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SHORT COMMUNICATION

Synthesis of the Novel Ligand Tris-(3,4-dimethoxylphenyl) phosphine and Its Catalytic Performance in 1-Dodecene Hydroformylation

YUAN Maolin, FU Haiyan, LI Ruixiang, CHEN Hua*, LI Xianjun

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China

Abstract: Tris-(3,4-dimethoxylphenyl)phosphine (TDMOPP) was synthesized and used as a ligand for the homogenous hydroformylation of 1-dodecene. The effects of the P/Rh molar ratio and reaction temperature on the activity and regioselectivity were investigated. The results showed that the activity of TDMOPP was about two times higher than that of the traditional triphenylphosphine at a low P/Rh and temperature.

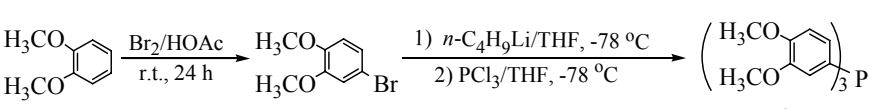
Key words: tris-(3,4-dimethoxylphenyl)phosphine; rhodium complex; 1-dodecene; hydroformylation

Hydroformylation is one of the most important industrial processes catalyzed by transition metal complexes, and over 8 million tons of oxo product aldehydes and their derivative alcohols are produced every year [1]. They are widely used as raw materials to produce plasticizers, surfactants, and detergents [2,3]. The design and preparation of ligands is an important part of transition metal complex research. The structure and properties of the ligand greatly influence the performance of the metal complexes [4–7]. For example, *ortho*-substituted triphenylphosphine as a rhodium complex ligand excludes the coordination of substrates to rhodium at low P/Rh molar ratios [8] resulting in low catalytic activity. However, electron-donating *para*-substituted triphenylphosphine allows strong coordination to rhodium and the formation of a complete saturation complex with low activity at relatively high P/Rh molar ratios [9]. In this paper, we report on the synthesis of a novel ligand tris-(3,4-dimethoxylphenyl)phosphine (TDMOPP) by the addition of a methoxy group to the *meta*- and *para*-positions on the phenyl ring of triphenylphosphine (TPP) for the first time. Our aim is to tune the electronic and steric properties to modulate the catalytic performance for hydroformylation.

Phosphine is air and moisture sensitive and all reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere. The synthetic route for the ligand TDMOPP is shown in Scheme 1.

^{1}H NMR and ^{31}P NMR spectra were recorded on a Bruker Avance 300 MHz NMR instrument with $CDCl_3$ as solvent and relative to internal Me_4Si and external H_3PO_4 (85%) standards. The multiplicities are indicated by s (singlet), d (doublet), t (triplet), and m (multiplet). MS spectra were obtained using a Finnigan MAT4510 instrument.

To a solution of 1,2-dimethoxybenezene (3.0 g, 22 mmol) in acetic acid (40 ml) was added a 20 ml acetic acid solution containing bromine (3.6 g, 23 mmol) at low temperature over a period of 3 h. The mixture was continuously stirred at room



Scheme 1. Synthetic route for tris-(3,4-dimethoxylphenyl) phosphine (TDMOPP).

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***Corresponding author.** Tel/Fax: +86-28-85412904; E-mail: scuhchen@163.com
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temperature for 24 h and then poured into 100 ml of ice-water. The aqueous phase was extracted with CH_2Cl_2 (30 ml × 3). The combined extracts were washed in turn with a saturated Na_2CO_3 solution, water, and brine. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated in vacuum. The residue was distilled under reduced pressure to give 4-bromo-1,2-dimethoxybenzene (3.5 g, 74.3%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 4.15 (s, 3H, CH_3O), 4.26 (s, 3H, CH_3O), 6.73–7.10 (m, 3H, Ar); MS: *m/z* 216/218 (M^+).

Subsequently, 5.2 ml of a hexane solution containing *n*-C_4H_9Li (2.89 mol/L, 15.0 mmol) was added dropwise to a solution of 4-bromo-1,2-dimethoxybenzene (3.2 g, 15.0 mmol) in THF (20 ml) at –78 °C over 30 min. Then, freshly distilled phosphorus trichloride (1.4 ml, 5.0 mmol) in 10 ml THF was added dropwise over 15 min at such a rate that the reaction temperature did not exceed –50 °C. The reaction mixture was warmed to room temperature within 1 h and left overnight. The mixture was then quenched with 20 ml of 10% aqueous NH_4Cl. The resulting light yellow solution was evaporated to dryness under reduced pressure. The residue was extracted with CH_2Cl_2 (30 ml × 3). The combined organic solution was washed with deoxygenated brine and the CH_2Cl_2 layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The crude product was recrystallized from C_2H_5OH to give TDMOPP as white needle-shaped crystals in good yield (4.7 g, 71.9%) based on 4-bromo-1,2-dimethoxybenzene. ^{1}H NMR ($CDCl_3$): δ 3.75 (s, 9H, OCH_3), 3.87 (s, 9H, OCH_3), 6.78–6.88 (m, 9H, Ar); ^{31}P NMR ($CDCl_3$): δ –4.48; MS: *m/z* 442 (M^+).

The catalytic performance of the ligand TDMOPP was investigated using a 60 ml stainless steel autoclave equipped with a magnetic stirrer. After being charged with the ligand, the catalyst precursor Rh(acac)$(CO)_2$, 1-dodecene, and toluene, the reaction mixture was degassed three times with syngas. The autoclave was then pressurized to the desired pressure with syngas. The catalyst was formed in situ with the ligand TDMOPP and Rh(acac)$(CO)_2$. After stirring for 1 h at the desired temperature, the autoclave was quickly cooled in an ice-water bath to room temperature and carefully depressurized. The hydroformylation products were analyzed using an HP 1890II GC equipped with an FID and a capillary column (SE-30, 30 m × 0.25 mm × 0.25 μm).

Because hydroformylation is highly dependent on the reaction conditions, the effect of P/Rh molar ratio was evaluated using 1-dodecene as a substrate. The conversion and the L/B ratio (molar ratio of linear aldehyde to branched aldehyde) are given in Table 1. At a lower P/Rh ratio, the catalytic system already showed a high reaction rate. The conversion of 1-dodecene increased with an increase in the P/Rh molar ratio and it showed a decline when the P/Rh ratio exceeded 7.5. The reason may be that TDMOPP contains six electron-donating methoxy groups, which coordinate to rhodium well and many catalytically active species are formed at a low P/Rh ratio and at low temperature resulting in high reactivity. The number of catalytically active species formed by TDMOPP and rhodium increased and in turn enhanced the catalytic activity further when the P/Rh ratio increased. When the P/Rh ratio increased, the charge and steric hindrance at the rhodium center increased and this increases the difficulty of 1-dodecene coordination to rhodium. As a result, the conversion of 1-dodecene decreased. The effect of the P/Rh ratio on L/B was also obvious and the L/B increased with an increase in the P/Rh molar ratio [10], especially over 7.5. Considering the conversion of 1-dodecene and L/B, the optimized P/Rh molar ratio was found to be 5.0 as the conversion of 1-dodecene was as high as 97.0%. The widely used TPP was also studied for comparison. From Table 1 the Rh-TDMOPP catalyst is shown to be superior to the Rh-TPP catalyst for the hydroformylation of 1-dodecene. The results show that the conversion of 1-dodecene for TDMOPP was about two times higher than that obtained for TPP at a low P/Rh molar ratio and temperature. We attribute the difference to two factors. One is that the TDMOPP that contains no *ortho*-substituent is capable of avoiding the exclusion of coordination of 1-dodecene to rhodium. The other may be that the bulky methoxy that is *meta*-substituted on the phenyl ring prevents the complete saturation coordination of TDMOPP at the rhodium center at a high P/Rh ratio. In the rhodium complex with a low coordination number, the shortage of charge at the rhodium center is satisfied by the electron-rich methoxy at the para position on the phenyl ring. As a result, the coordination of TDMOPP to rhodium forms a stable catalytically active species and promotes the reaction, which results in higher

Table 1 Effect of molar ratio of phosphine to rhodium on 1-dodecene hydroformylation

n(L)/*n*(Rh)	Conversion of 1-dodecene (%)	Product distribution (%)			L/B	TOF[d] (h^{-1})
		Aldehyde[a]	Isomerization[b]	Alkane[c]		
0.0	5.6	99.0	0.4	0.6	1.8	77
2.5	92.8	100.0	0.0	0.0	3.0	1276
5.0[e]	32.7	100.0	0.0	0.0	2.6	450
5.0	97.0	98.4	1.2	0.4	2.8	1334
7.5	90.0	100.0	0.0	0.0	2.9	1238
10.0	75.3	99.2	0.0	0.8	3.7	1035

Reaction conditions: [Rh] = 1.0×10^{-3} mol/L, toluene 5.0 ml, 1-dodecene 2.0 ml, 70 °C, initial pressure 1.5 MPa (CO/H_2 = 1), 1 h.

[a]Selectivity for aldehyde product of 1-dodecene. [b]Selectivity for isomerization product of 1-dodecene, mainly 2-dodecene. [c]Selectivity for hydrogenation product of 1-dodecene. [d]Mole of converted olefin per mole rhodium per hour. [e]TPP as ligand.

Table 2 Effect of temperature on 1-dodecene hydroformylation

Temperature (°C)	Conversion of 1-dodecene (%)	Product distribution (%)			L/B	TOF (h^{-1})
		Aldehyde	Isomerization	Alkane		
60[a]	29.8	100.0	0.0	0.0	2.6	410
60	72.6	100.0	0.0	0.0	3.0	998
70	97.0	98.4	1.2	0.4	2.8	1334
80	98.4	95.8	2.2	2.0	2.8	1353
100	91.2	92.1	5.1	2.8	2.7	1254
110	88.1	80.5	12.9	6.6	2.5	1211

Reaction conditions: n(L)/n(Rh) = 5.0, others are the same as in Table 1.

[a]A TPP was used instead of TDMOPP as a ligand.

reactivity. Because of the bulky catalytically active species formed by rhodium and TDMOPP containing three bulky methoxy groups *meta*-substituted on three phenyl rings, the L/B was a little higher for TDMOPP than that for TPP.

Temperature also has an important role in hydroformylation. The results listed in Table 2 demonstrate that the conversion of 1-dodecene increases with a rise in temperature and reaches 98.4% at 80 °C. It then declines with a further increase in the temperature. The optimum temperature ranged between 70 and 80 °C was achieved for 1-dodecene hydroformylation using Rh-TDMOPP as a catalyst. It has been shown that the reaction is controlled by the coordination and dissociation of the ligand at the metal center. At high temperature, the rate of TDMOPP dissociation from rhodium increases. The catalytic active species is, therefore, unstable and unfavorable for the catalytic cycle. In addition, the high temperature results in low solubility of syngas and 1-dodecene in toluene. Two factors cause a decrease in the conversion of 1-dodecene with a further rise in temperature. However, the selectivity for aldehydes always decreases with an increase in temperature [11]. The coordination number and steric hindrance at the rhodium center is reduced with rise in temperature resulting in a low L/B. Table 2 also indicates that TDMOPP still has excellent activity at temperatures as low as 60 °C.

In conclusion, the ligand TDMOPP that was studied in this work can be synthesized easily with relatively high yield in a two-step procedure starting from inexpensive 1,2-dimethoxybenzene. Its catalytic activity demonstrates that the ligand TDMOPP largely promotes the hydroformylation of 1-dodecene under mild conditions. The catalyst formed in situ with the rhodium precursor Rh(acac)$(CO)_2$ and the ligand TDMOPP was superior to that using TPP as a ligand. The conversion of 1-dodecene with TDMOPP is much higher than that with TPP at a low P/Rh molar ratio and at low temperature. We are investigating the use of TDMOPP in other fields.

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