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非膦钯催化 Suzuki 偶联反应

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摘要: 考察了非膦体系 Pd/哌嗪衍生物在超声波辅助下催化 Suzuki 偶联反应的催化活性。在以碳酸钾为碱助剂, 甲醇作溶剂, 超声波辅助, 30℃水浴中, 催化剂 Pd/哌嗪衍生物(1.0 mol%)能在短时间内催化芳溴衍生物和活化芳氯衍生物与苯硼酸偶联, 以优秀的收率得到相应的偶联产物。

关键词: 钯催化; Suzuki 偶联; 超声波; 哌嗪衍生物

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PHOSPHINE-FREE PALLADIUM CATALYZED SUZUKI CROSS-COUPLING REACTION

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Abstract: The catalytic activities of phosphine-free palladium/piperazine derivatives for Suzuki cross-coupling reaction assisted with ultrasound were investigated. The coupled products of aryl bromides and aryl chlorides derivatives coupled with phenylboronic acid were obtained with an excellent amount, which were catalyzed by phosphine-free palladium/piperazine derivatives (1.0 mol%) in shorter reaction time under 30℃, using K₂CO₃ as a base, methanol as a solvent and piperazine derivative as ligand.

Key words: palladium catalysis; Suzuki cross-coupling; ultrasound; piperazine derivative

近20多年来, Pd、Ni催化的卤代芳烃偶联反应取得巨大进展, 已广泛应用到工业和实验室规模的精细化学品的制备中^[1-2]。2010年诺贝尔化学奖颁发给因发展出“钯催化的交叉偶联方法”的三位科学家^[1,3-4]。Suzuki偶联反应是构筑联芳烃类化合物最常用的方法^[1-2,5], 已广泛应用于有机光电材料^[6-9]、天然产物^[10-17]及药物^[18-22]的制备中。钯催化 Suzuki偶联中最常见高效配体为单齿、高位阻和供

电子能力强的膦配体, 但含膦配体大多数对水和空气敏感, 不仅合成困难, 也使催化反应条件苛刻^[23-24]。非膦钯催化体系催化偶联反应一直是该领域的研究热点, 已经获得普遍使用^[25-26]。Mohanty报道含N, O配体能有效催化Suzuki和Heck偶联, 但反应温度高, 反应时间长^[27]。含N,O配体促进钯催化偶联反应顺利进行的关键在于能否生成催化活性物种。超声波是由超声波发生器发出的高频振荡信号, 由于

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超声波的空化作用所产生的局部高温高压可以促进电子转移,从而明显地加快反应速度。超声波在一些有机反应中有明显的促进作用^[28],在非磷配体催化的Suzuki偶联反应中也有不俗表现^[29]。本研究以超声波促进的4-甲基溴苯与苯硼酸偶联为探针反应,研究了易于合成、空气稳定、空间位阻大的N,O配体1,4-双(2-羟基-3,5-二-叔-丁基苯基)哌嗪作非磷钯在超声波促进的催化Suzuki偶联反应体系配体的催化规律。

1 实验部分

1.1 仪器与试剂

所有反应均在N₂气氛、Schlenk瓶中进行。溶剂用前经无水处理;四氢呋喃、1,4-二氧六环在N₂气氛下,在钠和二苯甲酮条件下蒸馏。溴苯、氯苯及其衍生物,苯硼酸, Pd₂(dba)₃, PdCl₂, Pd(OAc)₂等试剂从Aldrich或Arcos化学公司购买,未经纯化直接使用; Cs₂CO₃, KOBu^t, K₃PO₄, K₂CO₃, NaOBu^t, Na₂CO₃等碱助剂均为市售化学纯,未经进一步纯化;柱层析使用200~300目硅胶。核磁共振谱是在Bruker-400型核磁共振仪上测定(TMS为内标, CDCl₃为溶剂);超声波发生器选用上海超声波仪器厂的CQ-250型超声波仪(输出功率250 W,工作频率33 kHz);气相色谱分析用Agilent 6890气相色谱仪测定(SE-30毛细管柱,长50 m,内径0.32 mm,膜厚0.5 μm,内标正癸烷)。

1.2 合成及表征

1,4-双(2-羟基-3,5-二-叔-丁基苯基)哌嗪依据文献^[27]的方法制备,结合文献报道的¹H、¹³C NMR,辅以COSY和HSQC对化合物做出详尽归属。¹H NMR (400 MHz, CDCl₃): δ 10.70 (br s, 2H, OH), 7.22 (s, 2H, phenyl), 6.83 (s, 2H, phenyl), 3.71 (s, 4H, CH₂), 2.95-2.39 (br s, 8H, NC₄H₈N), 1.41 (s, 18H, 'Bu), 1.27 (s, 18H, 'Bu); ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 154.0 (s, phenyl), 140.8 (s, phenyl), 135.6 (s, phenyl), 123.5 (s, phenyl), 123.1 (s, phenyl), 120.3 (s, phenyl), 62.0 (s, CH₂), 52.1 (s, NCH₂), 34.9 (s, C(Me)₃), 34.2 (s, C(Me)₃), 31.7 (s, CH₃),

29.6 (s, CH₃)。

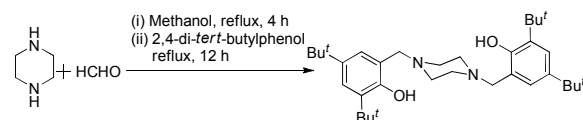


图1 1,4-双(2-羟基-3,5-二-叔-丁基苯基)哌嗪的合成

Fig.1 Synthesis of 1,4-bis(2-hydroxy-3,5-di-tert-butylbenzyl) piperazine

1.3 钯催化的Suzuki偶联反应

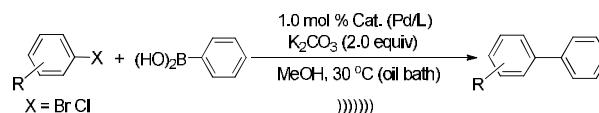


图2 Suzuki 偶联反应

Fig.2 Suzuki Cross Coupling reaction

实验步骤: 在N₂气氛下,干燥的Schlenk瓶中依次加入Pd(II)(1.0 mol%), 配体(1.3 mol%), 碱(1.0 mmol), 甲醇(3.0 mL), 30℃下, 搅拌反应半小时, 冷至室温, 依次加入卤代芳烃(0.5 mmol), 苯硼酸(0.75 mmol), 及内标正癸烷(0.5 mmol), 超声波清洗器中超声辐射一段时间, 气相色谱跟踪反应。反应结束后, 冷至室温, 加入5 mL水, 乙醚萃取水相(3 mL×3), 合并有机相, 无水硫酸钠干燥, 过滤浓缩, 柱层析分离提纯(乙酸乙酯/石油醚, V:V=1:10), 得到偶联产物, 结构经¹H NMR鉴定。

2 结果讨论

2.1 Suzuki 偶联产物表征

4-三氟甲基联苯: ¹H NMR(CDCl₃, 400 MHz, TMS): δ 7.33 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.62 (s, 4H)。

2-甲基联苯: ¹H NMR(CDCl₃, 400 MHz, TMS): δ 2.27 (s, 3H), 7.24~7.28 (m, 3H), 7.33 (t, *J* = 7.2 Hz, 4H), 7.41 (t, *J* = 7.4 Hz, 2H)。

联苯: ¹H NMR(CDCl₃, 400 MHz, TMS): δ 7.35 (t, *J* = 5.6 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 4H), 7.59 (d, *J* = 7.2 Hz, 4H)。

4-甲基联苯: ¹H NMR(CDCl₃, 400 MHz, TMS): δ 2.40 (s, 3H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H)。

4-乙酰基联苯: ^1H NMR(CDCl_3 , 400 MHz, TMS): δ 2.57 (s, 3H), 7.18 (s, 1H), 7.33~7.63 (m, 5H), 7.97 (d, J = 8.0 Hz, 2H), 8.19(d, J = 7.6 Hz, 1H)。

2,4-二甲基联苯: ^1H NMR(CDCl_3 , 400 MHz, TMS): δ 2.15 (s, 3H), 2.26 (s, 3H), 6.95~7.31 (m, 8H)。

4-甲氧基联苯: ^1H NMR(CDCl_3 , 400 MHz, TMS): δ 3.85 (s, 3H), 6.96~7.55 (m, 9H)。

2.2 钯源对Suzuki偶联的影响

钯源对Suzuki偶联反应的影响结果见表1。碳酸钾为碱助剂, 甲醇为溶剂, 考察了 $\text{Pd}(\text{OAc})_2$ 、 PdCl_2 、 $\text{Pd}_2(\text{dba})_3$ 、 $\text{Pd}(\text{COD})\text{Cl}_2$ 共4种钯源的影响。与文献报道相近^[16], 4种钯源的催化效果为: $\text{Pd}(\text{COD})\text{Cl}_2 > \text{Pd}(\text{OAc})_2 > \text{Pd}_2(\text{dba})_3 > \text{PdCl}_2$ 。

表1 钯源对4-溴甲苯与苯硼酸 Suzuki 偶联反应的影响
Table 1 Effect of different Pd(II) source on the Suzuki cross coupling reactions^a

Entry	Pd(II) source	Reaction time/min	$t/^\circ\text{C}$	Yield/% ^b
1	PdCl_2	30	30	15
2	$\text{Pd}(\text{OAc})_2$	30	30	67
3	$\text{Pd}_2(\text{dba})_3$	30	30	53
4	$\text{Pd}(\text{COD})\text{Cl}_2$	30	30	98

^aReaction conditions: 4-bromotoluene (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst 1.0 mol%, K_2CO_3 (2.0 equiv), methanol (3.0 mL), the catalyst was made from the palladium compounds and ligand. ^b GLC yield calibrated via internal standard, average of two runs.

2.3 碱助剂对Suzuki偶联反应的影响

碱助剂对钯催化Suzuki偶联反应的影响结果见表2。当Pd用量为1.0 mol%, 选择甲醇为溶剂, $\text{Pd}(\text{COD})\text{Cl}_2/\mathbf{1}$ (mole:mole = 1:1.3)的催化体系, 通过比较Suzuki偶联反应常用碱发现: 碳酸铯及含钾离子的碱效果好, 反应半小时就得到95%以上收率(Entries 1-6)。在本反应体系中产物收率随阳离子半径减小而减小, 这明显表现为所用3种碳酸盐的促进作用为 $\text{Cs}_2\text{CO}_3 > \text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3$, 与文献报道结果相近^[30]。说明该催化体系对碱助剂具有广适性。碳酸钾^[31]对Suzuki偶联反应也有很好的促进作用, 并且价格低廉。结合优化, 认为碳酸钾为该体系最

佳碱助剂。

表2 碱助剂对4-溴甲苯与苯硼酸 Suzuki 偶联反应的影响
Table 2 Effect of Base on the Suzuki cross coupling reactions^a

Entry	Base	Reaction time/min	$t/^\circ\text{C}$	Yield/% ^b
1	Cs_2CO_3	30	30	98
2	K_2CO_3	30	30	98
3	K_3PO_4	30	30	97
4	KF	30	30	95
5	KOH	30	30	96
6	KOBU^t	30	30	99
7	Na_2CO_3	30	30	86
8	NaOBU^t	30	30	89
9	NaOH	30	30	80
10	LiCl	30	30	25

^aReaction conditions: 4-bromotoluene (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst 1.0 mol %, Base (2.0 equiv), methanol (3.0 mL), the catalyst was made from the $\text{Pd}(\text{COD})\text{Cl}_2$ and ligand. ^bGLC yield calibrated via internal standard, average of two runs.

2.4 溶剂对Suzuki偶联反应的影响

表3 溶剂对4-溴甲苯与苯硼酸 Suzuki 偶联反应的影响
Table 3 Effect of solvent on the Suzuki cross coupling reactions^a

Entry	Solvent	Reaction time/min	$t/^\circ\text{C}$	Yield/% ^b
1	CH_3OH	30	30	98
2	$\text{CH}_3\text{OH}(50\%)$	30	30	70
3	EtOH	30	30	85
4	EtOH(95%)	30	30	90
5	H_2O	30	30	30
6	THF	30	30	60
7	Dioxane	30	30	78
8	DCM	30	30	35

^aReaction conditions: 4-bromotoluene (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst 1.0 mol %, K_2CO_3 (2.0 equiv), methanol (3.0 mL), the catalyst was made from the palladium compounds and ligand. ^bGLC yield calibrated via internal standard, average of two runs.

溶剂通常对钯催化的Suzuki偶联反应会有很大影响(表3)。在碳酸钾为碱, 当Pd用量为1.0 mol%, 选择甲醇为溶剂, $\text{Pd}(\text{COD})\text{Cl}_2/\mathbf{1}$ (mole:mole = 1:1.3)的催化体系, 在催化4-甲基溴苯与苯硼酸的Suzuki偶联反应时, 发现选择甲醇和乙醇(95%)催化效果最好, 30 min分别达到98%和90%收率(Entries 1, 4), 这可能是由于 $\text{Pd}(\text{COD})\text{Cl}_2/\mathbf{1}$ 在溶剂中溶解性好的缘

故^[16]。

2.5 Pd(COD)Cl₂/1催化芳基溴代物、芳基氯代物的 Suzuki 偶联反应的研究

通过选择一系列有不同取代基团的芳基溴代物和芳基氯代物,来考察甲醇为溶剂,碳酸钾为碱助剂,Pd用量为1.0 mol%,Pd(COD)Cl₂/1(mole:mole = 1:1.3)的催化体系在Suzuki偶联反应中的催化活性(表 4)。C—Cl键(Ph—X)的解离能^[32]:Cl, 402 kJ/mol; Br, 339 kJ/mol; I, 272 kJ/mol)的较高强度导致它们对零价Pd⁰物种的氧化加成反应不易进行,这也就是芳基氯代物的偶联较难进行的原因。

表 4 Pd(COD)Cl₂/1 催化芳基溴代物、芳基氯代物与苯硼酸的 Suzuki 偶联反应

Table 4 Pd(COD)Cl₂/1 catalyzed Suzuki reactions of aryl bromide and chlorides with phenylboronic acid^a

Entry	R	X	Reaction time/min	t/°C	Yield/% ^b
1	H	Br	30	30	99
2	4-Me	Br	30	30	96
3	2-Me	Br	30	30	93
4	4-CF ₃	Br	30	30	99
5	4-MeCO	Br	30	30	96
6	4-MeO	Br	30	30	97
7	2,4-dimethyl	Br	30	30	90
8	4-CF ₃	Cl	30	30	85
9	4-Me	Cl	30	30	33
10	2,4-dimethyl	Cl	30	30	20

^aReaction conditions: Aryl bromide (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst 1.0 mol %, K₂CO₃ (2.0 equiv), methanol (3.0 mL), the catalyst was made from the palladium compounds and ligand.

^bGLC yield calibrated via internal standard, average of two runs.

在超声波辅助、30℃水浴下,多种带活性吸电子基团及钝化供电子基团的溴苯与苯硼酸反应半小时均达到90%以上的收率。带性吸电子基团及钝化供电子基团的氯苯与苯硼酸反应收率却相差悬殊。表明N,O配体1作为钯催化剂配体对催化具有不同电子性和空阻基团溴苯衍生物的Suzuki偶联反应具有较广泛的适用性,而对于氯苯衍生物,对活化芳基氯代物催化活性适中,钝化的芳基氯代物催化活性不高。

3 小结

系统研究了超声波辅助下廉价易得的非膦N,O配体1,4-双(2-羟基-3,5-二-叔-丁基苯基)哌嗪促进的钯催化Suzuki偶联反应,实验表明,1.0 mol%的催化剂(Pd(COD)Cl₂/1 = 1:1.3),在甲醇中就能在30 min内催化芳溴和活化的芳氯衍生物与苯硼酸的偶联反应,高收率地获得对应产物,说明该空气稳定的配体中N,O-原子能够与催化剂钯金属中心进行很好的配位,同时特丁基提供了很大的空间位阻,提高了催化体系的活性,说明这类N,O-配体是钯催化Suzuki偶联反应体系的高效配体。

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