Chem. Pap.
DOI 10.1007/s11696-017-0153-4

SHORT COMMUNICATION

Rhodium complexes catalyze oxidative coupling between salicylaldehyde and phenylacetylene via C–H bond activation

Hongge Jia[1] · Yanan Tang[2] · Yongqiang Shi[1] · Liqun Ma[1] · Zijian He[1] · Weiwei Lai[1] · Yi Yang[1] · Yazhen Wang[1] · Yu Zang[1] · Shuangping Xu[1]

Received: 23 September 2016 / Accepted: 23 February 2017

Abstract A coupling reaction between salicylaldehyde and phenylacetylene was catalyzed by well-defined rhodium complexes, Rh(cod)(L-amino acid) (cod is 1,5-cyclooctadiene; L-amino acid is L-proline, L-phenylalanine and L-valine), to give a flavonoid in 40–88% yield, providing a method for flavonoid synthesis. The coupling reactions catalyzed by Rh(cod)(L-amino acid)s gave higher yields than those by $[Rh(cod)Cl]_2$ without L-amino acid ligands. The reaction mechanism may be that L-amino acid ligands of the rhodium complexes can provide an empty track for phenylacetylene to form a ring structure that fractures to produce the aim flavonoid and $Rh^{I}X$ species. Then, the active $Rh^{I}X$ specie is oxidized to regenerate $Rh^{III}X_3$ by $Cu(OAC)_2$.

Keywords Rhodium · Oxidation · Arene ligands · Carbonylation · Flavone

Electronic supplementary material The online version of this article (doi:10.1007/s11696-017-0153-4) contains supplementary material, which is available to authorized users.

✉ Hongge Jia
1542151015@qq.com

✉ Yanan Tang
1327260670@qq.com

✉ Liqun Ma
maliqun6166@163.com

[1] College of Materials Science and Engineering, Key Laboratory of Polymeric Composition and Modification, Qiqihar University, Wenhua Street 42, Qiqihar 161006, China

[2] College of Chemistry and Chemical Engineering, Qiqihar University, Wenhua Street 42, Qiqihar 161006, China

Introduction

In previous studies, transition-metal catalysts have been investigated in the polymerization of monomers and organic synthetic reactions (Baker et al. 2012; Riener et al. 2012). In both the synthesis of active bonds or functional groups and the asymmetric polymerization of substituted acetylenes, transition metals have always been used (Nishimura et al. 2012). Rh-diene complexes exhibit high catalytic activity in the asymmetric polymerization of various substituted acetylenes to give one-handed helical polymers (Jia et al. 2009; Liu et al. 2010; Teraguchi et al. 2010; Liu et al. 2013; Kaneko et al. 2013; Kim et al. 2016; Jin et al. 2016). Chiral well-defined rhodium complexes, Rh(cod)(L-Phe) (cod is 1,5-cyclooctadiene; Phe is phenylalanine) and Rh(cod)(L-Val) (Val is valine), were synthesized, isolated by recrystallization, and characterized (Jia et al. 2016). The helix-sense-selective polymerization (HSSP) of achiral 3,4,5-trisubstituted phenylacetylene, *p*-dodecyloxy-m,m-dihydroxyphenylacetylene (DoDHPA) was carried out using the two Rh complexes as catalysts. All these results indicate that these well-defined Rh complexes serve as excellent catalysts for the HSSP of DoDHPA (Jia et al. 2016). However, these new Rh complexes were not still used for other types of reactions, i.e., oxidative coupling reaction between aldehyde derivatives and phenylacetylene via C–H bond activation.

Some functionalized arenes have been obtained by oxidative coupling reactions with alkenes in the presence of a Pd catalyst and a Cu/air oxidant (Sahoo et al. 2012; Youn et al. 2011). Only a few rhodium catalysts have been used in oxidative coupling reactions (Shimizu et al. 2008; Kokubo et al. 1997, 1999; Huang et al. 2013; Luo et al. 2015a, b). Recently, Mikael Brasse and co-workers described the $[Cp^*RhCl]_2$ ($Cp^*= C_5Me_5$)-catalyzed

Published online: 08 March 2017

oxidative coupling of styrene with 2-phenylpyridine derivatives via C–H activation (Brasse et al. 2013). Their mechanistic study found that the turnover-limiting step is the migratory insertion of the alkene into the Rh-C(aryl) bond. Later, Yuki Fukui and co-workers reported that two tunable arylative cyclizations of 1,6-enynes were catalyzed by $[Cp^*RhCl]_2$ via C–H activation of O-substituted N-hydroxybenzamides (Fukui et al. 2014), and the mechanistic investigations of these two reactions clearly indicated that the C–H bond cleavage process was also involved in the turnover-limiting step.

However, the use of Rh-diene complexes, i.e., Rh(cod)(L-amino acid), has not been explored in oxidative coupling reactions. In this study, a chiral catalyst, Rh(cod)(L-Pro) (cod is 1,5-cyclooctadiene; L-pro is L-proline), was synthesized and purified by recrystallization, and the oxidative coupling reaction between salicylaldehyde and phenylacetylene was catalyzed by the rhodium and Cu(II) catalysts (See Scheme 1). The catalytic efficiencies and mechanisms of these catalysts are discussed.

Experimental

Synthesis of Rh(cod)(L-Pro), Rh(cod)(L-Val), and Rh(cod)(L-Phe) : The chiral Rh catalysts, Rh(cod)(L-Pro), Rh(cod)(L-Val) and Rh(cod)(L-Phe), were synthesized according to Scheme 2. The all reaction procedures were conducted under dry nitrogen.

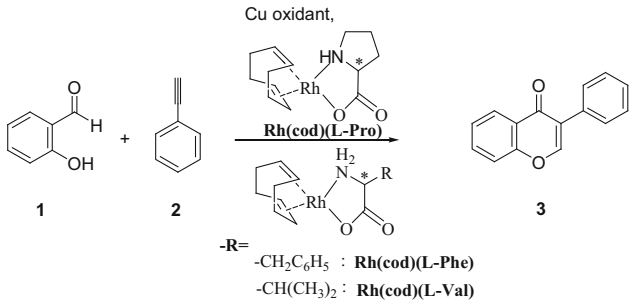
$[Rh(cod)Cl]_2$: This compound was synthesized and purified according to the literature procedure (Staubitz et al. 2015). Yield 55%. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS, δ): 4.42 (s, 8H, C*H*=CH), 2.50 (s, 8H, CHCH_2CH_2), 1.76 (s, 8H, CHCH_2CH_2). ^{13}C-NMR (150 MHz, $CDCl_3$, TMS, δ): 78.63, 30.85. IR (KBr): 3433, 2988, 2936, 2873, 2828, 1640, 1468, 1299, 1151, 994, 960, 867, 816, 775, 486 cm^{-1} (See Figs. S1–S3 in the Supporting Information).

Rh(cod)(L-Pro): A solution of L-proline (14.10 mg, 0.13 mmol) and NaOH (4.88 mg, 0.12 mmol) in H_2O (0.60 mL) was added with $[Rh(cod)Cl]_2$ (30.00 mg, 0.06 mmol) in methanol (2.00 mL). The obtained was stirred for 1 h at room temperature. The mixture was cooled, and then the precipitate was separated by centrifugation. The final product was a yellow powder, which was recrystallized from dichloromethane (Jia et al. 2016). Yield 52.7%. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS, δ): 4.46, 3.75 and 3.58 (3b, 4H, C*H*=CH); 3.86 (m, 1H, CH_2CH_2-C*H*COO); 2.96 (m, 2H, NCH_2CH_2); 2.55, 2.48 2.36 and 2.15 (4 m, 8H, HC=CHCH_2CH_2); 1.95 (m, 2H, CH_2CH_2-CH_2CHCOO); 1.89 (b, 1H, N*H*); 1.73 (b, 1H, COO*H*); 1.65 (m, 2H, NCH_2CH_2CH_2CH). ^{13}C-NMR (150 MHz, $CDCl_3$, TMS, δ): 206.96, 132.11, 63.89, 55.43, 49.94, 30.94, 29.90, 25.58. IR (KBr): 3427.87, 2930.79, 1719.43, 1619.13, 1375.66, 1282.79, 1194.70, 1085.57, 934.80, 802.01, 728.21 cm^{-1}. Elemental analysis for $C_{13}H_{19}NO_2Rh$: calcd. C 34.57, H 5.15, N 1.55; found C 34.65, H 5.24, N 1.50 (See Figs. S4–S6 in the Supporting Information).

Rh(cod)(L-Phe): This compound was prepared and purified by a method similar to that for Rh(cod)(L-Pro) (Jia et al. 2016). The ^{1}H-NMR, ^{13}C-NMR and IR spectra of Rh(cod)(L-Phe) see Figs. S7–S9 in the Supporting Information).

Rh(cod)(L-Val): This compound was prepared and purified by a method similar to that for Rh(cod)(L-pro) (Jia et al. 2016). The ^{1}H-NMR, ^{13}C-NMR and IR spectra of Rh(cod)(L-Pro) See Figs. S10–S12 in the Supporting Information).

Synthesis of 2-phenyl-4H-chromen-4-one (3): Rh(cod)(L-phenylalanine) (2.2 mg, 0.01 mmol), $C_5H_2Ph_4$ (7.2 mg, 0.02 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (200.0 mg, 1.00 mmol) were placed in a two-necked flask. Then, salicylaldehyde (0.50 mL, 0.50 mmol), phenylacetylene (0.50 mL, 0.50 mmol) and o-xylene (2.80 mL, 0.04 mmol) were added, and the resulting mixture was stirred under N_2 at 120 °C for 5.5 h. The raw product was extracted with ether, and the final product was isolated by column chromatography on silica gel with hexane. The solid products were recrystallized from hexane to give a yield of 88% (white crystals). GC spectrum appeared one peak at 11.196 min. ^{1}H-NMR (600 MHz, DMSO-d_6, TMS, δ): 7.62 (d, 2H, *H*C–C–C=O in Ph and C=C*H*–O), 7.61 (d, 2H, *H*C–C–C=C–O in o-Ph to alkenyl), 7.51 (m, 1H, *H*C=C–C–O in m-Ph to oxygen), 7.50 and 7.49 (2t, 2H, *H*C–C–C–C=C–O in m-Ph to alkenyl), 7.46 (s, 1H, *HC*–*C*–C–C–C=C–O in p-Ph to alkenyl), 7.45 (s, 1H, *H*C=C–C–C=O in m-Ph*H* to carbonyl), 7.44 (t, 1H, *H*C–C–O in Ph). ^{13}C-NMR (150 MHz, DMSO-d6, TMS, δ): 73.91, 76.81, 77.02, 77.23, 81.56, 121.82, 128.45, 129.22, 132.52 ppm. IR (KBr): 3049, 2952, 2925, 2854, 2190, 1740, 1484, 1251 cm^{-1} (see Figs. S13–S15). Anal Calcd for $C_{15}H_{10}O_2$: calcd. C 91.43, H 7.20, O 1.37; found C 91.08, H 6.50, O 2.42. Additional data for the products of catalysis by the rhodium catalysts are listed in Table 1.



Scheme 1 Oxidative coupling reaction of salicylaldehyde and phenylacetylene using Rh(cod)(L-Pro), Rh(cod)(L-Phe) and Rh(cod)(L-Val) and Cu(II) as catalysts

Scheme 2 Synthetic route to Rh(cod)(L-Pro)

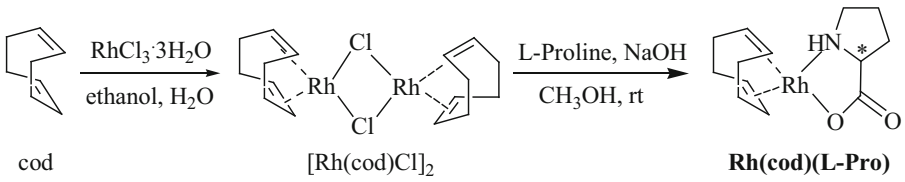


Table 1 Oxidative coupling reactions between salicylaldehyde (1) and phenylacetylene (2) using Rh(cod)(L-Phe), Rh(cod)(L-Val), Rh(cod)(L-Pro) and $[Rh(cod)Cl]_2$ as catalysts

No.	Rh catalyst	Amine cocatalyst	Yield (%)
1	Rh(cod)(L-Phe)	None	88.0
2	Rh(cod)(L-Val)	None	81.2
3	Rh(cod)(L-Pro)	None	76.2
4	$[Rh(cod)Cl]_2$	(S)-PEA	56.8
5	$[Rh(cod)Cl]_2$	TEA	55.5
6	$[Rh(cod)Cl]_2$	None	58.0
7	$RhCl_3$	None	0.0

In o-xylene at 120°C for 5.5 h with [1]/[2]/Rh catalyst]/[cocatalyst] = 1:1:0.02:0.1 (in mmol)

Materials

All the solvents were dried by standard methods and distilled over CaH_2 under reduced pressure before use. Commercially available compounds were used without further purification. $RhCl_3 \cdot 3H_2O$ and all other chemicals, including the L-amino acids, were purchased from Shanghai Darui Finechem Ltd.

Instruments

GC analysis was carried out 7280A GC System, HP-5 column (i.d. 30 m×320 μm×0.25 μm).Infrared (IR) spectra were recorded using a Perkin-Elmer Spectrum One B IR spectrophotometer. Mass spectrometric analysis was performed with a Thermo Q Exactive mass spectrometer (Thermo Fisher Scientific, United States). An NMR instrument [Bruker, Germany; ^1H (600 MHz) and ^{13}C (150 MHz)] was used to determine the molecular structures of the products. Elemental analysis was carried out on a Perkin-Elmer 2400 II CHNS/O instrument.Yield = Product weight ÷ (Mole number of feeding compound × Product molecular weight).

Results and discussion

Confirmation of Rh(cod)(L-pro): We refined the rhodium catalyst, Rh(cod)(L-Pro) by recrystallization to yield yellow solid (Jia et al. 2016). The ^1H-NMR spectrum of Rh(cod)(L-Pro) showed that the methyne peaks of the L-proline residue were detected at δ 3.86 ppm, and the methylene peaks of the L-proline residue were detected at δ 2.96, 1.95, and 1.65 ppm . The coordination of L-Phe to rhodium is confirmed. Judging from the IR spectra, ^{13}C-NMR spectra, and elemental analysis results, the novel chiral rhodium complex (Rh(cod)(L-Pro)) was synthesized .

Confirmation of 2-phenyl-4H-chromen-4-one (3): In an initial attempt to carry out the desired coupling reaction between salicylaldehyde (1) and phenylacetylene (2), these reagents were treated with Rh catalysts in o-xylene at 120 °C for 5.5 h (Scheme 1). The C–H bond of the aldehyde in salicylaldehyde was activated by the Rh catalysts and underwent oxidative coupling with the triple bond in phenylacetylene to give white crystals (3), which were recrystallized from hexane. In the ^1H-NMR spectrum of 2-phenyl-4H-chromen-4-one (3) in DMSO-d6, the chemical shifts of the aromatic residue that connects the carbonyl group occurred at δ 7.62, 7.51, 7.45 and 7.44 ppm. The aromatic peaks that connect the C=C bond were detected at δ 7.61, 7.50 and 7.66 ppm. The proton peak of the double bond was located at δ 7.62 ppm. Judging from the ^1H-NMR, ^{13}C-NMR and IR spectra, it is concluded that the novel compound (3) was successfully synthesized, providing a new method for the synthesis of flavonoids.

Rh catalysts possessing L-amino acids as ligands catalyzing the oxidative coupling of salicylaldehyde: When the new Rh(cod)(L-amino acid)s were used as the catalyst in the coupling reaction between salicylaldehyde and phenylacetylene, excellent results (Table 1, nos. 1–3; yields of 76.2–88.0%) were obtained that were much better than the results obtained using $[Rh(cod)Cl]_2$/(R)-phenylethylamine ((R)-PEA) or triethylamine (TEA) as a catalytic system (Table 1, entries 4–6; yields of 55.5–58.0%). Why is it that the introduction of an L-amino acid as a ligand in a Rh catalyst improves the yields so much? These Rh complexes are very active, unstable. It is easy to react with O atom, N atom or unsaturated bond to form a new active Rh species. We believe that the Rh-amino acid complex is the actual active species in the coupling reaction. L-Amino acids can form two coordination bonds with Rh, Rh-O and Rh-N bonds. In the reaction, because the Rh-N bond is active (Azpíroz et al. 2014), the O atom in the phenolic hydroxyl group of salicylaldehyde can replace the N atom to form a new Rh–O bond. The

original Rh–O bond in Rh(cod)(L-amino acid) may provide an empty track for phenylacetylene. Hence, the Rh(cod)(L-amino acid)s catalysts play an important role in the catalytic process. A detailed discussion of this reaction mechanism will be presented in a later section.

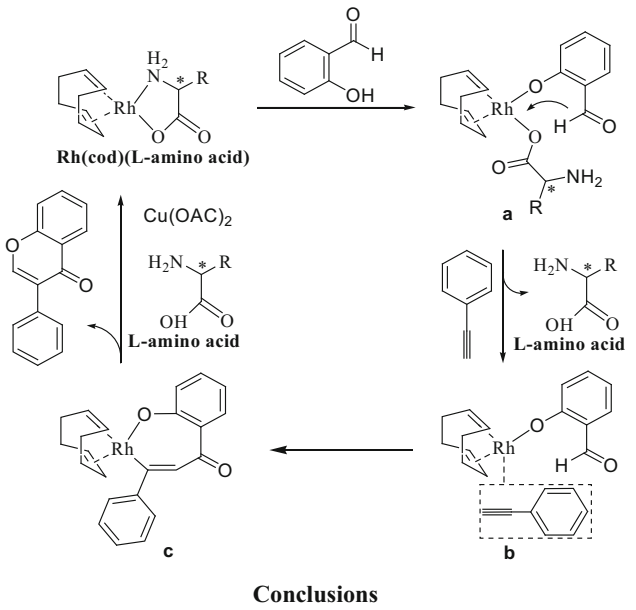
The new viewpoint that Rh–O can provide acetylene with an empty track in Rh is supported by the following results. Among the three types of Rh catalysts containing L-amino acids as ligands, Rh(cod)(L-Phe) has the largest aromatic side group. When Rh(cod)(L-Phe) was used as the catalyst, the reaction gave the highest yield (88.0%). The fact that L-phenylalanine, containing a large aromatic group, can dissociate easily form Rh and provide an empty track may be cause of this high yield.

In the Rh-catalyzed asymmetric polymerization of substituted phenylacetylene, a certain type of amine (such as (R)- or (S)-PEA, TEA or L-amino acids) is necessary as a cocatalyst (Jia et al. 2010). The amine can coordinate to the rhodium catalyst and form an active species in the asymmetric polymerization of the substituted phenylacetylene. The amine ligand of the catalyst does not dissociate in the initiation stage and remains a part of the propagating species (Staubitz et al. 2015). However, the yield of the oxidative coupling reaction catalyzed by $[Rh(cod)Cl]_2$ without an amine cocatalyst was close to those with $[Rh(cod)Cl]_2$/(R)-PEA or TEA (Table 1, nos. 4–6). Therefore, the amines did not play an important role in the coupling reaction between salicylaldehyde and phenylacetylene. We believe that the O atom of the phenolic hydroxyl group in salicylaldehyde takes priority over the N atom of the amine when coordinating to the rhodium atom. This opinion is consistent with our later mechanistic discussion.

When only $RhCl_3$ was used as the catalyst, the oxidative coupling reaction was not catalyzed (Table 1, no. 7). Comparison of this result to that obtained with $[Rh(cod)Cl]_2$ indicates that a diene ligand (cod) is necessary. The diene ligand may be retained throughout the whole catalytic process (See Scheme 3).

Mechanism

According to the above discussions, a plausible mechanism for the oxidative coupling reaction between salicylaldehyde and phenylacetylene is illustrated in Scheme 3 (Shimizu et al. 2008; Kokubo et al. 1997, 1999). First, because the O atom has stronger donating and accepting capacities than the N atom (Luo et al. 2015a, b), the R–N bond of Rh(cod)(L-amino acid) is replaced by the O atom of the phenolic hydroxyl group in salicylaldehyde to produce a rhodium(III) intermediate (a). Second, the electronegativity of the carbonyl in salicylaldehyde is improved by the ortho



Scheme 3 Plausible mechanism for the oxidative coupling reaction catalyzed by Rh(cod)(L-amino acid)s

hydroxyl groups, and the carbonyl attacks the Rh atom to give an empty track with ejection of the L-amino acid (b). Third, the triple bond of phenylacetylene enters into the empty track and coordinates to the rhodium catalyst to form a ring structure (c). Then, the Rh–O bond in the ring structure fractures to produce flavonoid (3) and $Rh^{I}X$ species. Finally, the active $Rh^{I}X$ specie is oxidized to regenerate $Rh^{III}X_3$ by $Cu(OAC)_2$ (Shimizu et al. 2008).

Conclusions

In summary, we have demonstrated that salicylaldehyde undergoes aldehyde C–H bond activation in the presence of novel rhodium catalysts with different ligands to produce 2-phenyl-4H-chromen-4-one. The role of L-amino acid ligands (L-pro, L-Phe or L-Val) in Rh complexes in oxidative coupling between salicylaldehyde and phenylacetylene via C–H bond activation was discussed in this paper. L-phe containing a large aromatic group can dissociate easily to form Rh and provide an empty track, which can improve catalytic activity of Rh complexes.

Acknowledgements This work was supported by the National Natural Science Foundation of China (U1162123) and (51103076), the Natural Science Foundation of Heilongjiang Province of China (LC2011C12), the Overseas Scholars Foundation of the Education Department of Heilongjiang Province of China (1251H012) and the New Century Excellent Talents of the Education Department of Heilongjiang Province of China (1253-NCET-24).

References

Azpíroz R, Rubio-Pérez L, Giuseppe A, Passarelli V, Lahoz F, Castarlenas R, Torrente J, Oro LA (2014) Rhodium(I)-N-heterocyclic carbene catalyst for selective coupling of N-vinylpyrazoles with alkynes via C–H activation. ACS Catal 4:4244–4253. doi:10.1021/cs501366q

Baker RW, Radzey H, Lucas NT, Turner P (2012) Stereospecific syntheses and structures of planar chiral Bidentateη5:κS-Indenyl-Sulfanyl and -Sulfinyl complexes of Rhodium(III). Organometallics 31:5622–5633. doi:10.1021/om300581r

Brasse M, Campora J, Ellman JA, Bergman RG (2013) Mechanistic study of the oxidative coupling of styrene with 2-phenylpyridine derivatives catalyzed by cationic Rhodium(III) via C–H activation. J Am Chem Soc 135:6427–6430. doi:10.1021/ja401561q

Fukui Y, Liu P, Liu Q, He Z, Wu NY, Tian P, Lin GQ (2014) Tunable arylative cyclization of 1,6-enynes triggered by Rhodium(III)-catalyzed C–H activation. ACS J Am Chem Soc 136:15607–15614. doi:10.1021/ja5072702

Huang JR, Zhang QR, Qu CH, Chen YC (2013) Rhodium(III)-catalyzed direct selective C(5)-H oxidative annulations of 2-substituted imidazoles and alkynes by double C–H activation. Org Lett. doi:10.1021/ol400537b

Jia H, Teraguchi M, Aoki T, Abe Y, Kaneko T, Hadano S, Namikoshi T, Marwanta E (2009) Two modes of asymmetric polymerization of phenylacetylene having a L-valinol residue and two hydroxy groups. Macromolecules 42:17–19. doi:10.1021/ma802313z

Jia H, Teraguchi M, Aoki T, Abe Y, Kaneko T, Hadano S, Namikoshi T, Ohishi T (2010) Three mechanisms of asymmetric polymerization of phenylacetylenes having an L-amino ether residue and two hydroxy groups. Macromolecules 43:8353–8362. doi:10.1021/ma101424x

Jia H, Shi Y, Ma L, Gao X, Wang Y, Zang Y, Peng J, Aoki T, Teraguchi M, Kaneko T, Masuda T (2016) Novel isolated, L-amino acid-ligated rhodium catalysts that induce highly helix-sense-selective polymerization of an achiral 3,4,5-trisubstituted phenylacetylene. J Poym Sci Part A 54:2346–2351. doi:10.1002/pola.28106

Jin Y, Kim H, Kim J, Heo N, Shin J, Teraguchi M, Kaneko T, Aoki T, Kwak G (2016) Asymmetric restriction of intramolecular rotation in chiral solvents. Cryst Growth Des 2016(16):2804–2809. doi:10.1021/acs.cgd.6b00128

Kaneko T, Abe H, Teraguchi M, Aoki T (2013) Folding-induced through-space magnetic interaction of poly(1,3-phenyleneethynylene)-based polyradicals. Macromolecules 2013(46):2583–2589. doi:10.1021/ma302314n

Kim H, Seo K, Jin Y, Lee C, Teraguchi M, Kaneko T, Aoki T, Kwak G (2016) Highly emissive, optically active poly(diphenylacetylene) having a bulky chiral side group. ACS Macro Lett 5:622–625. doi:10.1021/acsmacrolett.6b00184

Kokubo K, Matsumasa K, Miura M, Nomura M (1997) Rhodium-catalyzed coupling reaction of salicyl aldehydes with alkynes via cleavage of the aldehyde C–H bond. J Org Chem 62:4564–4565

Kokubo K, Matsumasa K, Nishinaka Y, Miura M, Nomura M (1999) Reaction of 2-hydroxybenzaldehydes with alkynes, alkenes, or allenes via cleavage of the aldehyde C–H bond using a rhodium catalyst system. Bull Chem Soc Jpn 72:303–311

Liu L, Zang Y, Hadano S, Aoki T, Teraguchi M, Kaneko T, Namikoshi T (2010) New achiral phenylacetylene monomers having an oligosiloxanyl group most suitable for helix-sense-selective polymerization and for obtaining good optical resolution membrane materials. Macromolecules 43:9268–9276. doi:10.1021/ma101999k

Liu L, Namikoshi T, Zang Y, Aoki T, Hadano S, Abe Y, Wasuzu I, Tsutsuba T, Teraguchi M, Kaneko T (2013) Top-down preparation of self-supporting supramolecular polymeric membranes using highly selective photocyclic aromatization of cis−cisoid helical poly(phenylacetylene)s in the membrane state. J Am Chem Soc 135:602–605. doi:10.1021/ja3113214

Luo C, Gandeepan P, Wu Y, Tsai C, Cheng C (2015a) Cooperative C(sp3)−H and C(sp2)−H activation of 2-ethylpyridines by copper and rhodium: a route toward quinolizinium salts. ACS Catal 5:4837–4841. doi:10.1021/acscatal.5b01244

Luo C, Jayakumar J, Gandeepan P, Wu Y, Cheng C (2015b) Rhodium(III)-catalyzed vinylic C−H activation: a direct route toward pyridinium salts. Org Lett 17:924–927. doi:10.1021/acs.orglett.5b00028

Nishimura T, Takiguchi Y, Hayashi T (2012) Effect of chiral diene ligands in rhodium-catalyzed asymmetric addition of arylboronic acids to α, β-unsaturated sulfonyl compounds. ACS J Am Chem Soc 134:9086–9089. doi:10.1021/ja303109q

Riener K, Hogerl MP, Gigler P, Kuhn FE (2012) Rhodium-catalyzed hydrosilylation of ketones: catalyst development and mechanistic insights. ACS Catal 2:613–621. doi:10.1021/cs200571v

Sahoo S, Banerjee A, Chakraborty S, Patel B (2012) Regioselective intramolecular arylthiolations by ligand free Cu and Pd catalyzed reaction. ACS Catal 2:544–551. doi:10.1021/cs200590p

Shimizu M, Tsurugi H, Satoh T, Miura M (2008) Rhodium-catalyzed oxidative coupling between salicylaldehydes and internal alkynes with C–H bond cleavage to produce 2,3-disubstituted chromones. Chem Asian J 3:881–886. doi:10.1002/asia.200800037

Staubitz A, Robertson APM, Sloan ME, Manners I (2015) Amine- and phosphine-borane adducts: new interest in old molecules. Chem Rev 110:4023–4078. doi:10.1021/cr100105a

Teraguchi M, Tanioka D, Kaneko T, Aoki T (2010) Helix-sense-selective polymerization of achiral phenylacetylenes with two N-alkylamide groups to generate the one-handed helical polymers stabilized by intramolecular hydrogen bonds. ACS Macro Lett 1:1258–1261. doi:10.1021/mz300309c

Youn SW, Bihn JH, Kim BS (2011) Pd-catalyzed intramolecular oxidative C–H amination: synthesis of carbazoles. Org Lett 13:3738–3741. doi:10.1021/ol201416u