b] [%]	n/i
1				>99	99	>98	208
2				>99	99	>98	183
3[c]				>99	99	>98	121
4				>99	99	>98	167
5[c]				>99	99	>98	140
6				>99	99	>98	250

[a] Reaction conditions: [Rh(acac)(CO)$_2$] (1 μmol), Tetrabi (4 μmol), olefin (1 mmol), amine (1 mmol), 2-propanol/ethanol (3 mL, 2:1), CO/H$_2$=7/35 bar at 125 °C, for 6 h. [b] Selectivity and yield was determined by GC analysis using 2-methoxyethyl ether (0.1 mL) as an internal standard, the average value of three repeated runs and two injections per run. [c] 125 °C for 12 h.

and ^{13}C NMR data to the previously reported data. New products were further characterized by HRMS.

General procedure for the hydroaminomethylation:[7, 11] All hydroaminomethylation experiments were performed in the nitrogen-filled glove box. Tetrabi (4 μmol, 3.8 mg) and [Rh (acac)$(CO)_2$] (1 μmol, 0.1 mL of 10 mmol solution in toluene) was added to a 10 mL long neck vial with a magnetic stirring bar. The mixture was stirred for 10 min; 1-hexene (1 mmol, 0.125 mL) and piperidine (1 mmol, 0.098 mL) was then added, followed by 2-methoxyethyl ether (0.1 mL) as internal standard, 2-propanol (2 mL) and ethanol (1 mL). The reaction mixture was transferred to an autoclave vial covered with a simple lid. The autoclave was purged with H_2 three times and subsequently charged with CO (7 bar) and H_2 (35 bar). The reaction was carried out at 125°C for 6 h. After 6 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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