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三氟甲磺酸铜(II)催化炔烃选择性转移氢化合成顺式烯烃

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摘要: 顺式烯烃是许多生物活性分子的基本结构单元, 在材料科学、药物化学和农药等领域都有着广泛的应用. 我们以异丙醇为氢源, 研究了 4,5-双二苯基膦-9,9-二甲基氧杂蒽配合三氟甲磺酸铜催化的炔烃选择性转移氢化反应, 实现了高选择性顺式烯烃 (*Z/E* >99/1) 的合成. 该反应体系不需要使用高压设备, 操作简便、安全, 对氟、氯和溴等卤素取代的炔烃表现出良好的底物兼容性. 最后, 进行了对比实验, 并提出了可能的反应机理.

关键词: 铜催化; 炔烃; 异丙醇; 转移氢化; 立体选择性

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顺式烯烃在药物分子、天然产物和香料等领域都有着广泛的应用 (图 1)^[1]. 炔烃的选择性还原是合成顺式烯烃最直接、有效的方式之一^[2]. 然而, 炔烃

在还原过程中往往存在异构化和过度还原的问题, 因此发展一种高选择性还原内炔制备顺式烯烃的方法是一个重要的挑战. 常见的炔烃选择性还原是以

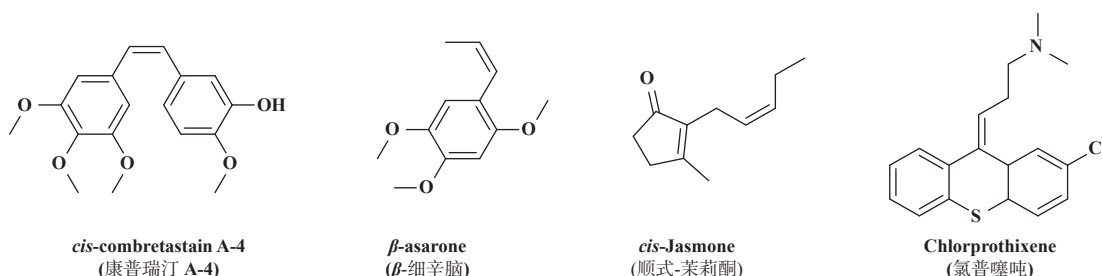


图 1 具有顺式烯烃结构的分子示例

Fig.1 Molecules with *cis*-alkenes structures

Lindlar 催化剂进行该反应^[3], Lindlar 催化剂由醋酸铅或喹啉修饰的钯/碳酸钙组成, 然而由于铅的剧毒性质以及存在可能从催化剂表现浸出的风险, 限制了其在食品、化妆品和药品制造等方面的应用; 另外金属钯的价格居高不下, 导致成本高昂. 因此, 探索廉价金属催化的顺式烯烃制备方法具有重要的意义. 近年来, 随着金属有机化学的发展, 基于锰^[4-6]、铁^[7-8]、钴^[9-11]、镍^[12-13]和铜^[14-17]等丰产金属催化剂不断被开发, 它们在炔烃的选择性还原反应中表现出了一定的活性, 但是目前还存在催化效率不足, 且需要用到特殊的配体等问题.

铜在地壳中具有丰富的储量, 约是铂族金属储量的 4.0×10^5 倍. 根据《中国矿产资源报告 2022》显示, 2021 年中国铜矿储量为 3.495×10^7 t. 除此之外, 铜作为催化剂已有一百多年的发展历史, 例如乌尔曼反应^[18]和酯的催化加氢^[19]等. 因此, 以铜作为催化剂实现炔烃的高选择性还原具有重要的意义 (图 2(a)). 1989 年, Ryu 等^[20]利用 200% 的铜(II)参与、以二乙基甲基硅烷为氢源对炔烃进行选择还原反应以来, Tsuji^[14a]、Lalic^[14b]、Teichert^[15a,16b,16c]、Grela^[15b]和 Nakao^[16a]等发展了多种金属铜催化策略, 利用硅烷、硼烷、氢气等多种氢源, 实现了由炔烃选择性

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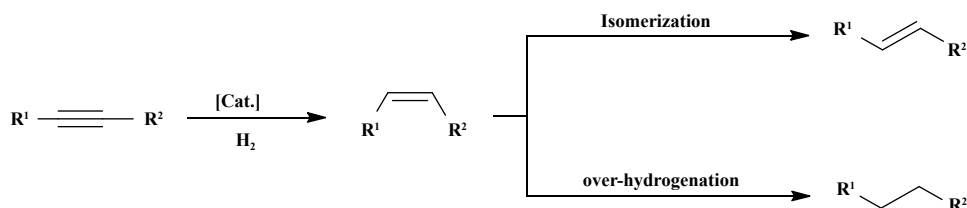
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还原制备顺式烯烃。但是,铜在催化炔烃选择性还原时,主要使用硅烷和硼烷作为氢源,会产生大量的废弃物。以氢气作为氢源时,低压氢的底物适应范围有限,为了实现好的底物适应性往往需要高温和高压(8.0~10.0 MPa),操作上较为繁琐。醇也可以作为一种氢源,以醇为原料通过“借氢”策略实现炔烃还原

具有原子经济性高、环境友好等优点,符合绿色化学的发展理念^[21]。目前,以异丙醇为氢源的铜催化炔烃选择性转移氢化反应有且仅有一例报道^[17a](图2(b)),但面临催化剂用量高、碱用量大、选择性差等问题。因此,探索高效、简便、选择性好的催化体系仍有很重要的研究价值。

(a) Challenges in *cis*-hydrogenation of alkynes to *cis*-alkenes



(b) Copper-catalyzed reduction of alkynes using alcohols as hydrogen source

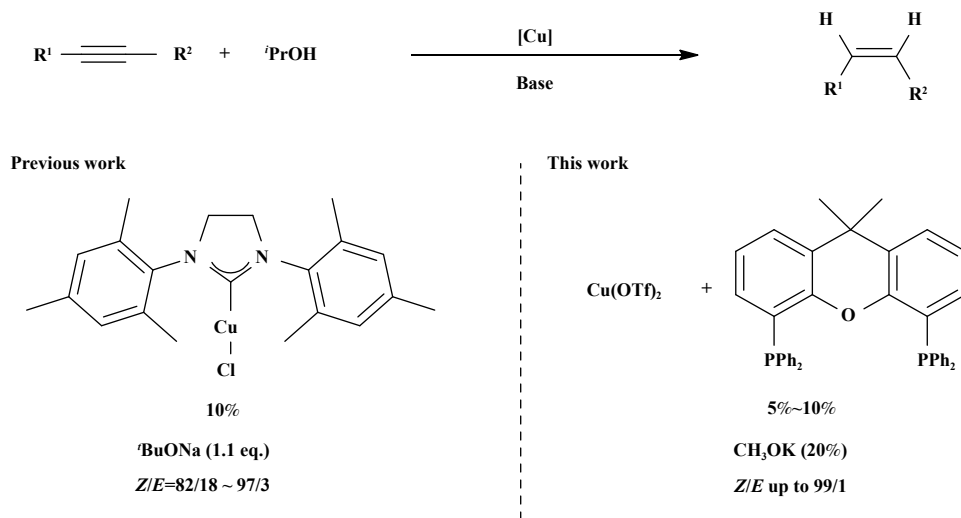


图2 铜催化的炔烃选择性还原反应

Fig.2 Copper-catalyzed selective reduction of alkynes

利用三氟甲磺酸铜($\text{Cu}(\text{OTf})_2$)作为催化剂前体, Xantphos作为配体, 以异丙醇作为氢源, 通过添加碱作为助剂, 即可实现炔烃的顺式选择性转移氢化反应, 高选择性地制备了顺式烯烃。

1 实验部分

1.1 试剂与仪器

二苯基乙炔购于安徽泽升科技有限公司, 通过柱层析纯化并用 EtOH 进行结晶纯化后使用; 炔烃 **1b**–**1n** 通过文献报道方法合成^[22]; 其他分析纯试剂通过市售渠道购买后直接使用。

核磁共振波谱仪 (型号: Bruker AVANCE III

400 MHz 型和 600 MHz 型, 瑞士 Bruker 公司); 气相色谱分析仪 (型号: Agilent 8860, 安捷伦科技有限公司); 气相-质谱联用仪 (型号: Agilent 8860/5977B, 安捷伦科技有限公司)。

1.2 炔烃选择性转移氢化反应步骤

在 N_2 气氛手套箱中, 向带有磁力搅拌子的 10 mL 干燥杨氏管中加入 $\text{Cu}(\text{OTf})_2$ (9.1 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol) 和异丙醇 (0.5 mL)。室温下搅拌 1 h 后加入甲醇钾 (7.0 mg, 0.1 mmol)。随后, 向反应管中加入二苯基乙炔 (89.1 mg, 0.5 mmol) 和异丙醇 (0.5 mmol)。将反应管带出手套箱置于油浴锅中, 在 130 °C 下反应 24 h。反应结束后, 将反应

管冷却至室温,取适量反应液用乙酸乙酯稀释,通过GC测量确定转化率和选择性.随后将反应液经过硅胶柱层析分离纯化(石油醚),得到产物2a-2c、2e-2l.

产物核磁数据如下:

(Z)-1,2-二苯基乙烯(2a): 收率: 85%; 无色液体; Z/E 值大于 99/1 是通过 GC 检测获得; ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.11 (m, 10H), 6.59 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 137.3, 130.3, 128.9, 128.2, 127.1.

(Z)-4-甲基二苯基乙烯(2b): 收率: 50%; 无色液体; Z/E 值为 98.5/1.5 是通过 GC 检测获得; ^1H NMR (400 MHz, CDCl_3) δ 7.27-7.13 (m, 7H), 7.02 (d, $J = 11.4$ Hz, 2H), 6.55 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 137.5, 136.9, 134.3, 130.2, 129.6, 128.9, 128.8, 128.2, 127.0, 21.2.

(Z)-3-甲基二苯基乙烯(2c): 收率: 71%; 无色液体; Z/E 值大于 99/1 是通过 GC 检测获得; ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.16 (m, 5H), 7.10-6.99 (m, 4H), 6.56 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 137.8, 137.4, 137.2, 130.4, 130.1, 129.6, 128.9, 128.2, 128.1, 127.9, 127.1, 125.9, 21.3.

(Z)-4-甲氧基二苯基乙烯(2e): 收率: 32%; 淡黄色固体; Z/E 值为 87/9/4 是通过 GC 检测获得; ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.16 (m, 7H), 6.77-6.73 (m, 2H), 6.55-6.48 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.7, 137.7, 130.2, 129.8, 129.7, 128.8, 128.8, 128.2, 126.9, 113.6, 55.2.

(Z)-4-氟二苯基乙烯(2f): 收率: 74%; 无色液体; Z/E 值大于 99/1 是通过 GC 检测获得; ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.18 (m, 7H), 6.92-6.88 (m, 2H), 6.60-6.52 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.1 (d, $J = 370.1$ Hz), 137.1, 133.2 (d, $J = 5.0$ Hz), 130.6 (d, $J = 12.1$ Hz), 130.3, 129.1, 128.8, 128.3, 127.2, 115.3, 115.0.

(Z)-4-氯二苯基乙烯(2g): 收率: 91%; 无色液体; Z/E 值大于 99/1 是通过 GC 检测获得; ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.14 (m, 9H), 6.60 (dd, $J_1 = 12.0$ Hz, $J_2 = 60.0$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 136.9, 135.7, 132.8, 131.0, 130.2, 128.9, 128.8, 128.4, 128.4, 127.3.

(Z)-4-溴二苯基乙烯(2h): 收率: 88%; 无色液体; Z/E 值大于 99/1 是通过 GC 检测获得; ^1H NMR

(400 MHz, CDCl_3) δ 7.33 (d, $J = 8.4$ Hz, 2H), 7.24-7.20 (m, 5H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.63 (d, $J = 12.2$ Hz, 1H), 6.50 (d, $J = 12.2$ Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 136.8, 136.1, 131.4, 131.0, 130.5, 128.9, 128.8, 128.4, 127.3, 120.9.

(Z)-1,1'-联苯-4-苯乙烯(2i): 收率: 85%; 白色固体; Z/E 值大于 99/1 是通过 GC 检测获得; ^1H NMR (400 MHz, CDCl_3) δ 7.60-7.57 (m, 2H), 7.47-7.40 (m, 4H), 7.34-7.18 (m, 8H), 6.62 (s, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 140.7, 139.8, 137.4, 136.3, 130.5, 129.8, 129.4, 128.9, 128.8, 128.3, 127.3, 127.2, 126.9, 126.9.

(Z)-1-苯基-3,3-二甲基丁烯(2j): 收率: 49%; 无色液体; Z/E 值大于 99/1 是通过 GC 检测获得; ^1H NMR (600 MHz, CDCl_3) δ 7.28-7.25 (m, 2H), 7.21-7.17 (m, 3H), 6.41 (d, $J = 12.6$ Hz, 1H), 5.60 (d, $J = 12.6$ Hz, 1H), 0.98 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 142.7, 139.4, 129.0, 127.6, 127.1, 126.2, 34.2, 31.2.

(Z)-1-(3,3-二甲基-1-丁烯)-4-甲基苯乙烯(2k): 收率 49%; 无色液体; Z/E 值大于 99/1 是通过 GC 检测获得; ^1H NMR (600 MHz, CDCl_3) δ 7.09-7.06 (m, 4H), 6.37 (d, $J = 12.6$ Hz, 1H), 5.57 (d, $J = 12.6$ Hz, 1H), 2.33 (s, 3H), 0.98 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 142.5, 136.4, 135.7, 128.9, 128.3, 127.1, 34.1, 31.3, 21.2.

(Z)-1-(3,3-二甲基-1-丁烯)-4-氟苯乙烯(2l): 收率: 40%; 无色液体; Z/E 值大于 99/1 是通过 GC 检测获得; ^1H NMR (600 MHz, CDCl_3) δ 7.14-7.11 (m, 2H), 6.97-6.94 (m, 2H), 6.34 (d, $J = 12.6$ Hz, 1H), 5.61 (d, $J = 12.6$ Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 162.3 (d, $J = 244.3$ Hz), 143.3, 130.4 (d, $J = 8.5$ Hz), 126.0, 114.5, 114.4, 34.2, 31.2.

2 结果与讨论

2.1 条件优化

首先,使用二苯基乙炔(1a)为标准底物、叔丁醇钾为碱、异丙醇为氢源和溶剂,当仅加入 $\text{Cu}(\text{OTf})_2$ 作为催化剂时,以 50% 的底物转化率和 92/8 的 Z/E 选择性得到顺式烯烃(表 1, Entry 1). 随后,测试了不同配体对该反应的影响(表 1, Entry 2-11). 结果表明,配体加入后能够调变反应的催化性能.当使用 dppb 和 Xantphos 为配体时,转化率

分别为 68%(*Z/E* = 94/6) 和 65%(*Z/E* = 99/1) 的收率(表 1, Entry 5 和 7), 使用其它配体反应收率都有所降低. 接下来以 Xantphos 为配体对碱的种类进行了考察, 其中以甲醇钾 (CH_3OK) 为碱的反应结果更好(表 1, Entry 14), 而当不加入碱时, 该反应不发生(表 1, Entry 16). 此外还对反应温度和时间进行了优化, 当温度为 140 °C 反应 12 h 时, 以 80% 的转化率得到了顺式烯烃(表 1, Entry 17), 继续延长时间至

24 h 后转化率也仅能达到 90%(表 1, Entry 18). 而当反应温度为 130 °C、反应时间为 24 h 时, 该反应以 91% 的转化率, 85% 的分离收率, *Z/E* 值大于 99/1 得到顺式烯烃(表 1, Entry 19). 最后, 还对比了以正丙醇和正丁醇为氢源, 分别仅能得到 11% 和 10% 的顺式烯烃(表 1, Entry 20 和 Entry 21). 由此, 确定了炔烃选择性转移氢化反应的最优反应条件: 以 $\text{Cu}(\text{OTf})_2$ 为铜前体、Xantphos 为配体、 CH_3OK 为

表 1 反应条件优化^aTable 1 Screening of reaction conditions^a

1a, 0.5 mmol 1 mL $\text{Cu}(\text{OTf})_2$ (5%) Ligand (6%) Base (20%) 130 °C, 12 h Z-2a E-2a				
DPEphos Xantphos dppf				
Entry	Ligand	Base	H-Source	Yield /% (<i>Z/E</i>)
1	—	<i>t</i> BuOK	<i>i</i> PrOH	50 (92/8)
2	dppm	<i>t</i> BuOK	<i>i</i> PrOH	11 (99/1)
3	dppe	<i>t</i> BuOK	<i>i</i> PrOH	7 (98/2)
4	dppp	<i>t</i> BuOK	<i>i</i> PrOH	8 (97/3)
5	dppb	<i>t</i> BuOK	<i>i</i> PrOH	68 (94/6)
6	dpppe	<i>t</i> BuOK	<i>i</i> PrOH	17 (98/2)
7	dpph	<i>t</i> BuOK	<i>i</i> PrOH	5 (94/6)
8	Xantphos	<i>t</i> BuOK	<i>i</i> PrOH	65 (>99/1)
9	DPEphos	<i>t</i> BuOK	<i>i</i> PrOH	27 (96/4)
10	BINAP	<i>t</i> BuOK	<i>i</i> PrOH	8(99/1)
11	dppf	<i>t</i> BuOK	<i>i</i> PrOH	39 (>99/1)
12	Xantphos	<i>t</i> BuOLi	<i>i</i> PrOH	17 (94/6)
13	Xantphos	<i>t</i> BuONa	<i>i</i> PrOH	55 (>99/1)
14	Xantphos	CH_3OK	<i>i</i> PrOH	66 (>99/1)
15	Xantphos	CH_3ONa	<i>i</i> PrOH	60 (98/2)
16	Xantphos	/	<i>i</i> PrOH	0
17 ^b	Xantphos	CH_3OK	<i>i</i> PrOH	80(>99/1)
18 ^{b,c}	Xantphos	CH_3OK	<i>i</i> PrOH	90(99/1)
19 ^c	Xantphos	CH_3OK	<i>i</i> PrOH	91 [85] ^d (>99/1)
20 ^c	Xantphos	CH_3OK	ⁿ PrOH	11 (>99/1)
21 ^c	Xantphos	CH_3OK	ⁿ BuOH	10 (>99/1)

a. Reaction conditions: **1a** (0.5 mmol), $\text{Cu}(\text{OTf})_2$ (0.025 mmol), Ligand (0.03 mmol), Base (0.1 mmol), Solvent (1 mL), oil bath 130 °C, 12 h, yields are determined by GC-analysis based on area normalization method; b. 140 °C; c. 24 h; d. Isolated yield

碱、 t -PrOH 为氢源和溶剂, 在 130 °C 下反应 24 h.

2.2 底物拓展

在确定最佳反应条件后, 对底物的适应范围进行了考察, 如表 2 所示. 首先, 考察了空间位阻效应, 分别以其中一个苯基有对位、间位或邻位甲基取代二芳基乙炔 (**1b–1d**) 为底物. 在标准条件下, 以含对位和间位甲基的 **1b** 和 **1c** 为底物是分别取得了 50%

和 71% 收率的顺式二芳基乙烯 **2b** 和 **2c**, Z/E 比分别为 98.5/1.5 和大于 99/1. 但是, 位阻相对较大的邻甲基取代二芳基乙炔需要通过加大催化量至 10% 后, 方能检测到有 68% 的顺式烯烃产生, Z/E 值大于 99/1. 其次, 考察了取代基的电子效应, 分别在二苯基乙炔其中一个苯基的对位引入甲氧基 (**1e**)、氟 (**1f**)、氯 (**1g**)、溴 (**1h**) 和苯基 (**1i**). 在标准条件下,

表 2 炔烃底物适应性考察^a

Table 2 Substrate scope for alkynes^a

$\text{R}^1 - \text{C} \equiv \text{C} - \text{R}^2 + t\text{PrOH} \xrightarrow[\text{130 } ^\circ\text{C, 12 h}]{\text{Cu(OTf)}_2 \text{ (5\%)}, \text{Xantphos (6\%)}, \text{CH}_3\text{OK (20\%)}}$		$\begin{matrix} \text{H} & \text{H} \\ \diagdown & / \\ \text{C} = \text{C} \\ / & \diagdown \\ \text{R}^1 & \text{R}^2 \end{matrix} + \begin{matrix} \text{H} & \text{R}^2 \\ \diagdown & / \\ \text{C} = \text{C} \\ / & \diagdown \\ \text{R}^1 & \text{H} \end{matrix} + \text{R}^1 - \text{CH}_2 - \text{CH}_2 - \text{R}^2$		
1	1 mL	Z-2	E-2	3
2a, 85%				
$Z/E > 99/1$				
2b, 50%				
$Z/E = 98.5/1.5$				
2c, 71%				
$Z/E > 99/1$				
2d, 68%^{b,c}				
$Z/E > 99/1$				
2e, 32%				
$Z/E/3 = 87/9/4$				
2f, 74%^b				
$Z/E > 99/1$				
2g, 91%^b				
$Z/E > 99/1$				
2h, 88%^b				
$Z/E > 99/1$				
2i, 85%				
$Z/E > 99/1$				
2j, 49%^b				
$Z/E > 99/1$				
2k, 49%^b				
$Z/E > 99/1$				
2l, 26%^{b,c}				
$Z/E > 99/1$				
2m, 40%^b				
$Z/E > 99/1$				
2n, 28%^c				
$Z/E > 99/1$				
2o, ND				

a. Reaction conditions: **1** (0.5 mmol), Cu(OTf)_2 (0.025 mmol, 9.1 mg), Xantphos (0.03 mmol, 17.4 mg), CH_3OK (0.1 mmol, 7.0 mg), t -PrOH (1 mL), 130 °C, 24 h, isolated yield. Z/E ratio is determined by GC analysis of the reaction mixture; b. Cu(OTf)_2 (0.05 mmol, 18.2 mg), Xantphos (0.06 mmol, 34.8 mg); c. Yields were determined by GC based on the area normalization method.

对甲氧基取代的二苯基乙炔有少量过度氢化的产物 **3e** 生成, 顺式烯烃 **2e** 收率为 32%, *Z/E* 值为 87/9/4. 含卤素的 3 个底物在以 10% 的铜为催化剂时, 分别取得了 74%(**2f**)、91%(**2g**) 和 88%(**2g**) 收率的顺式烯烃产物, *Z/E* 值均大于 99/1. 这些含卤素的产物可进一步转化成功能化的顺式烯烃. 当对位有苯基时 (**1i**), 在标准条件下以 85% 的收率获得顺式烯烃 **2i**, *Z/E* 值也大于 99/1. 接着, 对芳基烷基乙炔 (**1j**–**1n**) 进行了考察. 结果表明, 相较于二芳基乙

炔, 该反应体系对芳基烷基乙炔的活性较低. 在催化剂用量为 10% 时, 收率在 26%~49% 之间, 而 *Z/E* 值则依旧大于 99/1. 最后, 以二烷基炔烃 7-十四炔 (**1o**) 为底物时反应基本不进行, 可能是由于 7-十四炔更加富电子, 使迁移插入更加缓慢, 导致反应难以进行.

2.3 反应机理探究

考察了底物适用范围后, 对反应机理进行了初步探索 (图 3). 在最优反应条件下, 分别以顺式烯烃

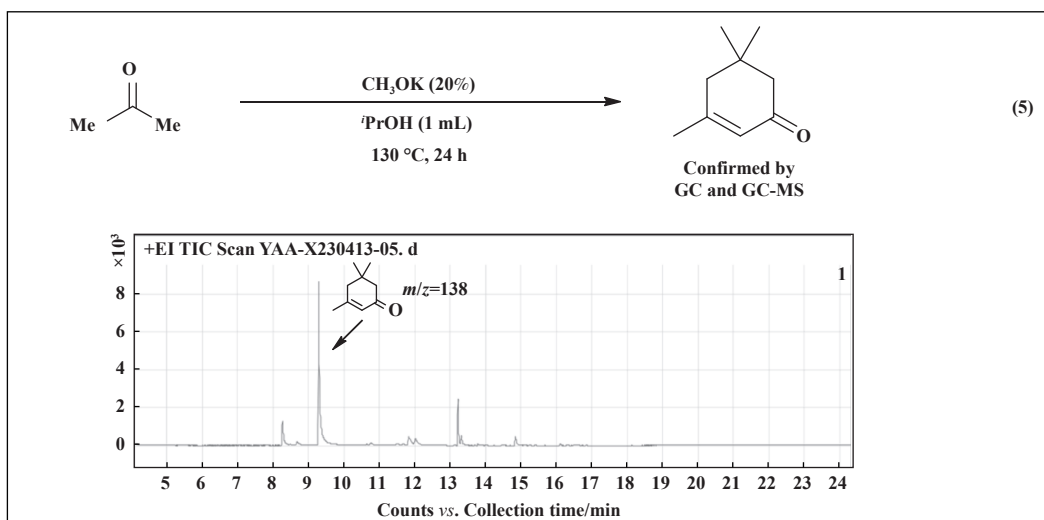
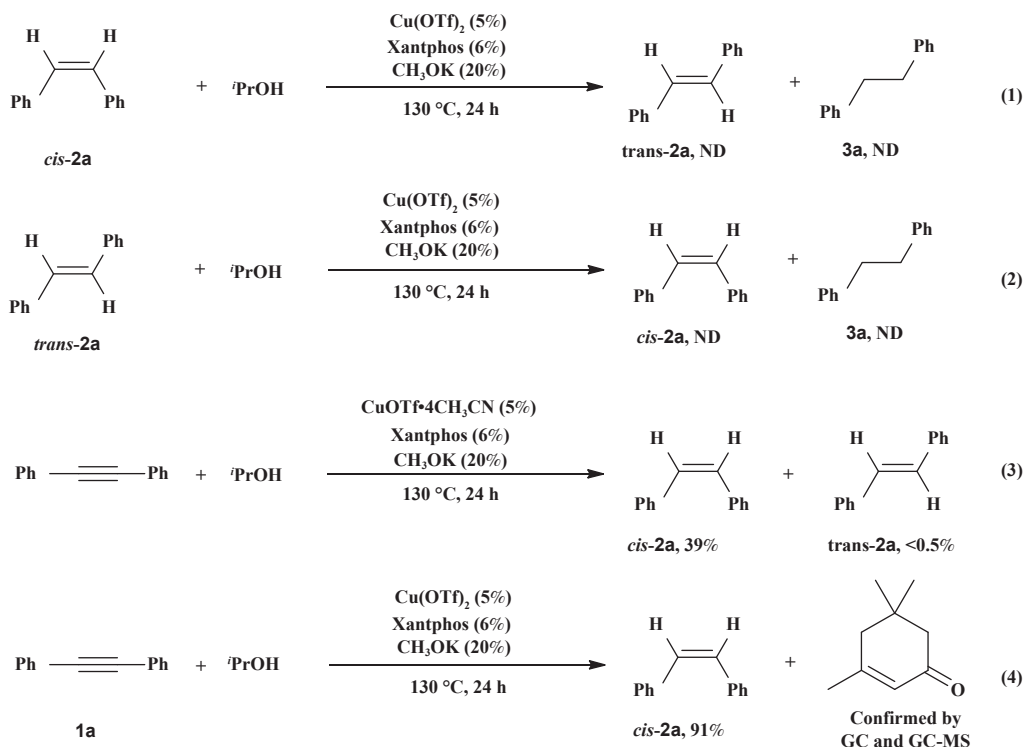


图3 机理探究

Fig.3 Mechanistic investigation

cis-**2a** 和反式烯烃 *trans*-**2a** 加入到反应体系中, 实验结果显示烯烃的构型并未发生翻转, 也未检测到有 1,2-二苯基乙烷生成, 表明烯烃在反应体系中不会发生异构化和过度还原 (方程式 (1) 和 (2)). 将最佳反应条件中的三氟甲磺酸铜 (II) 换成四 (乙腈) 三氟甲磺酸铜 (I) 时, 该反应仍能以 39% 的转化率得到 *cis*-**2a**, 表明 Cu(I) 可能是催化活性物种 (方程式 (3)). 通过对模板反应液进行 GC-MS 和 GC 分析, 以及与异佛尔酮标准样品色谱和质谱图进行比

对, 可以确认反应中有异佛尔酮生成 (方程式 (4)). 随后, 对生成异佛尔酮的反应条件进行了考察, 结果表明在碱存在条件下丙酮会缩合成异佛尔酮 (方程式 (5)). 由此, 可以推测在催化炔烃选择性转移氢化反应中会生成丙酮.

结合已有的文献报道和对比实验, 我们认为一价铜为真正的活性催化物种, 因此推测的反应机理如下 (图 4): 首先, 铜 (II) 配合物在碱性条件下与异丙醇反应生成异丙氧基铜 (I) 配合物 **A**^[6a]; 随后, 异

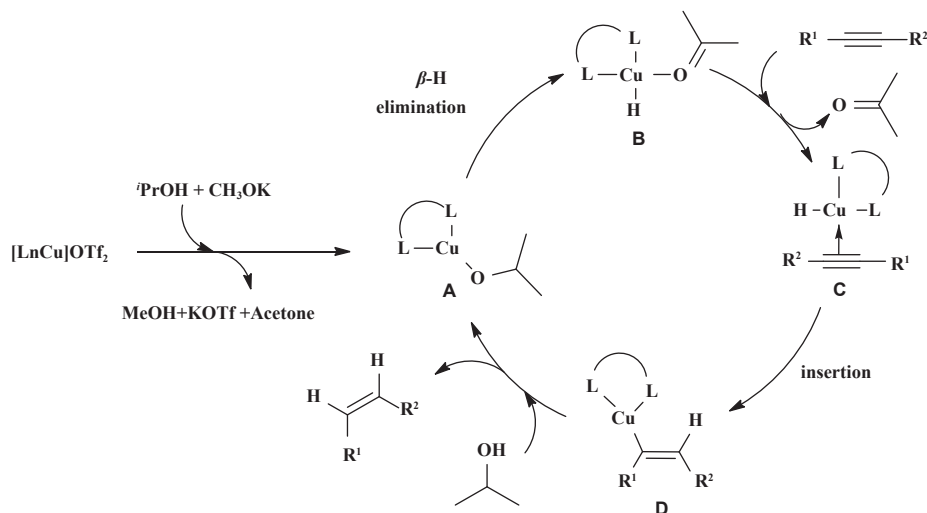


图 4 可能的反应机理

Fig.4 Proposed reaction mechanism

丙氧基铜 (I) 配合物 **A** 发生 β -H 消除, 生成 Cu(I)-H 物种 **B**^[23]; Cu(I)-H 物种 **B** 和炔烃发生配体交换^[14e], 生成炔基配位的 Cu(I)-H 物种 **C** 和丙酮; **C** 发生顺式的迁移插入得到烯基铜 (I) 物种 **D**^[14a-14c]; **D** 与异丙醇发生质子解, 得到异丙氧基铜 (I) 配合物 **A**, 完成了催化循环, 并生成产物顺式烯烃^[6b,10b].

3 结论

综上所述, 发展了一种以异丙醇为氢源、Xantphos 为配体和 Cu(OTf)₂ 为催化剂前体, 催化量的甲醇钾作为添加剂, 内炔选择性顺式还原的方法. 该方法可高选择性制备顺式烯烃, 烯烃顺反比普遍大于 99/1. 在该反应体系中, 不需要提前预制配合物, 相较于已报道的催化体系而言, 催化剂用量较低, 仅使用催化量的碱作为添加剂, 具有更加优异的收率和选择性. 该反应条件温和, 具有良好的官能团耐受性, 为顺式烯烃的绿色合成提供了一种新的方法.

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Copper(II) Triflate-Catalyzed Selective Transfer Hydrogenation of Alkynes for Synthesizing *Cis*-Alkenes

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Abstract: *Cis*-alkenes are essential structural units in many bioactive molecules and have a wide range of applications in the field of materials science, medicinal chemistry and pesticides. Herein, a copper-catalyzed selective transfer semi-hydrogenation of alkynes to *cis*-alkene (up to *Z/E* > 99/1) was developed, in which using ^tPrOH as a hydrogen source and Cu(OTf)₂/Xantphos as a catalyst. This reaction system does not require high-pressure equipment, which is simple and safe to operate and shows good compatibility with halogen-substituted alkynes such as fluorine, chlorine and bromine. Finally, the possible reaction mechanism was proposed on the basis of control experiments.

Key words: copper catalysis; alkyne; isopropanol; transfer hydrogenation; stereoselective