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Influence of electrostatic repulsive force and electron-withdrawing effect in ionic diphosphine on regioselectivity of rhodium-catalyzed hydroformylation of 1-octene

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ABSTRACT

The neutral diphosphine of **1** and the corresponding ionic diphosphine of **2** after quaternization **1** by MeOTf were prepared and investigated as the wide bite angle and bulky steric ligands to control the regioselectivity in $Rh(acac)(CO)_2$-catalyzed hydroformylation of 1-octene. As for **2**, due to the electrostatic repulsive force of the two positive charges, the involved two-PPh_2 were located in *trans*-position with the relatively longer *P*1...*P*2 distance [8.0231(11) Å] to prefer to aa-site coordination in trigonal bipyramid H(alkene)Rh(CO)(P–P) intermediate, which renders less bulky steric hindrance for the regioselectivity to linear aldehyde as a result of low *L*/*B* ratio of 1.9. Due to the strong electron-withdrawing effect from the positive-charged imidazolium rings on the neighbored P-atoms, **2** with strong π-acceptor ability can develop π-backdonation interaction between Rh and P linkage to favor the dissociation of CO ligand and facilitate the selectivity to nonanals. In contrast, **1** with no electrostatic repulsive effect and less steric hindrance, the two-PPh_2 were able to be conveniently located in *cis*-position with the relatively shorter *P*1...*P*2 distance [*P*1...*P*2, 6.2096(10) Å], which corresponded to the preferential linear regioselectivity with *L*/*B* = 7.1. The *in situ* high pressure spectroscopy analysis indicated that the involvement of **1** in $Rh(acac)(CO)_2$-catalyzed hydroformylation of 1-octene could greatly facilitate the formation and stability of the active Rh–H species (ν2047 cm^{-1}).

1. Introduction

Hydroformylation is an atom efficient route for the addition of syngas to alkenes toward aldehydes which is one of the most industrially important homogeneously catalyzed reactions [1–3]. Mononuclear rhodium complexes are the most efficient catalysts for this reaction and a great deal of work has been devoted to the improvement of reaction rates and selectivity by ligand design [1–9]. The *n*-regioselectivity of the catalyst can be enhanced by incorporation of sterically demanding substituents in the organic backbone of the ligands. Diphosphines/diphosphites have more preference for occupying specific sites in rhodium intermediate, in which the chelate backbone restricts the P–M–P bite angle [10–18]. The sterically hindered, chelating diphosphorus ligands were reported predominantly to induce the formation of *n*-aldehydes due to possessing the wide bite angle and the ability to form stereoisomers with temperature-dependent atropisomerism. For example, BISBI (with a bite angle near 120°) was firstly investigated by Casey et al. to show the good correlation between bite angle and high linear regioselectivity [14]. Later on, van Leeuwen and co-workers developed a series of tricyclic wide bite angle ligands like Xantphos with a range of bite angles from 102 to 131° to explore the effect of bite angles on linear selectivity of hydroformylation [15–18]. As summarizes in Table 1 [15,16], Xantphos with a bite angle near 110° gave the best regioselectivity (97.7% linear aldehyde), which was competitive to BISBI (89.6% linear aldehyde). Diphosphorus ligands with a preferred bite angle near 120° would be expected to preferentially occupy two equatorial sites (ee) on a trigonal bipyramid hydrido-rhodium intermediate for the preferential regioselectivity to the primary (alkyl)$Rh(CO)_2$(P–P) complex (corresponding to the linear aldehydes) according to the catalytic mechanism of hydroformylation [13,16]. Certainly, diphosphorus ligands in which the two phosphorous atoms demonstrate axial and axial sites (aa) or equatorial or axial sites (ea) in a trigonal

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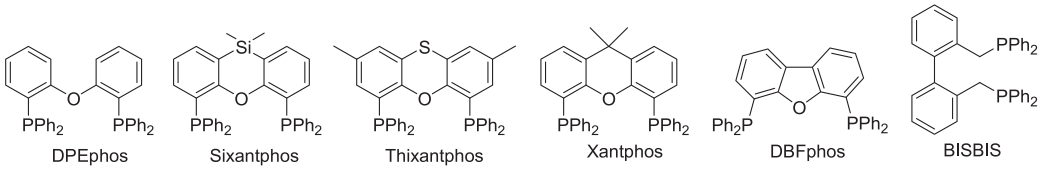
Table 1
Summary of the reported various diphosphines with their bite angles and linear aldehyde selectivity correlation for hydroformylation of 1-octnene at 80 °C.[a]



Ligand	Calcd. bite angle (β_n, °)	Flexibility range (°)	Normal/branched	*n*-Aldehyde (%)	Isomerization (%)	TOF (h^{-1})
DPEphos	102.2	86–120	6.7	87.0	0	250
Sixantphos	108.7	93–132	34	94.2	3	168
Thixantphos	109.4	94–130	41	93.0	4.7	445
Xantphos	111.7	97–135	53.5	97.7	0.5	800
DBFphos	131.1	117–147	3	71.0	5.5	125
BISBIS	122.6	101–148	80.5	89.6	9.3	850

[a] Refs. [15,16].

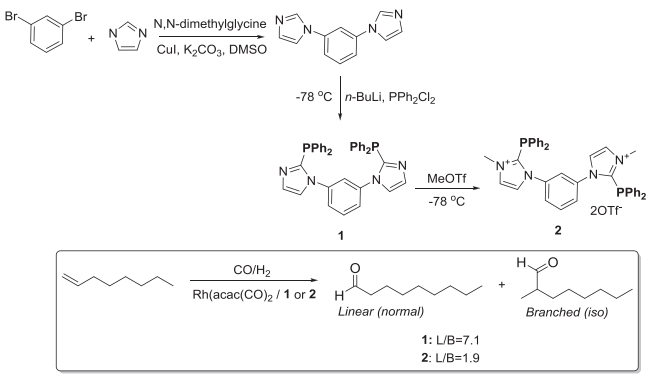
bipyramid hydrido-rhodium intermediate with a preferred bite angle near 180° or 90° account for the increased ratio to branched products.

The above mentioned information highlights us to study the affecting factors on the bite angle of diphosphorus ligands and then the corresponding relationship between bite angle and linear regioselelctivity. To our knowledge, the most examples to tune the bite angles of diphosphorus ligands are based on the modification of the organic backbones with different bulky organic groups [12–20]. In this paper, the effect of electric charges in diphosphines was considered for the first time to control the bite angle to tailor the regioselectivity of hydroformylation. For this purpose, the neutral and ionic diphosphines of **1** and **2** was synthesized according the method reported by Barthes et al. [21]. **2** was the resultant compound of **1** after quaternization **1** by MeOTf (methyltrifluoromethane sulfonate) at 3N-position of imidazolyl ring, in which the two-PPh_2 groups were vicinal to the two positive charged imidazolium rings (Scheme 1). The technique of *in situ* high pressure spectroscopy was applied to investigate the state of the active Rh–H intermediate under 'real' reaction condition to correlate to the observed activity over **1** and **2** for hydroformylation of 1-octene.

2. Experimental

2.1. Reagents and analysis

The chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co., Ltd. and Alfa Aesar China, and used as received. FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. The ^1H and ^{31}P NMR spectra for the analyses of the common compounds were recorded on a Bruker Avance 400 spectrometer. The ^{31}P NMR spectra for the analyses of the phosphine-selenides (Fig. 2) were recorded on a Bruker Avance 500 spectrometer. The ^{31}P NMR spectra were referenced to 85% H_3PO_4 sealed in a capillary tube as an internal standard. The electrospray ionization mass spectra (ESI-MS) were performed on a TSQ Quantum Access MAX mass spectrometer (Thermo Scientific). Elemental analyses (CHN) were obtained by using an Elementar Vario EL III instrument. Gas chromatography (GC) was performed on a SHIMADZU-2014 equipped with a DM-1 capillary column (30 m × 0.25 mm × 0.25 μm). GC–mass spectrometry (GC–MS) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector.



Scheme 1. Synthesis of the diphoshines of **1** and **2** for rhodium-catalyzed hydroformylation of 1-octene.

2.2. Synthesis

1 and **2** were prepared according to the procedures reported by Barthes et al. [21] with some modifications.

2.2.1. 1, 3-Bis(2′-diphenylphosphino-3′-methylimidazolium) benzene (*1*)

Under N_2 atmosphere, imidazole (8.4 g, 125 mmol), K_2CO_3 (27.6 g, 200 mmol), *N*,*N*-dimethylglycine (2.06 g, 20 mmol), CuI (2.4 g, 12.5 mmol), and 1,3-dibromobenze (11.8 g, 50 mmol) were added sequentially into the distilled DMSO (100 mL) and then the obtained mixtures were stirred vigorously at 125 °C for 48 h. After cooled down to room temperature, the reaction mixture was treated with 400 mL deionized water, and then extracted with ethyl acetate (200 × 4 mL). The combined organic phase was dried with anhydrous sodium sulfate. The residue after removal of the organic solvent in vacuo was then purified through silica gel column chromatography with eluent of dichloromethane/ethyl acetate (4:1) to give 1,3-bis(1-imidazolyl) benzene as the white powder (5.8 g, yield 55 wt%). ^1H NMR (δ, ppm, acetone-d_6): 8.24 (s, 2H, NC*H*N), 7.95–7.94 (t, 1H, *J* = 2 Hz, NCC*H*CN), 7.75–7.74 (t, 2H, *J* = 1.5 Hz, NCHC*H*NPh), 7.71–7.63 (m, 3H, NCC*HCHCH*CN), 7.15 (s, 2H, NC*H*CHNPh).

Under nitrogen atmosphere, a solution of 1,3-bis(1-imidazolyl) benzene (3.15 g, 15 mmol), tetramethylethylenediamine (TMEDA, 3.84 g, 33 mmol) in 65 mL of absolute THF (refluxed with sodium and distilled freshly before use) was cooled to −78 °C, and then 15 mL of *n*-BuLi (2.2 M in hexane, 33 mmol) was added dropwise. The obtained reaction mixture after stirring vigorously for 1 h was added with chlorodiphenylphosphine (PPh_2Cl, 7.28 g, 33 mmol) dropwise. The resultant suspension was stirred for another 1 h at −78 °C and then warmed up to room temperature naturally. After quenching excess *n*-BuLi with 100 mL deionized water, the mixture was stripped of solvent in vacuo and then extracted with dichloromethane (100 × 3 mL). The combined organic phase was dried by anhydrous sodium sulfate and