Electronic Supplementary Information

Position-Selective Intramolecular Aromatic C-H Bond Activation of 1,2,3-Triazol-5-ylidene (tzNHC) Ligands in (p-Cymene)Ruthenium(II) Complexes

Kenichi Ogata, Sayuri Inomata and Shin-ichi Fukuzawa*

Department of Applied Chemistry, Institute of Science and Engineering, Chuo University
1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

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1. Experimental Procedures

1.1 General Procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under a nitrogen atmosphere by using a standard Schlenk tube or high vacuum techniques. CH₂Cl₂ was distilled over calcium hydride under nitrogen atmosphere prior to use. THF was distilled over sodium-benzophenone under nitrogen atmosphere prior to use. 2,6-dimethyl phenyl azide, 1,2-methyl phenyl azido, 1a, 3 1d were prepared according to literature procedures. Other reagents employed in this research were commercially available and used without further purification. Column chromatography was performed on silica gel (spherical, 60 μm) and alumina (spherical, 75 μm). The 1H and 13C NMR spectra recorded with a Varian Mercury-300 or Varian 400-MR spectrometer at ambient temperature. The chemical shifts were reported in δ units downfield from the internal reference (Me₄Si). All coupling constants were recorded in Hz. Elementary analysis were measured on a Perkin-Elmer 2400 series II CHN analyzer.

1.2 Synthesis of triazole and triazolium salt

1.2.1 Preparation of the 1-(2,6-xylyl)-4-phenyl-1,2,3-triazole.

\[
\text{N}_3 + \text{Ph} \text{-C} = \text{C} \text{-CH}_3 + \text{CuSO}_4, \text{Na ascorbate} \xrightarrow{\text{tert-BuOH}, \text{H}_2\text{O}} \text{N}_3 \text{-C} = \text{C} \text{-CH}_3
\]

The mixture of Phenylacetylene (0.37 mL, 3.3 mmol), 2,6-xylylazido (450 mg, 3.1 mmol), sodium ascorbate (1450 mg, 3.6 mmol), anhydrous copper sulfate (579 mg, 3.6 mmol), H₂O (5.0 mL) and tert-BuOH (20 mL) were charged in a 100 mL round-bottomed flask. After stirring at room temperature for 43 h under air, the mixture was extracted with ethyl acetate, washed with conc. NH₄Cl aq. dried over MgSO₄, and the volatile was removed under reduced pressure. The residual solid was purified by silica gel chromatograph (eluted with hexane first, then with ethyl acetate) to yield the 1-(2,6-xylyl)-4-phenyl-1,2,3-triazole as a white solid (721 mg, 2.89 mmol, 93%). 1H NMR (300 MHz, CDCl₃) δ 7.94 (d, J = 7.0 Hz, 2H, Ar), 7.87 (s, 1H, triazol C=CH), 7.5 (m, 2H, Ar), 7.4-7.3 (m, 2H, Ar) 7.21 (d, J = 7.7 Hz, 2H, Ar), 2.07 (s, 6H, xylyl-CH₃). 13C NMR (75 MHz, CDCl₃) δ 147.6, 135.8, 135.4, 130.3, 130.0, 128.9, 128.4, 128.3, 125.7, 121.3 (s, Ar, triazole C=C), 17.3 (s, xylyl-CH₃). Anal. Calcd for C₁₆H₁₅N₅: C, 77.08; H, 6.06; N, 16.85. Found: C, 77.34; H, 6.04; N, 16.96%.

1.2.2 Preparation of the 1-(2-methyl phenyl)-4-phenyl-1,2,3-triazole.

\[
\text{N}_3 + \text{Ph} \text{-C} = \text{C} \text{-CH}_3 + \text{CuSO}_4, \text{Na ascorbate} \xrightarrow{\text{tert-BuOH}, \text{H}_2\text{O}} \text{N}_3 \text{-C} = \text{C} \text{-CH}_3
\]

The mixture of Phenylacetylene (0.85 mL, 7.7 mmol), 2-methyl phenyl azido (1.02 g, 7.7 mmol), sodium ascorbate (153 mg, 0.77 mmol), copper sulfate pentahydrate (96.3 mg, 0.39 mmol), H₂O (11.0 mL) and tert-BuOH (11.0 mL) were charged in a 100 mL round-bottomed flask. After stirring at room temperature for overnight under air, the mixture was extracted with ethyl acetate, washed with conc. NH₄Cl aq. dried over MgSO₄, and the volatile was removed under reduced pressure. The residual solid was purified by silica gel chromatograph (eluted with hexane first, then with ethyl acetate) to yield the 1-(2-methyl phenyl)-4-phenyl-1,2,3-triazole as a white solid (1.02 g, 7.7 mmol, 93%). 1H NMR (300 MHz, CDCl₃) δ 7.98 (d, J = 7.0 Hz, 1H, Ar), 7.87 (s, 1H, triazol C=CH), 7.7 (m, 2H, Ar), 7.4-7.3 (m, 2H, Ar) 7.24 (d, J = 7.7 Hz, 2H, Ar), 2.07 (s, 6H, xylyl-CH₃). 13C NMR (75 MHz, CDCl₃) δ 147.6, 135.8, 135.4, 130.3, 130.0, 128.9, 128.4, 128.3, 125.7, 121.3 (s, Ar, triazole C=C), 17.3 (s, xylyl-CH₃). Anal. Calcd for C₁₆H₁₅N₅: C, 77.08; H, 6.06; N, 16.85. Found: C, 77.34; H, 6.04; N, 16.96%.
removed under reduced pressure. The residual solid was purified by silica gel chromatograph (eluted with hexane first then with ethyl acetate) to yield the compound as a white solid (1.51 g, 6.42 mmol, 83%). The compound was prepared by modified method for previous report which have been synthesized this compound.\textsuperscript{5} Spectroscopic data also was compared to data for previous report.\textsuperscript{2}

1.2.3 Preparation of the triazolium salt 1b

The mixture of 1-(2-methyl phenyl)-4-phenyl-1,2,3-triazole (186 mg, 0.79 mmol), Me\textsubscript{3}OBF\textsubscript{4} (159 mg, 1.03 mmol) and CH\textsubscript{2}Cl\textsubscript{2} (10 mL) were charged in a 50 mL Schlenk tube. After stirring at room temperature for overnight, the reaction was quenched with MeOH, and the volatile was removed under reduced pressure. The residual solid was washed with Et\textsubscript{2}O and dried to yield 1b as a white solid (252 mg, 2.89 mmol, 95%). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 8.35 (s, 1H, triazolium CH), 7.8-7.7 (m, 3H, Ar), 7.6 (m, 3H), 7.6-7.5 (m, 1H, Ar), 7.43 (dd, \( J \) = 6.3, 6.3 Hz, 2H, Ph), 4.39 (s, 3H, N-CH\textsubscript{3}), 2.38 (s, 3H, o-tolyl-CH\textsubscript{3}). \textsuperscript{13}C NMR (75 MHz, (CD\textsubscript{3})\textsubscript{2}SO) \( \delta \) 142.7 (triazolium CH), 134.2, 133.4, 132.1, 131.7, 130.4, 129.5, 129.5, 127.6, 126.2, 122.6 (s, Ar, triazole), 39.0 (s, N-CH\textsubscript{3}), 17.0 (s, xylyl-CH\textsubscript{3}). Anal. Calcd for C\textsubscript{16}H\textsubscript{16}N\textsubscript{3}: C, 57.00; H, 4.78; N, 12.46. Found: C, 57.08; H, 4.75; N, 12.54%

1.2.4 Preparation of the triazolium salt 1c.

The mixture of 1-xylyl-4-phenyl 1,2,3-triazole (125 mg, 0.50 mmol), Me\textsubscript{3}OBF\textsubscript{4} (99.7 mg, 0.67 mmol) and CH\textsubscript{2}Cl\textsubscript{2} 10 mL were charged in a 50 mL Schlenk tube. After stirring at room temperature for overnight, the reaction was quenched with MeOH, and the volatile was removed under reduced pressure. The residual solid was washed with Et\textsubscript{2}O and dried to yield 1c as a white solid (161 mg, 0.46 mmol, 92%). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 8.33 (s, 1H, triazolium CH), 7.81 (dd, \( J \) = 6.7, 3.1 Hz, 2H, Ar), 7.7-7.6 (m, 3H, Ar), 7.48 (d, \( J \) = 8.0 Hz, 1H, Ar), 7.3 (m, 2H, Ar), 4.47 (s, 3H, N-CH\textsubscript{3}), 2.22 (s, 6H, xylyl-CH\textsubscript{3}). \textsuperscript{13}C NMR (100 MHz, (CD\textsubscript{3})\textsubscript{2}SO) \( \delta \) 143.2 (s, triazolium CH), 134.9, 133.7, 132.0, 131.7, 130.9, 129.7, 129.4, 129.1, 122.7 (s, Ar, triazole), 39.1 (s, N-CH\textsubscript{3}), 16.9 (s, xylyl-CH\textsubscript{3}). Anal. Calcd for C\textsubscript{17}H\textsubscript{18}N\textsubscript{3}: C, 58.15; H, 5.17; N, 11.97. Found: C, 58.14; H, 5.06; N, 11.94%

S3
1.3 Synthesis of ruthenium NHC complexes

1.3.1 Synthesis of ruthenium complex 2a.

The mixture of a triazolium salt 1a (171 mg, 0.53 mmol), Ag₂O (74.3 mg, 0.32 mmol), Me₄NCl (69.7 mg, 0.64 mmol) and CH₂Cl₂/CH₃CN (1:1, 20 mL) were charged in a 50 mL Schlenk tube. After stirring at room temperature for 2 h, the volatile was removed under reduced pressure. The residual solid was extracted with CH₂Cl₂ and filtered, and the volatile was removed under reduced pressure. To this residue, [RuCl₂(p-cymene)]₂ (162 mg, 0.26 mmol) and CH₂Cl₂ 15 mL were added. After stirring for 3 h at room temperature, the volatile was concentrated in reduced pressure and purified by alumina column chromatography (CH₂Cl₂/acetone = 9/1) to yield 2a as a yellow solid (142 mg, 0.28 mmol, 53%). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from CH₂Cl₂ and Et₂O. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (dd, J = 7.4, 1.1 Hz, 1H, Ar), 7.9 (m, 2H, Ar), 7.6 (m, 4H, Ar), 7.12 (ddd, J = 7.4, 7.3, 1.4 Hz, 1H, Ar), 7.02 (ddd, J = 7.6, 7.5, 1.4Hz, 1H, Ar), 5.26 (d, J = 7.0 Hz, p-cymene ring), 5.25 (d, J = 7.0 Hz, 1H, p-cymene ring), 4.83 (d, J = 5.8 Hz, 1H, p-cymene ring), 4.80 (d, J = 5.8 Hz, 1H, p-cymene ring), 4.11 (s, 3H, N-CH₃), 2.14 (sep, 1H, J = 6.9 Hz, p-cymene-CH(CH₃)₂), 1.94 (s, 3H, p-cymene-CH₃), 0.81 (d, J = 6.9 Hz, 3H, p-cymene-CH(CH₃)₂), 0.81 (d, J = 6.9 Hz, 3H, p-cymene-CH(CH₃)₂). ¹³C NMR (100 MHz, CDCl₃) δ 173.0 (s, Ru-C(Ar)), 166.3 (s, carbene carbon), 145.7 144.9, 142.0, 130.6, 129.7, 128.9, 128.7, 127.4, 122.3, 113.8 (s, Ph, triazole), 102.1, 99.6, 89.7, 89.6, 88.4, 84.3 (s, p-cymene ring), 37.0, 30.9, 23.1, 21.5, 18.9 (s, p-cymene-CH₃, p-cymene-CH(CH₃)₂, N-CH₃). Anal. Calcd for C₂₃H₂₆ClN₃Ru: C, 59.46; H, 5.19; N, 8.32. Found: C, 59.42; H, 5.11; N, 8.28%

1.3.2 Synthesis of ruthenium complexes 2b.

Complex 2b was prepared from triazolium salt 1b (80.7 mg, 0.24 mmol), Ag₂O (33.9 mg, 0.15 mmol), Me₄NCl (31.6 mg, 0.29 mmol) and [RuCl₂(p-cymene)]₂ (73.9 mg, 0.12 mmol) in the same manner as that for 2a except for purification method. Complex 2b was isolated by recrystallization from CH₂Cl₂/Et₂O as an orange solid (50.3 mg, 0.10 mmol, 40%). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from 1,2-C₂H₄Cl₂ and Et₂O. ¹H NMR (300 MHz, CDCl₃) δ 8.13 (d, J = 6.9 Hz, 1H, o-toly), 7.9 (m, 2H, Ph), 7.6 (m, 3H,
Ph), 6.98 (dd, 1H, J = 7.4, 7.4 Hz, o-tolyl), 6.80 (d, J = 7.2 Hz, 1H, o-tolyl), 5.21 (s, 2H, p-cymene ring), 4.80 (d, J = 5.8 Hz, 1H, p-cymene ring), 4.74 (d, J = 5.8 Hz, 1H, p-cymene ring), 4.11 (s, 3H, N-CH₃), 2.62 (s, 3H, o-tolyl-CH₃), 2.12 (sep, J = 6.9 Hz, 1H, p-cymene-CH(CH₃)₂), 1.92 (s, 3H, p-cymene-CH₃), 0.80 (d, J = 6.9 Hz, 3H, p-cymene-CH(CH₃)₂), 0.73 (d, J = 6.9 Hz, 3H, p-cymene-CH(CH₃)₂). ¹³C NMR (75 MHz, CDCl₃) δ 174.2 (s, Ru-C(Ar)), 167.6 (s, carbene carbon), 144.5, 143.6, 139.7, 130.8, 129.8, 128.8, 126.6, 126.1, 125.9 (s, Ar, triazole), 102.1, 99.5, 90.1, 88.6, 84.7 (s, p-cymene ring), 37.1, 30.8, 23.0, 21.5, 20.8, 18.9 (s, p-cymene-CH(CH₃)₂), p-cymene-CH(CH₃)₂, N-CH₃, o-tolyl-CH₃). Anal. Calcd for C₂₇H₂₆Cl₁₃Ru-0.25CH₂Cl₂: C, 58.36; H, 5.32; N, 7.78. Found: C, 58.46; H, 5.21; N, 7.88% 

### 1.3.3 Synthesis of ruthenium complexes 3c.

Complex 3c was prepared from triazolium salt 1c (231 mg, 0.66 mmol), Ag₂O (92.6 mg, 0.40 mmol), Me₃NCl (86.6 mg, 0.79 mmol) and [RuCl₂(p-cymene)]₂ (203 mg, 0.33 mmol) in the same manner as that for 2b. Complex 3c was isolated as an orange solid (300 mg, 0.53 mmol, 80%). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from CH₂Cl₂ and Et₂O. ¹H NMR (300 MHz, CDCl₃) δ 8.0 (m, 2H, Ar), 7.6 (m, 3H, Ar), 7.23 (t, J = 7.5 Hz, 1H, Ar), 7.05 (d, J = 7.5 Hz, 2H, Ar), 5.13 (d, J = 5.9 Hz, 2H, p-cymene ring), 4.22 (d, 2H, J = 5.9 Hz, p-cymene ring), 3.97 (s, 3H, N-CH₃), 2.85 (sep, J = 6.9 Hz, 1H, p-cymene-CH(CH₃)₂), 1.80 (s, 3H, p-cymene-CH₃), 1.16 (d, J = 6.9 Hz, 6H, p-cymene-CH(CH₃)₂). ¹³C NMR NMR (300 MHz, CDCl₃) δ 162.4 (s, carbene carbon), 147.7, 140.1, 135.4, 131.8, 130.1, 129.8, 129.3, 128.6, 127.3 (s, Ar, triazole), 106.6, 97.0, 88.6, 80.4 (p-cymene ring), 37.6, 30.3, 22.4, 18.5, 18.4 (s, p-cymene-CH(CH₃)₂), p-cymene-CH(CH₃)₂, N-CH₃, xylyl). Anal. Calcd for C₂₇H₂₆Cl₃N₂Ru-1/3CH₂Cl₂: C, 54.91; H, 5.34; N, 7.03. Found: C, 54.63; H, 5.27; N, 6.99% 

### 1.3.4 Synthesis of ruthenium complexes 3d.

Complex 3d was prepared from 1d (186 mg, 0.55 mmol), Ag₂O (77.3 mg, 0.33 mmol), Me₃NCl (72.3 mg, 0.66 mmol) and [RuCl₂(p-cymene)]₂ (169 mg, 0.28 mmol) in the same manner as that for 2b. Complex 3d was isolated as an orange solid (297 mg, 0.53 mmol, 97%). ¹H NMR (300 MHz, CDCl₃) δ 7.72 (dd, J = 6.5, 3.1 Hz, 2H, Ar), 7.5 (m, 3H, Ar), 7.4-7.3 (m, 5H, Ar), 6.28 (s, 2H, Bn-CH₂), 5.13 (d, J = 6.0 Hz, 2H, p-cymene ring), 4.74 (d, J = 6.0
Hz, 2H, p-cymene ring), 3.74 (s, 3H, N-CH$_3$), 2.47 (sep, $J = 6.9$ Hz, 1H, p-cymene-CH(CH$_3$)$_2$), 1.59 (s, 3H, p-cymene-CH$_3$), 1.07 (d, $J = 6.9$ Hz, 6H, p-cymene-CH(CH$_3$)$_2$). $^{13}$C NMR (75MHz, CDCl$_3$) δ 161.3 (s, carbene carbon), 148.5, 136.4, 131.9, 128.6, 128.5, 127.9 (s, Ar, triazole), 105.5, 96.4, 84.7, 83.2 (s, p-cymene ring), 57.1 (s, Bn-CH$_2$), 37.1, 30.3, 22.4, 17.9 (s, p-cymene-CH$_3$), 1.82 (s, 3H, cymene-CH$_3$), 1.07 (d, $J = 6.9$ Hz, 3H, p-cymene-CH(CH$_3$)$_2$), 0.92 (d, $J = 6.9$ Hz, 3H, p-cymene-CH(CH$_3$)$_2$).

**1.3.5 Synthesis of ruthenium complexes 4c.**

The mixture of the ruthenium complex 3c (89.5 mg, 0.16 mmol), K$_2$CO$_3$ (35.0 mg, 0.25 mmol) and THF 5 mL were charged in a 20 mL Schlenk tube. After stirring at reflux for 6 h, the volatile was removed under reduced pressure. The residual solid was extracted with CH$_2$Cl$_2$ and filtered. The volatile was removed under reduced pressure and the residue was recrystallized (CH$_2$Cl$_2$/Et$_2$O) to yield 4c as a yellow solid (61.6 mg, 0.12 mmol, 75%). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.27 (d, $J = 7.4$, Hz, 1H, Ph), 7.47 (dd, $J = 7.6$, 7.6 Hz, 1H, Ph), 7.4-7.3 (m, 3H, xylyl), 7.06 (dd, $J = 7.4$, 7.2 Hz, 1H, Ph), 6.96 (dd, $J = 7.6$, 7.6 Hz, 1H, Ph), 5.53 (d, $J = 6.0$ Hz, 1H, p-cymene ring), 4.91 (d, 1H, $J = 6.0$ Hz, p-cymene ring), 4.55 (d, 1H, $J = 5.5$ Hz, p-cymene ring), 4.28 (d, 1H, $J = 5.5$ Hz, p-cymene ring), 4.27 (s, 3H, N-CH$_3$), 2.39 (s, 3H, p-cymene-CH$_3$), 2.30 (sep, $J = 6.9$ Hz, 1H, p-cymene-CH(CH$_3$)$_2$), 2.10 (s, 3H, xylyl-CH$_3$), 1.82 (s, 3H, xylyl-CH$_3$), 0.92 (d, $J = 6.9$ Hz, 3H, p-cymene-CH(CH$_3$)$_2$), 0.52 (d, $J = 6.9$ Hz, 3H, p-cymene-CH(CH$_3$)$_2$). $^{13}$C NMR NMR (300 MHz CDCl$_3$) δ 180.8, 178.4 (s, Ru-C(Ar), carbene carbon), 152.9 (s, triazole), 142.2, 138.1, 137.9, 136.5, 135.2, 130.2, 128.9, 127.8, 127.4, 121.8, 120.8 (s, Ar), 100.9, 99.8, 93.6, 90.8, 89.5, 75.9 (s, p-cymene ring), 37.3, 30.6, 23.9, 20.7, 18.9, 18.4, 17.6 (s, p-cymene-CH(CH$_3$)$_2$, p-cymene-CH(CH$_3$)$_2$, xylyl, N-CH$_3$). HR-MS (ESI) calcd for C$_{28}$H$_{30}$ClN$_3$Ru [M+Na]$^+$ 556.1069, found 556.1068.
2. X-ray Crystallographic data

Crystal data for 2a: C_{25}H_{20}ClN_{4}Ru, \( M = 505.02 \), monoclinic, \( a = 7.9014(19) \), \( b = 23.660(6) \), \( c = 11.737(3) \) Å, \( V = 2187.0(9) \) Å\(^3\), \( T = 123 \) K, space group \( P2_1/n \) (no. 14), \( Z = 4 \), \( \mu(\text{Mo}–\text{K}\alpha) = 8.562 \) cm\(^{-1}\), 16427 measured reflections, 4990 unique reflections. \( R_1 = 0.0303 \), \( wR_2 = 0.0703 \), for 4550 reflections. For 2b-CH\(_2\)Cl\(_2\): C\(_{25}\)H\(_{32}\)Cl\(_3\)N\(_3\)Ru, \( M = 618.01 \), monoclinic, \( a = 29.7166(6) \), \( b = 11.3579(2) \), \( c = 21.1834(4) \) Å, \( V = 5507(2) \) Å\(^3\), \( T = 198 \) K, space group \( C2/c \) (no. 15), \( Z = 8 \), \( \mu(\text{Mo}–\text{K}\alpha) = 8.822 \) cm\(^{-1}\), 25744 measured reflections, 6277 unique reflections. \( R_1 = 0.0365 \), \( wR_2 = 0.0917 \), for 5904 reflections. For 3c-2CH\(_2\)Cl\(_2\): C\(_{29}\)H\(_{35}\)Cl\(_4\)N\(_3\)Ru, \( M = 739.40 \), monoclinic, \( a = 22.430(5) \), \( b = 13.091(3) \), \( c = 23.693(3) \) Å, \( V = 6449(3) \) Å\(^3\), \( T = 123 \) K, space group \( P2_1/n \) (no. 14), \( Z = 8 \), \( \mu(\text{Mo}–\text{K}\alpha) = 10.070 \) cm\(^{-1}\), 48952 measured reflections, 14715 unique reflections. \( R_1 = 0.0779 \), \( wR_2 = 0.2052 \), for 11198 reflections. For 4c-CH\(_2\)Cl\(_2\): C\(_{29}\)H\(_{32}\)Cl\(_3\)N\(_3\)Ru, \( M = 618.01 \), monoclinic, \( a = 10.8748(3) \), \( b = 9.4047(2) \), \( c = 26.8586(6) \) Å, \( V = 2739.6(2) \) Å\(^3\), \( T = 198 \) K, space group \( P2_1/n \) (no. 14), \( Z = 4 \), \( \mu(\text{Mo}–\text{K}\alpha) = 8.867 \) cm\(^{-1}\), 25313 measured reflections, 6266 unique reflections. \( R_1 = 0.0302 \), \( wR_2 = 0.0541 \), for 5599 reflections. CCDC numbers: 901766 (2a), 901767 (2b), 901768 (3c) and 901934 (4c).

3. References