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Rh-Catalyzed Hydroformylation of Alkynes to α,β-Unsaturated Aldehydes

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Abstract: A couple of pyrrolyl-based phosphoramidites featuring a binaphthyl backbone have been used as bidentate ligands in Rh-catalyzed hydroformylation of alkynes, to afford a range of α,β-unsaturated aldehydes in generally good yields (up to 94%) with excellent chemo- and stereoselectivities (E/Z up to > 99/1) under mild reaction conditions.

Key words: rhodium; hydroformylation; alkynes; α,β-unsaturated aldehyde

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The hydroformylation is commonly referred to the addition of hydrogen and carbon monoxide across olefins to generate oxygenated products, which are valuable chemicals in industry and versatile intermediates for synthesis[1-2]. Hydroformylation is also currently the largest industrial homogeneous catalytic process, with a global annual production of ca 10 million tons of oxo chemicals[3]. So far most of the works in this area from both academia and industry have focused on the hydroformylation of olefins, whereas the corresponding hydroformylation reaction of alkynes has been much less explored[4-5]. Hydroformylation of alkynes can provide a straightforward access to enals that are versatile synthetic intermediates, however, pioneering studies in 1970s on this reaction furnished the enals only in low yields with poor chemoselectivity. One of the major hurdles that hampers the further development in alkyne hydroformylation is the hard suppression of the byproduct formation, e. g., saturated aldehydes and alkenes, generated by over-reduction[6]. Since 1995, significant breakthroughs have been achieved in this reaction with transition metal catalysts based on Rh[7], Co[8], or Pd[9]. In 1995s, Buchwald and coworkers reported the use of a Rh/Biphephos catalytic system for the hydroformylation of symmetrical dialkyl-substituted alkynes to the corresponding enals with good chemoselectivities[7a]. Later on, Breit et al developed a chemo- and stereoselective hydroformylation of dialkyl- and diaryl-substituted alkynes as well as some terminal alkynes, using a rhodium complex with an electron-poor phosphine ligand bearing self-assembling H-bonding moieties[7d]. Very recently, Zhang and coworkers reported a Rh-catalyzed hydroformylation of symmetrically disubstituted alkynes using a tetraphosphoramidite ligand, to afford the corresponding α,β-unsaturated aldehydes in high yields with excellent efficiency[7f]. Significant progresses in the hydroformylation of alkynes have also been made using Pd complexes as the catalysts. Hidai et al developed a heterobimetallic catalyst, $[PdCl_2(PCy_3)_2]/[Co_2(CO)_8]$ for catalytic

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hydroformylation reaction of alkynes by taking advantage of the synergistic effect between the two metals[8]. Recently, Beller and coworkers reported an efficient hydroformylation of alkynes with a palladium catalyst bearing a *N*-phenylpyrrole-based bisphosphine ligand, wherein hydrogenation of alkynes were largely suppressed[9]. In the context of hydroformylation of alkynes, further development of readily accessible catalysts with a wide substrate adaptability is highly desirable. As an ongoing effort of our studies on Rh-catalyzed hydroformylation reactions[10], herein we report a readily accessible rhodium/phosphoramidite catalyst for efficient hydroformylation of alkynes. Under mild conditions, a range of enals were synthesized in generally high yields with good to excellent chemo- and stereoselectivities.

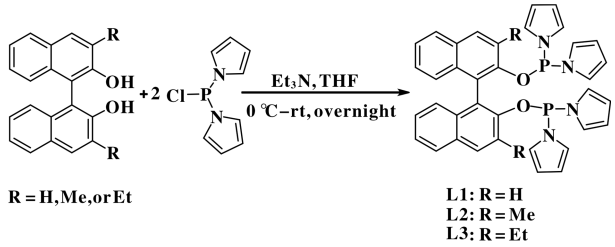
1 Experimental

1.1 General

Unless otherwise noted, all manipulations involving air- or moisture-sensitive compounds were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. Solvents were dried according to standard procedures. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on an Agilent or Varian (400 MHz) spectrometers. GC analyses were carried out on an Agilent 6890N or an Agilent 7820A gas chromatograph using a DM-Wax column or HP-5 column. High resolution mass spectra (HRMS-ESI) were recorded on BRUKER DALTONICS APEX III. BIPHEPHOS, Xantphos, Rh(acac)$(CO)_2$, phenylacetylene and diphenylacetylene were purchased from commercial sources and were used as received without further purification, while the other alkynes used in this study were synthesized according to the reported procedures[11].

1.2 The synthesis of ligands L1-L3

Ligands **L1-L3** were synthesized by following a literature procedure[12]. A solution of the racemic diol (1.0 mmol) in THF (2 mL) was added dropwise to a solution of 1,1′-(chlorophosphinediyl) bis (1*H*-pyrrole) (595.7 mg, 3.0 mmol) and triethylamine (0.42 mL, 3.0 mmol) in THF (1 mL) at 0 ℃. After stirring the mixture at room temperature for 12 h, the precipitated $Et_3N \cdot HCl$ salt was filtered off, and the filtrate was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE/EA = 10/1) to afford the product.



1.3 Characterization data for Ligand L1-L3[12]

2,2′-Bis (di (1*H*-pyrrol-1-yl) phosphinooxy)-1,1′-binaphthyl (**L1**): White solid, 73% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 8.8 Hz, 4H), 7.43-7.39 (m, 2H), 7.33-7.21 (m, 4H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.48-6.45 (m, 8H), 6.13-6.07 (m,8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.1, 149.0, 133.6, 130.8, 130.5, 128.1, 127.1, 125.8, 125.2, 122.36, 122.34, 122.32, 121.1, 121.06, 120.96, 210.89, 119.3, 119.2, 112.09, 112.06, 112.04, 112.0. ^{31}P NMR (161 MHz, $CDCl_3$): 109.0 ppm.

1,1′,1″,1‴-(3,3′-Dimethyl-1,1′-binaphthyl-2,2′diyl) bis (oxy) bis (phosphinetriyl) tetrakis (1*H*-pyrrole) (**L2**): White solid, 70% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.15-7.13 (m, 2H), 6.71-6.49 (m, 8H), 6.18-6.06 (m, 8H), 1.89 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.18, 150.13, 150.07, 133.0, 131.0, 130.7, 130.3, 127.2, 126.4, 125.8, 125.2, 122.47, 122.44, 122.41, 121.2, 121.1, 121.07, 120.9, 120.8, 120.7, 111.89, 111.87, 111.85, 111.33, 111.31, 111.28, 17.2. ^{31}P NMR (161 MHz, $CDCl_3$): 106.2 ppm.

1,1′,1″,1‴-(3,3′-Diethyl-1,1′-binaphthyl-2,2′-diyl) bis (oxy) bis (phosphinetriyl) tetrakis (1*H*-pyrrole) **L3**: White solid, 75% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.55 (s, 2H), 7.40-7.36 (m, 2H), 7.25-7.21 (m, 2H), 7.15-7.13 (m, 2H), 6.66-6.49 (m, 8H), 6.12-

6.04 (m, 8H), 2.32-2.13 (m, 4H), 1.04 (t, J = 7.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.92, 149.85, 149.79, 135.7, 132.9, 131.1, 128.7, 127.4, 126.3, 125.9, 125.1, 122.38, 122.34, 122.31, 121.1, 121.04, 120.9, 120.8, 120.7, 120.6, 111.78, 111.76, 111.73, 111.36, 111.33, 111.31, 23.3, 13.4. ^{31}P NMR (161 MHz, $CDCl_3$): 105.7 ppm.

1.4 Typical procedure for the hydroformylation of alkynes

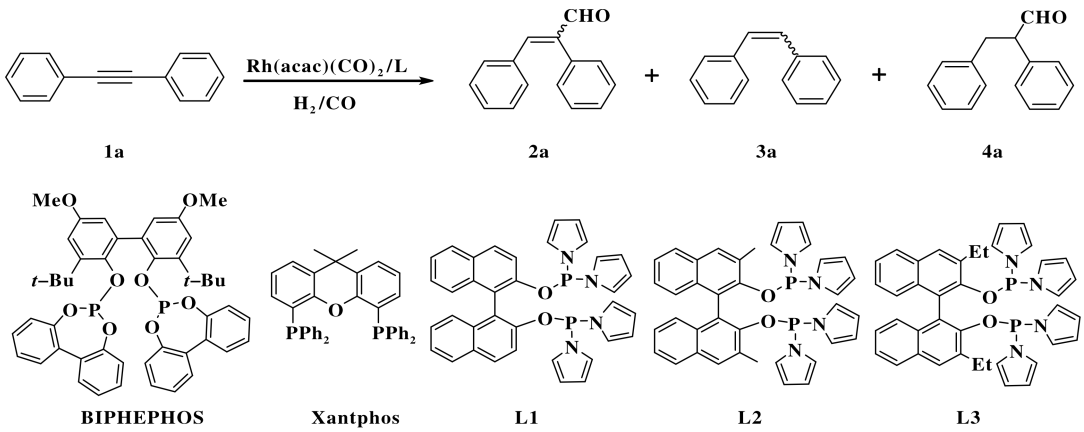
In a glove box, a Parr autoclave equipped with a magnetic stirring bar was charged with the alkyne (0.5 mmol), **L1** (0.005 mmol), Rh(acac)$(CO)_2$(0.01 M in toluene, 0.25 mL, 0.002 5 mmol), and toluene (1.0 mL). The autoclave was sealed and purged three times with H_2 gas, and subsequently charged with H_2 (10 bar) and CO (10 bar). The autoclave was then heated at 60 ℃ (oil bath) for 12 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The conversion, the quantity of the hydrogenation product, and E/Z ratio of the enal were determined by GC analysis of an aliquot of the mixture using p-xylene (31 μL, 0.25 mmol) as the internal standard. The reaction mixture was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel with EA/petroleum ether as the eluent to give the enal.

2 Results and discussion

2.1 Optimization of reaction conditions

We initially examined the effect of different P-ligands using Rh(acac)$(CO)_2$ as the catalyst precursor for the hydroformylation of 1,2-diphenylethyne (**1a**). The reactions were conducted in toluene in the presence of 0.5% of the catalyst (Rh/ligand molar ratio 1∶2) under 20 bar syngas pressure (H_2/CO = 10∶10) at 60 ℃, and the results were summarized in Table 1. It is notable that under otherwise identical conditions, ligands with enhanced π-acidity, e. g., bisphosphite BIPHEPHOS and bisphosphoramidites

Table 1 Optimization of reaction conditions [a]



Entry	Ligand	Conv. / % [b]	**2a**(Yield/%, E/Z) [b]	**2a/3a/4a** [b]
1	BIPHEPHOS	94	78 (97.5/2.5)	83.4/15.9/0.7
2	XantPhos	67	49 (95.6/4.4)	92.3/7.5/0.2
3[c]	**L1**	>99	93 (98.8/1.2)	94.4/5.3/0.3
4	**L2**	95	90 (94.6/5.4)	92.6/7.1/0.3
5	**L3**	91	85 (97.0/3.0)	92.6/7.0/0.4
6[d]	**L1**	>99	90 (98.2/1.8)	89.8/9.0/1.2

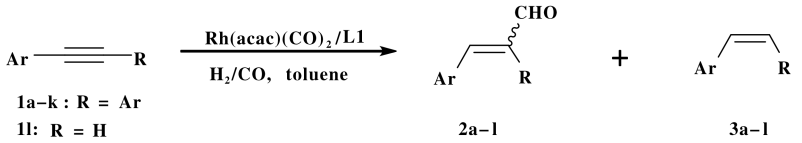
a. Reaction conditions: **1a**(0.5 mmol), H_2/CO = 10∶10 (bar/bar), s/c = 200, Rh(acac)$(CO)_2$(0.5 mol%), molar ratio of Rh/L = 1∶2, toluene (1.0 mL), 60 ℃, 12 h; b. Conversion of **1a**, yield and E/Z ratio of **2a**, and molar ratios of **2a/3a/4a** were determined by GC using p-xylene as the internal standard; c. The yield of isolated **2a** was 90%; d. T= 80 ℃

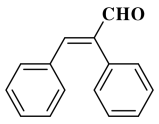
L1-L3, exhibited a significantly higher catalytic activity (conversions of **1a**> 91%, entries 1, 3-5) than that of bisphosphine XantPhos (conversion 67%, entry 2). For all the tested ligands the formation of saturated aldehyde **4a** was negligible (< 0.5%), and in each case the sterereoselectivity was excellent (> 94.6/5.4, entries 1-5). The bisphosphate BIPHEPHOS furnished the enal **2a** in reasonably good yield (78%), albeit somehow compromised by co-generation of a significant amount of hydrogenation byproduct **3a** (16%, entry 1). The BINOL-derived bis-*N*-pyrrolyphosphoramidites **L1-L3**, on the other hand, generally demonstrated a remarkably high yield of enal **2a** (> 85%) and much better chemoselectivity (**2a/3a/4a**>92.6/7.1/0.3, entries 3-5). Overall, **L1**, without any substituents on the 3,3'-positions of its binaphthyl skeleton, turned out to be optimal in terms of catalytic activity, chemo- and stereoselectivities. In this case, full conversion of 1,2-diphenylethyne **1a** was achieved, delivering **2a** in high yield (93%) with excellent *E/Z* ratio (98.8/1.2) and chemoselectivities (**2a/3a/4a** = 94.4/5.3/0.3, entry 3). Further examination of this system by elevation of the reaction temperature to 80 ℃, however, led to a slight decline in the chemoselectivity for **2a**, as a result of the increased formation of hydrogenation byproduct **3a** (entry 6).

2.2 Substrate scope of alkynes

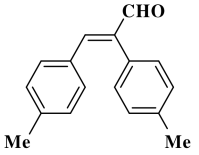
With the optimized conditions in hand, we proceeded to study the substrate scope of this reaction, using 0.5% Rh(acac)$(CO)_2$ and 1% **L1** as catalyst in the presence of CO/H_2 (10 : 10 bar) at 60 ℃ for 12 h. As shown in Table 2, a variety of symmetrically disubstituted alkynes, including alkynes with diaryl-

Table 2 Synthesis of the α,β-unsaturated aldehydes [a]

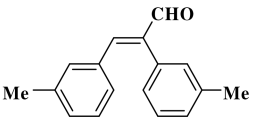




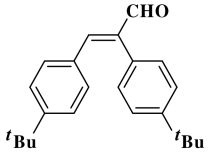
100% conv., 2a/3a 95:5
2a: 90%, E/Z = 98.8/1.2



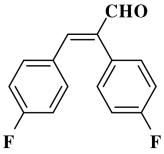
100% conv., 2b/3b 97:3
2b: 94%, E/Z > 99/1



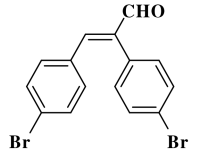
100% conv., 2c/3c 96:4
2c: 92%, E/Z > 99/1



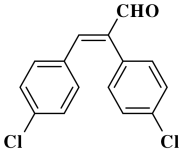
100% conv., 2d/3d 97:3
2d: 93%, E/Z = 94/6



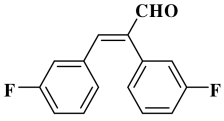
100% conv., 2e/3e 98:2
2e: 88%, E/Z = 98.8/1.2



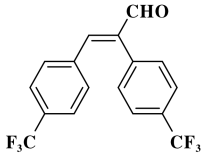
100% conv., 2f/3f 87:13
2f: 84%, E/Z > 99/1



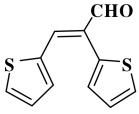
100% conv., 2g/3g 87:13
2g: 85%, E/Z > 99/1



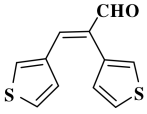
97% conv., 2h/3h 86:14
2h: 83%, E/Z > 99/1



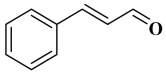
100% conv., [b]2i/3i 64:36
2i: 64%, E/Z > 99/1



100% conv., 2j/3j 84:16
2j: 83%, E/Z = 98/2



100% conv., 2k/3k 95:5
2k: 93%, E/Z = 97/3



66% conv., 2l: 15%

a. Reaction conditions: Substrate **1** (0.5 mmol), H_2/CO = 10 : 10 (bar/bar), s/c = 200, Rh(acac)$(CO)_2$(0.5 mol%), Rh/**L1** = 1 : 2, toluene (1.0 mL), 60 ℃, 12 h. The yields were for the isolated enals **2a-l**. The conversion values, molar ratios of **2/3**, and *E/Z* ratios of enals **2** were determined by GC using *p*-xylene as the internal standard. The saturated aldehyde was found to be negligible in each case; b. 24 h

and diheteroaryl-substitutuents (**1a-k**), are amenable to the procedure, to afford the corresponding (*E*)-enals **2a-k** in good to excellent yields (64% ~94%) with excellent *E*/*Z* ratios (≥ 94/6). In these cases, the formation of saturated aldehydes was found to be negligible. Electron-donating substituents on the aromatic ring were well tolerated, and the corresponding enals **2b-2d** were obtained in excellent yields, and the alkene formation was effectively suppressed (**2**/**3** ≥ 96/4). In the cases of diarylalkynes with halogens (F, Cl, Br) on the aryl rings, chemoselectivity towards the formation of corresponding enals **2e-2h** were also quite high (**2**/**3** = 86/14 to 98/2). The reaction with the diarylalkyne bearing CF_3 groups on the aryl rings was less satisfactory, however, furnished the corresponding enal **2i** in moderate yield (64%) along with some amount of the alkene. Furthermore, 2- or 3-thienyl disubstituted alkynes were also compatible with the protocol, affording the corresponding enals **2j-2k** in excellent yields with high selectivities. We have also examined the hydroformylation of phenylacetylene, a terminal arylacetylene that was known to be challenging for this transformation owing to the many potential by-products involved (>5). Unfortunately, under the otherwise identical conditions, the corresponding *E*-enal **2l** was only isolated in modest yield (15%).

2.3 Experimental characterization data for products

(*E*)-2, 3-diphenylacrylaldehyde (**2a**)[7d]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.79 (s, 1H), 7.43 (s, 1H), 7.41-7.39 (m, 3H), 7.29-7.26 (m, 1H), 7.24-7.19 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.9, 150.2, 141.8, 134.0, 133.3, 130.7, 130.2, 129.3, 128.8, 128.5, 128.3 ppm.

(*E*)-2, 3-di-p-tolylacrylaldehyde (**2b**)[7d]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.73 (s, 1H), 7.32 (s, 1H), 7.24-7.20 (m, 2H), 7.14-7.03 (m, 6H), 2.39 (s, 3H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.2, 150.1, 140.9, 140.7, 137.9, 131.4, 130.7, 130.4, 129.6, 129.2, 129.1, 21.4, 21.3 ppm.

(*E*)-2, 3-di-m-tolylacrylaldehyde (**2c**)[7d]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.75 (s, 1H), 7.34 (s, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.21-7.19 (m, 1H), 7.11-6.97 (m, 6H), 2.36 (s, 3H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.1, 150.3, 141.8, 138.4, 138.0, 133.9, 133.3, 131.7, 131.0, 129.7, 129.0, 128.7, 128.3, 127.7, 126.2, 21.4, 21.2 ppm.

(*E*)-2,3-bis(4-(tert-butyl)phenyl)acrylaldehyde (**2d**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.76 (s, 1H), 7.49-7.47 (m, 2H), 7.36 (s, 1H), 7.30-7.28 (m, 2H), 7.23-7.17 (m, 4H), 1.40 (s, 9H), 1.31 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.3, 153.8, 151.0, 150.2, 140.8, 131.3, 130.7, 130.4, 128.8, 125.7, 125.4, 34.8, 34.6, 31.3, 31.0 ppm. HRMS (ESI) m/z: Calcd. For $C_{23}H_{29}O^+$: 321.2213, Found: 321.2212 $[M+H]^+$.

(*E*)-2, 3-bis (4-fluorophenyl) acrylaldehyde (**2e**)[7d]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.75 (s, 1H), 7.37 (s, 1H), 7.23-7.10 (m, 6H), 6.98-6.93 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.5, 163.5 (d, J_{C-F} = 252 Hz), 162.7 (d, J_{C-F} = 247 Hz), 149.2, 140.4 (d, J_{C-F} = 1.4 Hz), 132.6 (d, J_{C-F} = 8.0 Hz), 131.2 (d, J_{C-F} = 7.5 Hz), 130.0 (d, J_{C-F} = 3.3 Hz), 128.7 (d, J_{C-F} = 3.1 Hz), 116.1 (d, J_{C-F} = 21 Hz), 115.8 (d, J_{C-F} = 21.6 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ −108.4, −112.9 ppm.

(*E*)-2, 3-bis (4-bromophenyl) acrylaldehyde (**2f**)[7d]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.73 (s, 1H), 7.55-7.53 (m, 2H), 7.41-7.39 (m, 2H), 7.34 (s, 1H), 7.08-7.05 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.0, 148.9, 141.0, 132.5, 132.2, 132.0, 131.9, 131.0, 124.9, 122.9 ppm.

(*E*)-2, 3-bis (4-chlorophenyl) acrylaldehyde (**2g**)[7d]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.75 (s, 1H), 7.42-7.39 (m, 2H), 7.37 (s, 1H), 7.27-7.24 (m, 2H), 7.16-7.13 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.1, 148.9, 140.8, 136.4, 134.6, 132.1, 131.7, 131.2, 130.8, 129.2, 128.9 ppm.

(*E*)-2, 3-bis (3-fluorophenyl) acrylaldehyde (**2h**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.77 (s, 1H), 7.43-7.38 (m, 2H), 7.28-7.23 (m, 1H), 7.14-7.09 (m, 1H), 7.06-6.85 (m, 5H). ^{13}C

NMR ($CDCl_3$, 100 MHz): δ 193.0, 163.0 (d, J_{C-F} = 247 Hz), 162.4 (d, J_{C-F} = 245 Hz), 148.8 (d, J_{C-F} = 3.0 Hz), 141.4 (d, J_{C-F} = 2.1 Hz), 135.6 (d, J_{C-F} = 8.7 Hz), 134.8 (d, J_{C-F} = 8.2 Hz), 130.6 (d, J_{C-F} = 7.7 Hz), 130.1 (d, J_{C-F} = 8.2 Hz), 126.5 (d, J_{C-F} = 3.1 Hz), 125.0 (d, J_{C-F} = 3.0 Hz), 117.3 (d, J_{C-F} = 20.7 Hz), 116.9 (d, J_{C-F} = 22 Hz), 116.3 (d, J_{C-F} = 21.6 Hz), 115.6 (d, J_{C-F} = 20.8 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ -111.9 ppm. HRMS (EI) m/z: Calcd. For $C_{15}H_{10}F_2O^+$: 244.0700, Found: 244.0696 $[M]^+$.

(*E*)-2,3-bis(4-(trifluoromethyl)phenyl)acrylaldehyde (**2i**)[7d]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.82 (s, 1H), 7.69-7.67 (m, 2H), 7.54 (s, 1H), 7.52-7.49 (m, 2H), 7.33-7.29 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.7, 148.6, 142.1, 136.8, 136.3, 131.8 (q, J_{C-F} = 32.5 Hz), 130.7 (q, J_{C-F} = 32.8 Hz), 130.6, 129.9, 125.9 (q, J_{C-F} = 4.1 Hz), 125.6 (q, J_{C-F} = 3.8 Hz), 123.9 (q, J_{C-F} = 271 Hz), 123.5 (q, J_{C-F} = 271 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ -62.7, -63.1 ppm.

(*Z*)-2, 3-di (thiophen-2-yl) acrylaldehyde (**2j**)[7d]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.69 (s, 1H), 7.73 (s, 1H), 7.55 (dd, *J* = 1.6, 5.6 Hz, 1H), 7.45-7.43 (m, 1H), 7.39-7.38 (m, 1H), 7.18 (dd, *J* = 3.6, 8.4 Hz, 1H), 7.06-7.03 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.8, 144.2, 137.6, 135.2, 133.0, 132.1, 131.7, 128.9, 128.3, 127.6, 127.2 ppm.

(*E*)-2, 3-di (thiophen-3-yl) acrylaldehyde (**2k**)[7d]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.70 (s, 1H), 7.44-7.40 (m, 3H), 7.30 (dd, *J* = 1.2, 2.8 Hz, 1H), 7.20 (dd, *J* = 2.8, 5.2 Hz, 1H), 6.98 (dd, *J* = 1.2, 4.8 Hz, 1H), 6.81 (dd, *J* = 1.2, 5.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.4, 143.7, 136.4, 135.3, 132.8, 130.7, 128.2, 128.0, 126.1, 125.9, 125.2 ppm.

Cinnamaldehyde (**2l**)[7d]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.70 (d, *J* = 8.0 Hz, 4H), 7.58-7.56 (m, 2H), 7.50-7.42 (m, 4H), 6.70 (dd, *J* = 7.6, 16 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.6, 152.7, 133.9, 131.2, 129.0, 128.5, 128.4 ppm.

3 Conclusions

In summary, we have developed an efficient rhodium/phosphoramidite catalyst system for hydroformylation of alkynes. Under mild conditions, a variety of symmetrically diaryl- or diheteroaryl-substituted alkynes were smoothly transformed into the corresponding enals in good yields with excellent chemo- and stereoselectivities. Further extension of the catalyst system to other alkynes are ongoing in our labs.

References:

[1] a. Roelen Otto. US [P] 2327066, 1943; GE [P] 849548, 1938/1952.

b. Zhu Wei-jun(朱维君), Liu Da-cai(刘大财), Yang Nian-fa(阳年发), *et al.* Synthesis of enantiopure C3-symmetric lig and derived from BINO land its application in enantioselective addition of diethylzinc to aromatic aldehydes(联萘酚衍生 C3 对称的手性配体的合成及其在诱导二乙基锌与芳基醛的不对称加成反应中的应用)[J]. *J Mol Catal (China)*(分子催化), 2015, **29**(4): 299-306.

c. Liao Ben-ren(廖本仁), Fan Man-man(范曼曼), Gong Lei(龚 磊), *et al.* Study on hydroformylation of butene with diphosphite and diphosphine mixed-ligands modified catalysts(双亚磷酸酯和双膦混合配体在丁烯氢甲酰化反应中的应用研究)[J]. *J Mol Catal (China)*(分子催化), 2015, **29**(1): 19-26.

[2] a. Weissermel K, Arpe H J. Industrial Organic Chemistry [M]. VCH: New York, 1993.

b. Roelen O. GE [P] 949, 548, 1938.

c. Breit B, Seiche W. Recent advances on chemo-, regio- and stereoselective hydroformylation [J]. *Synthesis*, 2001, **1**: 1-36.

d. Claver C, van Leeuwen P W N M. Rhodium Catalyzed Hydroformylation [M]. Kluwer Academic Publishers, Dordrecht, The Netherlands, 2002.

e. Ungváry F. Application of transition metals in hydroformylation annual survey covering the year 2004 [J]. *Coord Chem Rev*, 2005, **249**(24): 2946-2961.

[3] a. Tolman C A, Faller J W. Homogeneous Catalysis with Metal Phosphine Complexes [M]. 81, ed. Pignolet, L. H. Plenum, New York, 1983.

b. Kohlpaintner C W, Frohning C D. Applied Homogeneous Catalysis with Organometallic Compounds 1 [M]. ed. Cornils B, Herrmann W A. VCH, Weinheim, 1996,

vol. 1.

c. Franke R, Selent D, Börner A. Applied hydroformylation [J]. *Chem Rev*, 2012, **112**(11): 5675-5732.

[4] a. Castillón S, Fernández E. Rhodium Catalyzed Hydroformylation [M]. ed. van Leeuwen P W N M, and Claver C. Kluwer, Dordrecht, 2000. 178-182.

b. Wang Li-ping(王丽苹), Wang Gong-ying(王公应). Progress in metal-organic frameworks based on the carboxyl ligands as the catalyst(羧基配体金属有机骨架材料作为催化剂的研究进展) [J]. *J Mol Catal (China)* (分子催化), 2015, **29**(3): 275-287.

[5] a. Glorius E F. Science of Synthesis [M], Vol. 25 (Ed.: R. Bruckner), Georg Thimeme, Stuttgart, 2007. 733.

b. Shao Zheng-feng(邵正锋), Li Chuang(李 闯), Liang Chang-hai(梁长海). Preparation of Pd-Fe catalysts via galvanic replacement reaction and their catalytic hydrogenation performance(置换反应制备 Pd-Fe 双金属催化剂及其催化加氢性能) [J]. *J Mol Catal (China)* (分子催化), 2014, **28**(1): 47-53.

[6] a. Fell B, Beutler M. Hydroformylation of alkynes with rhodiumcarbonyl triphenylphosphine complex catalysts [J]. *Tetrahedron Lett*, 1972, **13**: 3455-3456.

b. Botteghi C, Salomon C. Conclusive evidence for direct hydroformylation of triple bond catalyzed by chiral rhodium-complexes [J]. *Tetrahedron Lett*, 1974, **15**: 4285-4288.

c. Doyama K, Joh T, *et al*. Carbonylation of enynes under hydroformylation conditons catalyzed by rhodium carbonyl-A new method for synthesis of cyclic enones [J]. *Bull Chem Soc Jpn*, 1988, **61**(12): 4353-4360.

d. Wuts P G M, Ritter A R. Anovel synthesis of spironolactone. an application of the hydroformylation reaction [J]. *J Org Chem*, 1989, **54**(21): 5180-5184.

e. Campi E M, Jackson W R, *et al*. A hydroformylation route to β-substituted pyrroles [J]. *Tetrahedron Lett*, 1991, **32**(8): 1093-1094.

f. Nombel P, Lugan N, *et al*. Vinyl group transfer via insertion: cluster-mediated production of poly(phenylacetylene), enynes, and α,β-unsaturated aldehydes [J]. *Organometallics*, 1994, **13**(12): 4673-4675.

[7] a. Johnson J R, Cuny G D, *et al*. Rhodium-catalyzed hydroformylation of internal alkynes to α,β-unsaturated aldehydes [J]. *Angew Chem Int Ed*, 1995, **34**(16): 1760-1761.

b. Van den Hoven B G, Alper H. Regioselective hydroformylation of enynes catalyzed by a zwitterionic rhodium complex and triphenyl phosphite [J]. *J Org Chem*, 1999, **64**(11): 3964-3968.

c. Van den Hoven B G, Alper H. The first regioselective hydroformylation of acetylenic thiophenes catalyzed by a zwitterionic rhodium complex and triphenyl phosphite [J]. *J Org Chem*, 1999, **64**(20): 9640-9645.

d. Agabekov V, Seiche W, *et al*. Rhodium-catalyzed hydroformylation of alkynes employing a self-assembling ligand system [J]. *Chem Sci*, 2013, **4**(6): 2418-2422.

e. Zhang Z P, Wang Q, *et al*. Selective rhodium-catalyzed hydroformylation of alkynes to α,β-unsaturated aldehydes with a tetraphosphoramidite ligand [J]. *Org Lett*, 2016, **18**(13): 3290-3293.

[8] Ishii Y, Miyashita K, *et al*. Selective hydroformylation of internal acetylenes by $PdCl_2(PCy_3)_2$: Remarkable synergistic effect of cobalt [J]. *J Am Chem Soc*, 1997, **119**(27): 6448-6449.

[9] Fang X J, Zhang M, *et al*. Selective palladium-catalyzed hydroformylation of alkynes to α,β-unsaturated aldehydes [J]. *Angew Chem Int Ed*, 2013, **52**(52): 4645-4649.

[10] a. Jia X F, Wang Z, *et al*. Spiroketal-based phosphorus ligands for highly regioselective hydroformylation of terminal and internal olefins [J]. *Chem Eur J*, 2012, **18**(48): 15288-15295.

b. Jia X F, Wang Z, *et al*. Novel spiroketal-based diphosphite ligands for hydroformylation of terminal and internal olefins [J]. *Catal Sci Technol*, 2013, **3**(8): 1901-1904.

[11] Chuentragool P, Vongnam K, *et al*. Calcium carbide as a cost-effective starting material for symmetrical diarylethynes via Pd-catalyzed coupling reaction [J]. *Tetrahedron*, 2011, **67**(42): 8177-8182.

[12] Jia Xiao-fei (贾肖飞). Doctoral dissertion of lanzhou institute of chemical physics chinese academy of sciences (中国科学院兰州化学物理研究所博士论文) [D]. 2013.

铑催化炔烃氢甲酰化反应合成 α, β-不饱和醛

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摘要: 以一类 BINOL 衍生的双齿亚磷酰胺为配体, 用于铑催化的炔烃氢甲酰化反应中. 在温和的反应条件下, 对于一系列对称的双芳基或双杂芳环取代的炔烃底物的催化反应, 以较高的产率(最高 94%)以及优秀的化学和立体选择性($E/Z > 99/1$)得到相应的 α, β-不饱和醛.

关键词: 铑; 炔烃; 氢甲酰化; α, β-不饱和醛

欢迎订阅《分子催化》

《分子催化》是由中国科学院主管、科学出版社出版, 由中国科学院兰州化学物理研究所主办的向国内外公开发行的学术刊物. 主要报导有关分子催化方面的最新进展与研究成果. 辟有学术论文、研究简报、研究快报及进展评述等栏目. 内容侧重于络合催化、酶催化、光助催化、催化过程中的立体化学问题、催化反应机理与动力学、催化剂表面态的研究及量子化学在催化学科中的应用等. 工业催化过程中均相催化剂、固载化的均相催化剂、固载化的酶催化剂等的活化、失活和再生, 以及用于新催化过程的催化剂的优选与表征等方面的稿件, 本刊也很欢迎. 读者对象主要是科研单位及工矿企业中从事催化工作的科技人员、研究生、高等院校化学系和化工系师生. 欢迎相关专业人员投稿.

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