新型配体三(3,4-二甲氧基苯基)膦的合成及其 Rh 配合物在 1-十二烯氢甲酰化反应中的催化性能

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摘要: 将合成的三(3,4-二甲氧基苯基)膦(TDMOPP)用作 Rh 催化剂配体, 并用于 1-十二烯氢甲酰化反应, 考察了膦/铑比和反应温度对 Rh-TDMOPP 催化剂活性和选择性的影响。结果表明, 在膦/铑比与反应温度较低时, Rh-TDMOPP 活性是 Rh-三苯基膦催化剂的 3 倍。

关键词: 三(3,4-二甲氧基苯基)膦; 铑配合物; 1-十二烯; 氢甲酰化反应

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

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Abstract: Tris-(3,4-dimethoxyphenyl)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-dimethoxyphenyl)phosphine; rhodium complex; 1-dodecene; hydroformylation

烯烃氢甲酰化反应是工业上最重要的过渡金属络合催化过程之一^[1], 由其生产的醛及其衍生物醇的年产量超过了 800 万吨, 广泛用作合成增塑剂、表面活性剂和洗涤剂等的原料^[2,3]。在过渡金属络合催化研究中, 膦配体的设计合成是重要内容之一。膦配体结构和性质对络合催化剂性能影响很大^[4~7]。例如, 在低膦/铑比下, 配合物中邻位取代三苯基膦配体的邻位取代基就产生封闭底物向金属配位的现象^[8], 导致催化剂活性低; 在较高膦/铑比下, 对位供电取代的三苯基膦又会与金属发生强配位而生成低活性的饱和配合物^[9]。本文将甲氧基引入三苯基膦

中苯环的对位和间位, 首次合成了新型的三(3,4-二甲氧基苯基)膦配体(TDMOPP), 以期提高 Rh-TDMOPP 在烯烃氢甲酰化反应中的催化性能。

利用传统方法合成 TDMOPP 膦配体, 路线如图式 1 所示。¹H 和 ³¹P 核磁共振(NMR)谱采用 Bruker Avance 300 MHz 型核磁共振仪测试, 以 CDCl₃ 作溶剂。¹H NMR 以 TMS 作内标, ³¹P NMR 以 85% H₃PO₄ 作外标。质谱用 Finnigan MAT4510 型质谱仪测定。

首先将 3.0 g 1,2-二甲氧基苯(AR, 成都长征试剂)溶于 40 ml 冰醋酸中。在冰水浴冷却下, 于 3 h

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图式 1 TDMOPP 的合成路线

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

内将 3.6 g 溴 (AR, 成都科龙试剂) 与少量冰醋酸配成的溶液经恒压滴液漏斗漫漫滴加到反应瓶中. 室温反应 24 h 后, 将反应液倒入 100 ml 冰水浴中, 用 30 ml CH_2Cl_2 萃取三次, 分出有机层. 有机层分别用水和饱和食盐水洗涤、无水 MgSO_4 干燥、过滤. 滤液蒸除 CH_2Cl_2 后, 减压蒸馏, 收集 178 °C, 1 333 Pa 的馏分, 得无色液体 4-溴-1,2-二甲氧基苯 3.5 g, 产率 74.3%. ^1H NMR (CDCl_3): δ 4.15 (s, 3H, OCH_3), 4.26 (s, 3H, OCH_3), 6.73~7.10 (m, 3H, C_6H_3); MS: m/z 216/218 (M^+).

在氮气保护下, 将 3.2 g 4-溴-1,2-二甲氧基苯和 20 ml 经脱水去氧的 THF (AR, 成都长征试剂) 加入到 50 ml 干燥的两颈烧瓶内. 在 -78 °C 向瓶中慢慢滴加 5.2 ml $n\text{-C}_4\text{H}_9\text{Li}$ 的己烷溶液 (2.89 mol/L, Acros), 反应 0.5 h 后, 滴加 1.4 ml PCl_3 的 THF 溶液, 1 h 内升至室温, 反应过夜. 向瓶中滴加 20 ml 脱氧的 10% NH_4Cl 水溶液水解终止反应, 减压除去 THF. 用 30 ml 脱氧的 CH_2Cl_2 萃取三次, 合并有机相. 有机相用无水 MgSO_4 干燥, 过滤. 滤液真空去除 CH_2Cl_2 , 然后用脱氧处理的乙醇重结晶, 得白色针状晶体 TDMOPP 4.7 g, 产率 71.9%. ^1H NMR (CDCl_3): δ 3.75 (s, 9H, OCH_3), 3.87 (s, 9H, OCH_3), 6.78~6.88 (m, 9H, C_6H_3); MS: m/z 442 (M^+); ^{31}P NMR (CDCl_3): δ -4.48.

烯烃氢甲酰化反应在 60 ml 自制的高压釜中进行. 将一定量的乙酰丙酮羰基铑 (纯度 > 99.5%, Acros)、膦配体、甲苯 (AR, 成都长征试剂) 和 1-十二烯 (纯度 > 95%, Fluka) 加入高压釜中, 用合成气 (西南化工研究院, 99.99%, $n(\text{H}_2)/n(\text{CO}) = 1$) 置换 3~5 次, 再充合成气至设定压力, 催化剂原位生成. 升至反应温度, 搅拌, 反应一定时间后终止反应. 用惠普上海分析仪器公司的 HP1890 II 型气相色谱仪分析产物组成, SE-30 毛细管色谱柱 (30 m $\times$ 0.25 mm $\times$ 0.25 μm), FID 检测器, SC1100 色谱工作站, 按归一化法定量.

表 1 为膦/铑摩尔比对催化剂活性与选择性的影响. 由表 1 可见, 在较低膦/铑比时, 催化体系表现出较高的 1-十二烯转化率, 并随膦/铑比的增加而增加, 至 7.5 以后略有下降. 这是由于配体 TDMOPP 分子中含有 6 个供电子甲氧基, 具有强的配位能力, 因此, 在膦/铑摩尔比和温度较低时即能形成大量催化活性物种, 表现出高的催化活性. 随着膦/铑比的增加, 膦与铑配位形成的催化活性物种增多, 使催化活性进一步提高. 但当膦/铑比增大到一定程度后, 中心原子铑周围电荷增加、空间位阻增大, 反应物分子不易与活性中心络合, 反而使活性下降. 另外, 正/异比随膦/铑比增加而增加^[10], 在膦/铑比 > 7.5 以后增加较快. 综合考虑, 最佳膦/铑摩尔比为 5.0.

表 1 膦/铑摩尔比对 1-十二烯氢甲酰化反应的影响

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

$n(\text{L})/n(\text{Rh})$	Conversion of 1-dodecene (%)	Product distribution (%)			L/B ^d	TOF ^e (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 ^f	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: $[\text{Rh}]$ 1.0×10^{-3} mol/L, toluene 5.0 ml, 1-dodecene 2.0 ml, 70 °C, initial pressure 1.5 MPa ($\text{CO}/\text{H}_2 = 1$), 1 h.

^aSelectivity for aldehyde product of 1-dodecene. ^bSelectivity for isomerization product of 1-dodecene, mainly 2-dodecene. ^cSelectivity for hydrogenation product of 1-dodecene. ^dMolar ratio of linear to branched aldehyde. ^eMole of converted olefin per mole rhodium per hour. ^fTPP (triphenylphosphine) as ligand.

由表 1 还可以看出, 以 TDMOPP 为配体的铑催化剂其活性和选择性都优于以三苯基膦 (TPP) 为配体的铑催化剂, 前者的活性是后者的近 3 倍. 一方面, 由于 TDMOPP 分子中不存在邻位甲氧基, 因而可避免因邻位取代而导致 1-十二烯向金属铑配位的封闭现象; 另一方面, 具有空间位阻的间甲氧基可防止配体在较高膦/铑比时生成低活性的饱和配合物, 在未饱和配位的金属络合物中, 间甲氧基的供电不足可由对位的甲氧基来弥补. 因此, TDMOPP 与 Rh 配位形成稳定的活性中间体, 从而表现出较高的催化活性. 同时, TDMOPP 分子中 3 个间甲氧基的存在又使得空间位阻较大, 易形成体积较大的催化活性物种, 因而产物醛的正/异比略高于以 TPP 为配体的铑催化剂.

表 2 为反应温度对 Rh-TDMOPP 催化 1-十二

烯氢甲酰化反应性能的影响. 由表可见, 当反应温度低于 80 °C 时, 升高温度可加快催化活性物种的形成, 催化剂活性随温度升高而增加, 80 °C 时, 1-十二烯转化率达最高, 为 98.4%. 反应温度高于 80 °C 时, 催化剂活性开始下降. 可见, 适宜反应温度为 70~80 °C. 研究表明, 反应是由配体的配位和解离两个因素共同决定的. 温度过高, 配体的解离加快, 催化活性组分中间态不稳定, 不利于催化循环, 表现为催化剂活性随温度的进一步升高而下降. 另外, 高温将导致合成气和 1-十二烯溶解度下降, 也会造成 1-十二烯转化率下降. 而成醛选择性则随温度的升高而逐渐下降^[11]. 温度升高, 配位数减小, 中心 Rh 原子周围空间位阻减小, 正/异比下降. 还可以看出, 在 60 °C 低温下, Rh-TDMOPP 催化剂仍表现出较 Rh-TPP 高的催化性能.

表 2 温度变化对 1-十二烯氢甲酰化反应的影响

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: $n(\text{L})/n(\text{Rh}) = 5.0$, others are the same as in Table 1. ^aA TPP was used instead of TDMOPP as a ligand.

综上所述, 配体 TDMOPP 可由廉价的 1,2-二甲氧基苯原料经两步直接合成, 产率较高. 在 Rh-TDMOPP 催化的 1-十二烯氢甲酰化反应中, 通过间甲氧基和对甲氧基的电子效应与空间效应的共同作用, 配体 TDMOPP 能在膦/铑比和反应温度均较低条件下与 Rh 形成稳定的催化活性物种, 表现出较 Rh-TPP 高的催化性能. 目前, 我们正在寻找该配体在其它催化领域中的应用.

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英 译 文

English Text

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-dimethoxyphenyl)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.

^1H 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-dimethoxybenzene (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 temperature for 24 h and then poured into 100 ml of ice-water. The aqueous phase was extracted with CH_2Cl_2 (30 ml $\times$ 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. ^1H 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 $n\text{-C}_4\text{H}_9\text{Li}$ (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 $\times$ 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 $\text{C}_2\text{H}_5\text{OH}$ to give TDMOPP as white needle-shaped crystals in good yield (4.7 g, 71.9%) based on 4-bromo-1,2-dimethoxybenzene. ^1H 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 $\text{Rh}(\text{acac})(\text{CO})_2$, 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 $\text{Rh}(\text{acac})(\text{CO})_2$. 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 $\times$ 0.25 mm $\times$ 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 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 $\text{Rh}(\text{acac})(\text{CO})_2$ 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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