

Introducing Axial Chirality into Mesoionic 4,4'-Bis(1,2,3-triazole) Dicarbenes

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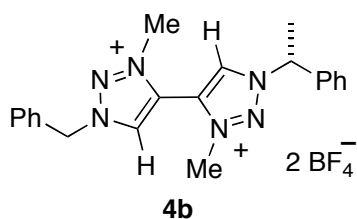
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1. Preparation Details and Physical and Spectroscopic Data of Compounds 3a-c, 4a-c

1.1. General. All reactions were carried out under an atmosphere of nitrogen in oven or flame-dried glassware with magnetic stirring. Solvents were distilled prior to use. Acetonitrile (CH₃CN) and dichloromethane (CH₂Cl₂) were distilled from calcium hydride. Methanol (MeOH) was dried over magnesium metal and iodine. Purification of reaction products was carried out by flash chromatography using silicagel 60 (230-400 mesh, from Merck 60F PF254). Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F plates. Melting points were measured with a Büchi SMP-20 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Bruker Alpha-P spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance DPX300 and Bruker Avance500 spectrometers and are reported as δ values (ppm) relative to residual CHCl₃ δH (7.26 ppm) and CDCl₃ δC (77.16 ppm) as internal standards, respectively. Mass spectra were obtained with an Agilent HP 5973 mass spectrometer using a TOF analyzer (GCT Micromass). The preparation of some bis(1,2,3-triazole) compounds was previously reported: **4a**,¹ **8a**² and **9a**¹.

1.2. Synthesis of 4,4'-bis(1*H*-1,2,3-triazolium) tetrafluoroborates 4b-c



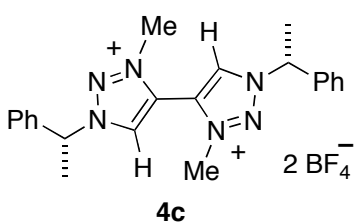
Compound 4b: CuSO₄·5H₂O (0.15 mmol, 37 mg) and sodium ascorbate (0.30 mmol, 59 mg) were added to a solution of 1-benzyl-4-ethynyl-1*H*-1,2,3-triazole² (0.76 mmol, 105 mg) and (*R*)-α-methylbenzyl azide (1.14 mmol, 168 mg) in H₂O:^tBuOH:THF 1:1:1 (9 mL) and the mixture was stirred at room temperature overnight.

The solvent was evaporated *in vacuo*, the residue was suspended in aqueous 10% NH₃ and the mixture was extracted with CH₂Cl₂ (3 x10 mL). The combined organic layer was dried (MgSO₄) and the solvent was evaporated under reduced pressure to afford the intermediate 1-benzyl-1'-

¹ Aizpurua, J. M.; Sagartzazu-Aizpurua, M.; Monasterio, Z.; Azcune, I.; Miranda, J. I.; García-Lecina, E.; Fratila, R. M. *Synthesis*, **2011**, 2737-2742.

² Monkowius, U.; Ritter, S.; König, B.; Zabel, M.; Yersin, H. *Eur. J. Inorg. Chem.*, **2007**, 4597-4606.

(*R*)- α -methylbenzyl-4,4'-bis-1*H*-1,2,3-triazole [Yield: 190 mg (76%); m.p. = 172.1-173.3°C; $[\alpha]_D^{20} = -19.52^\circ$ (c= 1.04, CH₂Cl₂); IR (cm⁻¹): 1455 (trz); ¹H NMR (500 MHz, CDCl₃) δ 7.97 (s, 2H), 7.42 – 7.30 (m, 10H), 5.88 (q, *J* = 6.8, 1H), 5.58 (s, 2H), 2.02 (d, *J* = 7.0, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 140.6, 140.0, 139.5, 134.3, 129.2, 129.1, 128.9, 128.7, 128.2, 126.6, 120.5, 119.4, 60.4, 54.3, 21.2; HRMS (ESI+): *m/z* [M]⁺ calcd for C₁₉H₁₉N₆⁺: 331.1671; found: 331.1665]. To this material (0.30 mmol, 100 mg) dissolved under nitrogen atmosphere in anhydrous CH₂Cl₂ (3 mL), was added trimethyloxonium tetrafluoroborate (1.20 mmol, 228 mg) and the reaction mixture was stirred at room temperature overnight. The solvent was evaporated and the product was purified by crystallization from MeOH/Et₂O as a white powder. Yield: 140 mg (87%); m.p. = 77.1-78.2°C; $[\alpha]_D^{20} = -6.70^\circ$ (c= 1.68, acetone); IR (cm⁻¹): 1455 (trz), 1065 (BF₄); ¹H NMR (500 MHz, DMSO) δ 9.46 (s, 1H), 9.45 (s, 1H), 7.56-7.48 (m, 10H), 6.40 (q, *J* = 6.9, 1H), 6.02 (s, 2H), 4.35 (s, 3H), 4.34 (s, 3H), 2.05 (d, *J* = 7.0, 3H); ¹³C NMR (126 MHz, DMSO) δ 137.3, 133.0, 132.5, 131.8, 129.5, 129.4, 129.1, 129.0, 127.2, 127.0, 64.4, 56.8, 39.5, 20.1; HRMS (ESI+): *m/z* [M·2·BF₄-H]⁺ calcd: 359.1984; found: 359.1982.



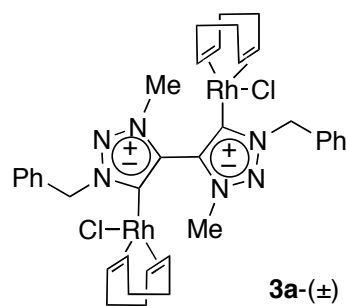
Compound 4c: To a solution of 1,4-bis(trimethylsilyl)-1,3-butadiyne (1.37 mmol, 266 mg) and (*R*)- α -methylbenzyl azide (2.87 mmol, 422 mg) in H₂O:BuOH 1:1 (20 mL), CuSO₄·5H₂O (1.15 mmol, 402 mg), sodium ascorbate (2.30 mmol, 456 mg), pyridine (13.70 mmol, 1.10 mL) and K₂CO₃ (2.74 mmol, 379 mg)

were added and the reaction mixture was stirred vigorously for 24 hours. The solvent was evaporated *in vacuo*, the residue was suspended in aqueous 10% NH₃ (10%) and it was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic layer was dried (MgSO₄) and the solvent was evaporated under reduced pressure to afford the intermediate 1,1'-bis[(*R*)- α -methylbenzyl]-4,4'-bis-1*H*-1,2,3-triazole [Yield: 414 mg (88%); m.p. = 168.8°C; $[\alpha]_D^{20} = -37.8^\circ$ (c= 1.05, CH₂Cl₂); IR (cm⁻¹): 1456 (trz); ¹H NMR (500 MHz, CDCl₃) δ 7.98 (s, 2H), 7.43 - 7.30 (m, 10H), 5.89 (q, *J* = 7.1, 2H), 2.09 – 1.97 (d, *J* = 7.1, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 139.5, 129.0, 128.6, 126.5, 119.4, 60.4, 21.2; HRMS (ESI+): *m/z* [M]⁺ calcd for C₁₉H₁₉N₆⁺: 331.1671; found: 331.1665]. To this material (1.08 mmol, 371 mg) dissolved in anhydrous CH₂Cl₂ (11 mL), was added trimethyloxonium tetrafluoroborate (4.31 mmol, 838 mg) and the reaction mixture was stirred at room temperature overnight. The solvent was evaporated and the product was purified

by crystallization from MeOH/Et₂O as a white powder. Yield: 325 mg (55%); m.p. = 148.1-148.9°C; $[\alpha]_D^{20} = -81.85^\circ$ (c = 0.56, acetone); IR (cm⁻¹): 1459 (trz), 1050 (BF₄). ¹H NMR (500 MHz, DMSO) δ 9.47 (s, 2H), 7.59 – 7.41 (m, 10H), 6.41 (q, *J* = 6.9 Hz, 2H), 4.36 (s, 6H), 2.07 (d, *J* = 7.0 Hz, 6H); ¹³C NMR (126 MHz, DMSO) δ 137.3, 131.9, 129.4, 129.1, 127.1, 64.4, 39.5, 20.1; HRMS (ESI+): *m/z* [M-2·BF₄-H]⁺ calcd: 373.2141 ; found: 373.2145.

1.3. Synthesis of 4,4'-bis(1*H*-1,2,3-triazol-5,5'-diylidene)di[rhodium(I)(cod)chloride] complexes **3a-c**

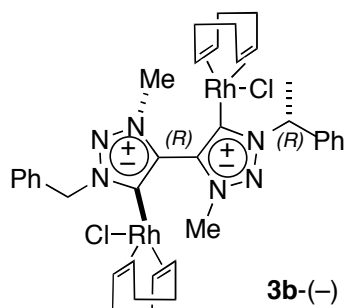
General procedure: To a solution of the corresponding 4,4'-bis(1*H*-1,2,3-triazolium) ditetrafluoroborate **4a-c** (1.0 mmol) in anhydrous MeCN (15 mL) was added Ag₂O (3.0 mmol) and the mixture was refluxed for 24 hours at 80°C. The suspension was filtered through a celite pad, washed with anhydrous methanol (3 x 5 mL) and the combined filtrate was evaporated *in vacuo* to afford the corresponding intermediate Ag(I) dicarbene complex. The product was used in the next reaction without further purification. Dimer complex [Rh(I)Cl(cod)]₂ (2.0 mmol) and tetramethylammonium chloride (2.0 mmol) were added to a solution of the corresponding Ag(I) dicarbene complex (1.0 mmol) in dried MeCN (15 mL) and the mixture was stirred for 2 hours at room temperature. Upon completion, it was filtered through a celite pad, which was rinsed with dichloromethane and the filtrate was evaporated *in vacuo*. The product was purified by column chromatography (silica gel, CH₂Cl₂:MeOH 95:5) to afford a yellow solid.



Compound 3a: The general procedure 1.3. was followed starting from 3,3'-dimethyl-1,1'-dibenzyl-4,4'-bis-1*H*-1,2,3-triazolium ditetrafluoroborate **4a** (0.31 mmol, 160 mg) and Ag₂O (1.23 mmol, 284 mg) in anhydrous acetonitrile (5.30 mL). [Intermediate dicarbene Ag(I) complex: yellowish oil, yield: 187 mg (94%); ¹H NMR (400 MHz, CD₃CN) δ 7.27 – 7.09 (m, 10H), 5.57 (d, *J* = 14.2, 2H), 5.41 (d, *J* = 14.3, 2H), 4.22 (s, 6H); ¹³C NMR (101 MHz, CD₃CN) δ

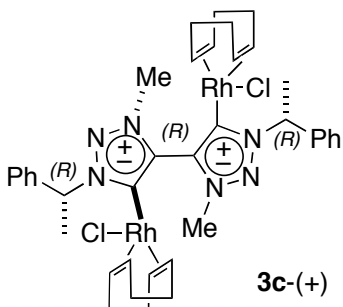
169.8 (carbene Ag-C), 137.4, 134.2, 128.9, 128.4, 128.2, 58.1, 37.7]. The Ag(I) dicarbene complex (0.02 mmol, 10 mg) was reacted with the dimer complex [Rh(I)Cl(cod)]₂ (0.02 mmol, 8

mg) and tetramethylammonium chloride (0.03 mmol, 3 mg) in acetonitrile (0.50 mL). Yield: 11 mg (85%); m.p.: 140°C dec. (CH₂Cl₂/pentane); IR (cm⁻¹): 2921(cod), 1455 (trz); ¹H NMR (500 MHz, CDCl₃) δ 7.56-7.40 (m, 10H), 6.56 (d, *J* = 14.5, 2H), 5.77 (d, *J* = 14.5, 2H), 5.10 – 5.02 (m, 2H), 4.95 – 4.87 (m, 2H), 4.82 (s, 6H), 2.37 – 2.24 (m, 4H), 2.09-2.04 (m, 4H), 1.85 – 1.82 (m, 2H), 1.71 – 1.53 (m, 8H), 1.35-1.34 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 171.9 (d, ¹*J*_{RhC} = 46.3), 135.5, 133.2, 128.8, 128.45, 128.3, 98.8 (d, *J* = 6.8), 96.3 (d, *J* = 7.3), 69.7 (d, *J* = 14.6), 68.1 (d, *J* = 14.3), 58.3, 40.4, 34.0, 31.8, 29.0, 27.8; HRMS (ESI+): *m/z* [M-Cl]⁺ calcd for: 801.1426; found: 801.1454.



Compound 3b: The general procedure 1.3. was followed starting from 3,3'-dimethyl-1-benzyl-1'-(*R*)- α -methylbenzyl-4,4'-bis-1*H*-1,2,3-triazolium ditetrafluoroborate **4b** (0.19 mmol, 100 mg) and Ag₂O (0.63 mmol, 146 mg) in anhydrous acetonitrile (5.30 mL). [Intermediate dicarbene Ag(I) complex: yellowish oil, yield 125 mg (72%); ¹H NMR (400 MHz, CD₃CN) δ 7.27-7.00 (m, 10H), 5.89 (m, 1H), 5.55 (d, *J* = 15.2, 2H), 5.41 (d, *J* = 13.5, 2H), 4.23 (s, 6H),

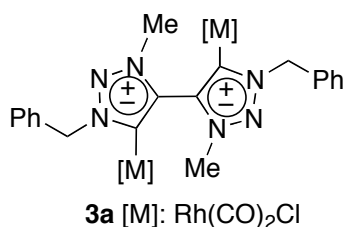
1.90 (d, *J* = 6.8, 3H); ¹³C NMR (101 MHz, CD₃CN) δ 170.1, 168.4 (carbene Ag-C), 138.6, 137.9, 137.4, 134.5, 129.2, 128.7, 128.5, 128.1, 127.5, 63.7, 58.4, 38.0, 20.4]. The Ag(I) dicarbene complex (0.04 mmol, 30 mg) was reacted with the dimer complex [Rh(I)Cl(cod)]₂ (0.04 mmol, 18 mg) and tetramethylammonium chloride (0.07 mmol, 8 mg) in acetonitrile (1.50 mL). Yield: 27 mg (87%); m.p.: 160°C dec. (CH₂Cl₂); [α]_D²⁰ = -128.6° (c= 0.65, CH₂Cl₂); IR (cm⁻¹): 2921(cod), 1455 (trz); ¹H NMR (500 MHz, CDCl₃) δ 7.56-7.37 (m, 10H), 7.08 (q, *J* = 6.7, 1H), 6.56 (d, *J* = 14.5, 1H), 5.76 (d, *J* = 14.5, 1H), 5.06 (m, 2H), 4.90 (m, 2H), 4.86 (s, 3H), 4.83 (s, 3H), 2.43-2.23 (m, 4H), 2.08 (d, *J* = 6.9, 3H), 2.05-1.97 (m, 4H), 1.89-1.78 (m, 2H), 1.76-1.49 (m, 8H), 1.40-1.28 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 172.7 (d, ¹*J*_{RhC} = 46.1), 172.2 (d, ¹*J*_{RhC} = 46.2), 142.2, 136.0, 133.7 (d, *J* = 3.0), 133.0 (d, *J* = 3.0), 129.2, 129.1, 128.9, 128.7, 128.5, 127.0, 99.2 (d, *J* = 6.9), 99.1 (d, *J* = 6.8), 96.7 (d, *J* = 7.4), 96.5 (d, *J* = 7.4), 70.2 (d, *J* = 14.6), 70.0 (d, *J* = 14.7), 68.6 (d, *J* = 14.3), 68.3 (d, *J* = 14.4), 66.4, 58.8, 41.0, 40.8, 34.4, 34.2, 32.2, 32.1, 29.6, 29.4, 28.3, 28.2, 23.0; HRMS (ESI+): *m/z* [M-Cl]⁺ calcd: 815.1583; found: 815.1584.



Compound 3c: The general procedure 1.3. was followed starting from 3,3'-dimethyl-1,1'-bis((*R*)- α -methylbenzyl)-4,4'-bis-1*H*-1,2,3-triazolium ditetrafluoroborate **4c** (0.18 mmol, 100 mg) and Ag₂O (0.54 mmol, 125 mg) in anhydrous acetonitrile (4 mL). [Intermediate dicarbene Ag(I) complex: ¹H NMR (400 MHz, CD₃CN) δ 7.22 – 7.01 (m, 10H), 5.89 (q, *J* = 7.0, 2H), 4.25 (s, 6H), 1.90 (d, *J* = 7.0, 6H); ¹³C NMR (101 MHz, CD₃CN) δ 138.6, 137.7,

128.5, 128.0, 127.5, 63.7, 38.0, 20.4³]. The Ag(I) dicarbene complex (0.04 mmol, 30 mg) was reacted with dimer complex [Rh(I)Cl(cod)]₂ (0.04 mmol, 18 mg) and tetramethylammonium chloride (0.07 mmol, 8 mg) in acetonitrile (1.5 mL). Yield = 30 mg (98%), m.p. = 222°C dec. (CH₂Cl₂); [α]_D²⁰ = +364.4° (c = 0.56, CH₂Cl₂); IR (cm⁻¹): 2926(cod), 1454 (trz); ¹H NMR (400 MHz, CDCl₃) δ 7.56–7.29 (m, 10H), 7.07 (q, *J* = 7.0, 2H), 5.10 – 5.03 (m, 2H), 4.94–4.87 (m, 2H), 4.85 (s, 6H), 2.41–2.16 (m, 4H), 2.08 (d, *J* = 7.1, 6H), 2.06 – 1.94 (m, 4H), 1.69–1.48 (m, 10H), 1.38 – 1.25 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 172.3 (d, ¹*J*_{RhC} = 46.2), 141.8, 132.7 (d, *J* = 2.6), 128.8, 128.1, 126.6, 98.7 (d, *J* = 7.0), 96.1 (d, *J* = 7.5), 69.7 (d, *J* = 14.6), 68.0 (d, *J* = 14.4), 66.0, 40.6, 33.9, 31.8, 29.2, 27.9, 22.6; HRMS (ESI+): *m/z* [M-Cl]⁺ calcd: 829.1739; found: 829.1743.

1.4. Determination of the Tolman Electronic Parameter in dicarbene complex **3a** [M = Rh(CO)₂Cl]



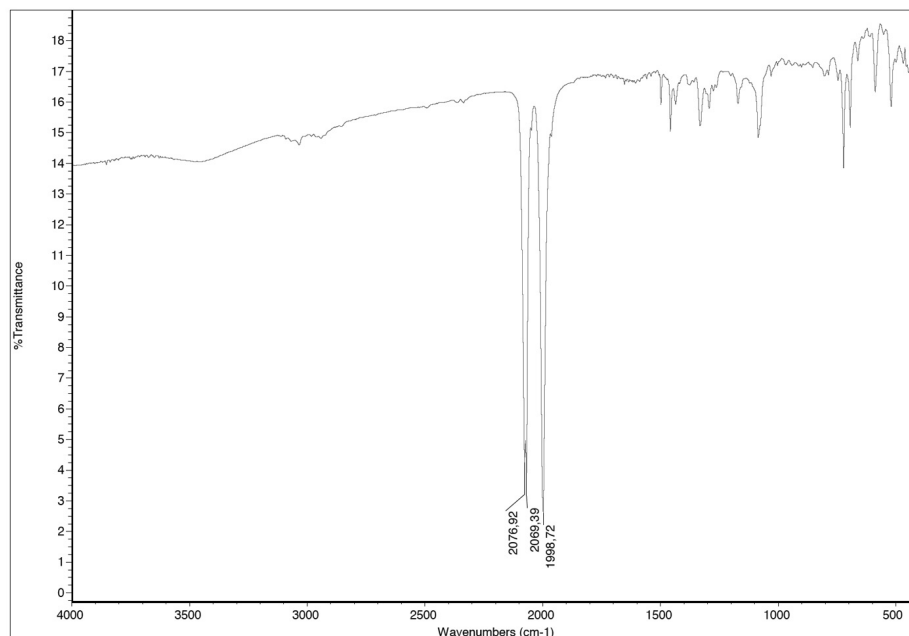
Dimer complex **3a** [M]: Rh(Cod)Cl (8 mg, 10 μ mol) was dissolved in *ca.* 1 mL of dichloromethane and CO was bubbled through it for 1 hour, after which time the volume was reduced *in vacuo* and a light yellow precipitate appeared upon addition of hexane. The solid was decanted, further washed with hexane and dried *in vacuo*. Yield: 5.9 mg (79%); IR (cm⁻¹): 2077, 2069, 1999 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 7.50 – 7.15 (m, 10H), 6.17 (d, *J* = 14.4, 2H), 5.80 (d, *J* = 14.4, 2H), 4.45 (s, 6H).

³ Carbene signal not observed. For similar examples, see Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978–4008.

The TEP value for **3a** [M= Rh(CO)₂Cl] was calculated from equation (1),⁴ correlating the Tolman parameter with the carbonyl stretch frequency $\nu_{\text{average}}(\text{CO})\text{Ir}$ in $\text{L}(\text{CO})_2\text{Cl}$ complexes, and equation (2),⁵ correlating the stretch frequencies $\nu_{\text{average}}(\text{CO})\text{Ir}$ and $\nu_{\text{average}}(\text{CO})\text{Rh}$.

$$(1) \quad \text{TEP (cm}^{-1}\text{)} = 0.847 \nu_{\text{average}}(\text{CO})\text{Ir} - 336 \text{ cm}^{-1}$$

$$(2) \quad \nu_{\text{average}}(\text{CO})\text{Ir} = 0.8695 \nu_{\text{average}}(\text{CO})\text{Rh} - 250.7 \text{ cm}^{-1}$$



3a [M= Rh(CO)₂Cl]

$$\nu_{\text{a}}(\text{CO})\text{Rh} = 2076.92$$

$$\nu_{\text{b}}(\text{CO})\text{Rh} = 2069.39$$

$$\nu_{\text{c}}(\text{CO})\text{Rh} = 1998.72$$

$$\nu_{1_{\text{av}}}(\text{CO})\text{Ir} = 2022.7$$

$$\nu_{2_{\text{av}}}(\text{CO})\text{Ir} = 2019.2$$

$$\boxed{\text{TEP}_1 = 2049.2 \text{ cm}^{-1}}$$

$$\boxed{\text{TEP}_2 = 2046.2 \text{ cm}^{-1}}$$

Figure S1. FT-IR spectrum of compound **3a** [M= Rh(CO)₂Cl]

The TEP values for 4,4'-bis(1*H*-1,2,3-triazole-5,5'-ylidene) ligand in the complex **3a** were very similar to previously reported 1*H*-1,2,3-triazole-5-ylidenes ($\approx 2047 \text{ cm}^{-1}$) or 1,3-imidazole-2-ylidenes ($\approx 2049 \text{ cm}^{-1}$).⁶

⁴ Kelly III, R. A.; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics*, **2008**, *27*, 202-210.

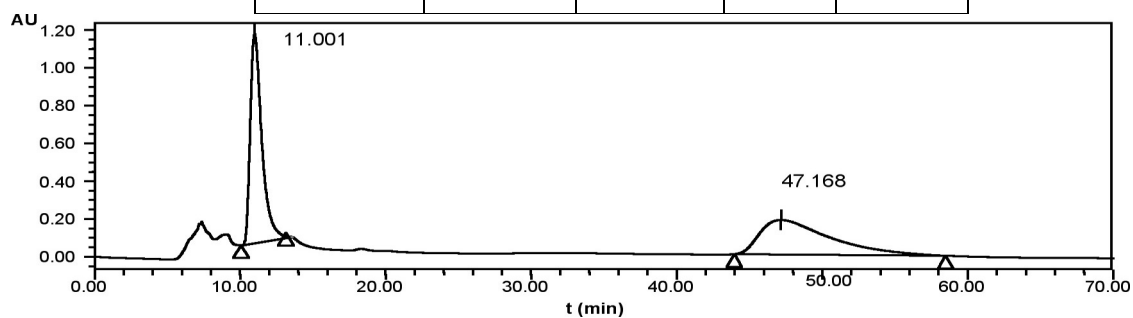
⁵ Wolf, S.; Plenio, H. *J. Organomet. Chem.*, **2009**, *694*, 1487-149.

⁶ Mathew, P.; Neels, A.; Albrecht, M. *J. Am. Chem. Soc.* **2008**, *130*, 13534-13535.

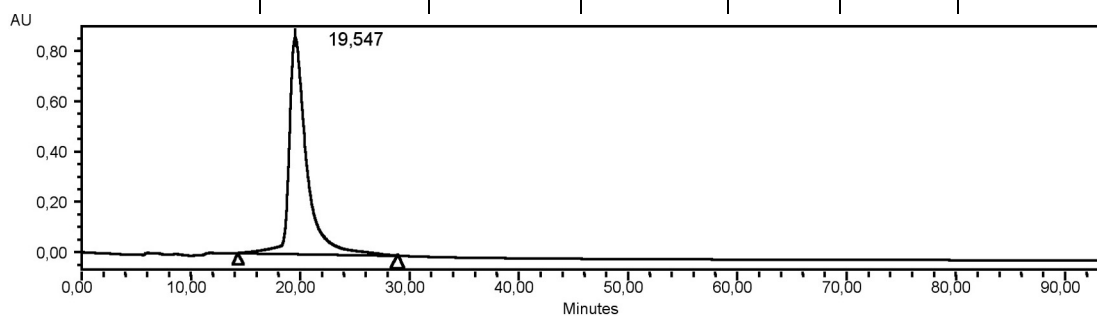
1.5. Optical purity (chiral HPLC) of complexes 3a-c

Analytical HPLC was performed on a Waters-600E chromatograph (diode array UV detector), using a Daicel Chiralpak OD-H column. Eluent: *i*PrOH/hexane 30/70; 0.5-1 mL/min, $\lambda = 227\text{nm}$.

Compound	R.T. (min)	Area	%Area	Height
3a-(<i>R</i>)	11.001	63756468	49.98	1210838
3a-(<i>S</i>)	47.168	63807494	50.02	196734



Compound	R.T. (min)	Area	%Area	Height
3b-(<i>R</i>)	19.547	95702995	100.00	859502



Compound	R.T. (min)	Area	%Area	Height
3c-(<i>R</i>)	8.617	32918554	100.00	493635

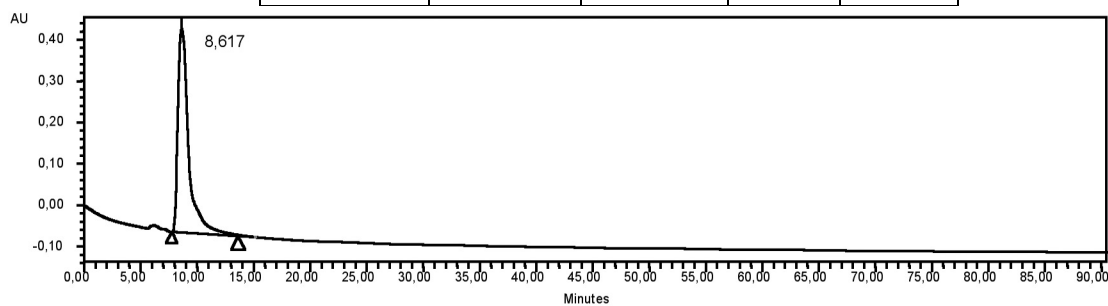


Figure S2. HPLC chromatograms of compound 3a-c [M= Rh(cod)Cl]

2. ^1H and ^{13}C NMR Spectra of Compounds **3a-c** [$\text{M} = \text{Ag}$] and **3a-c** [$\text{M} = \text{Rh}(\text{cod})\text{Cl}$]

The transient formation of the Ag(I)-complexed intermediate cation carbene **6a** is evidenced by ^1H -NMR spectroscopy (Figure S3). Spectrum 1 (reaction time 0h); Spectrum 2 (reaction time 3h); Spectrum 3 (reaction time 24h). Benzylic protons in **4a** are magnetically equivalent (singlet at δ 5.89 ppm). Benzylic protons in **6a** are also magnetically equivalent for each methylene group (singlet at δ 5.92 ppm; broad singlet at δ 5.65 ppm;). Benzylic protons in **3a** are not magnetically equivalent (double doublet at δ 5.50 ppm), proving the creation of a chiral axis around the C4-C4' bond. The chemical shift of the triazole CH protons (around 8.7-8.9 ppm) and N-methyl groups (4.0-4.2 ppm) are also consistent.

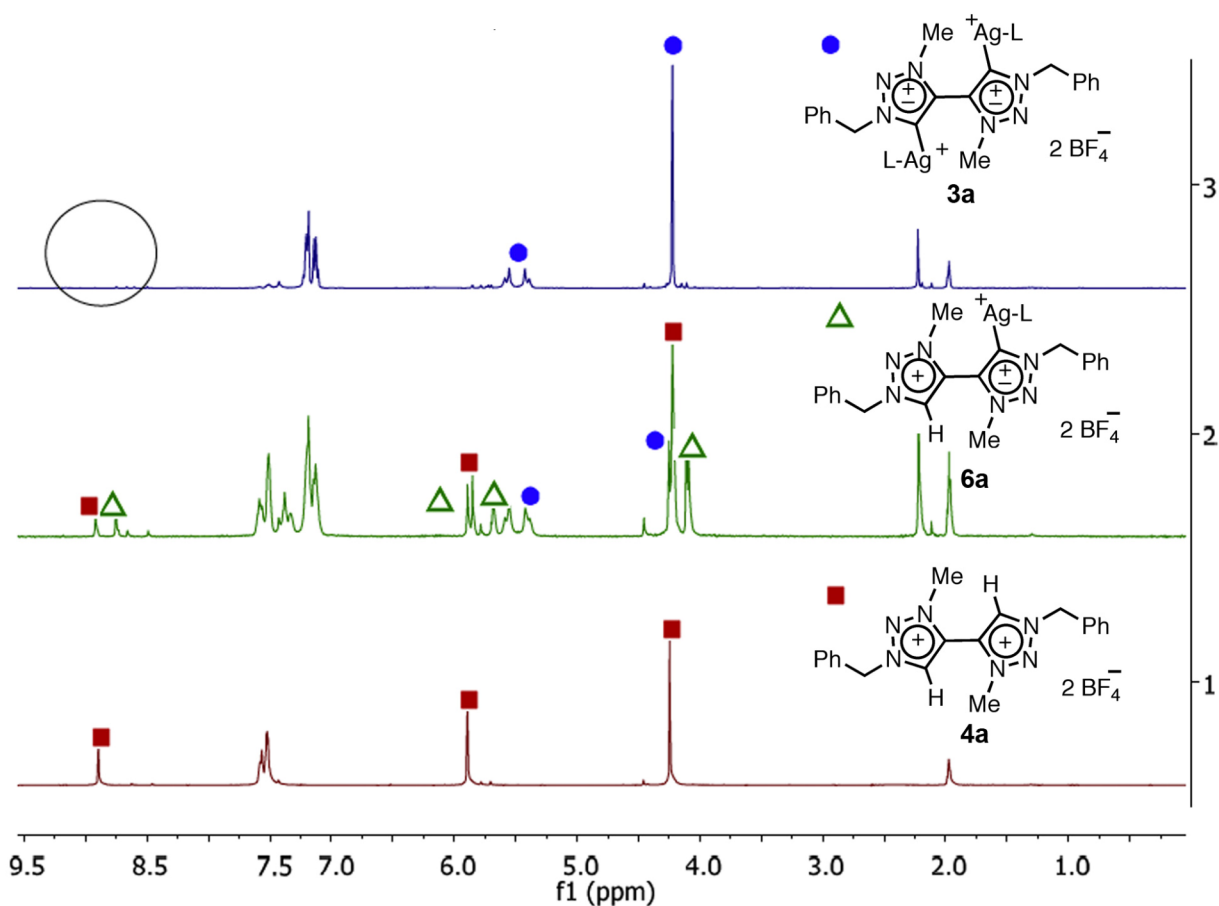


Figure S3. ^1H -NMR Spectra (500MHz, CD_3CN) of the conversion of **4a** into the Ag(I) complex of **3a** [$\text{L} = \text{MeCN}$]. The transient cation carbene complex **6a** is formed.

The thermodynamic equilibration of the diastereomeric Ag(I) dicarbene complexes **3b**-(*R*) and **3b**-(*S*) checked by ¹H-NMR spectroscopy (Figure S4). Spectrum 1 (reaction time 8h); Spectrum 2 (reaction time 24h). Benzylic CH₂ diastereotopic protons of **3b**-(*R*) and **3b**-(*S*) show as double doublets around δ 5.50 ppm. Benzylic CH(Me)Ph protons appear at 5.90 ppm for **3b**-(*R*) and 5.70 ppm for **3b**-(*S*). Slightly different methyl groups bonded to the triazole nitrogen appear at 4.2 ppm. After 24h, the peaks of **3b**-(*S*) vanished to give only diastereomer **3b**-(*R*).

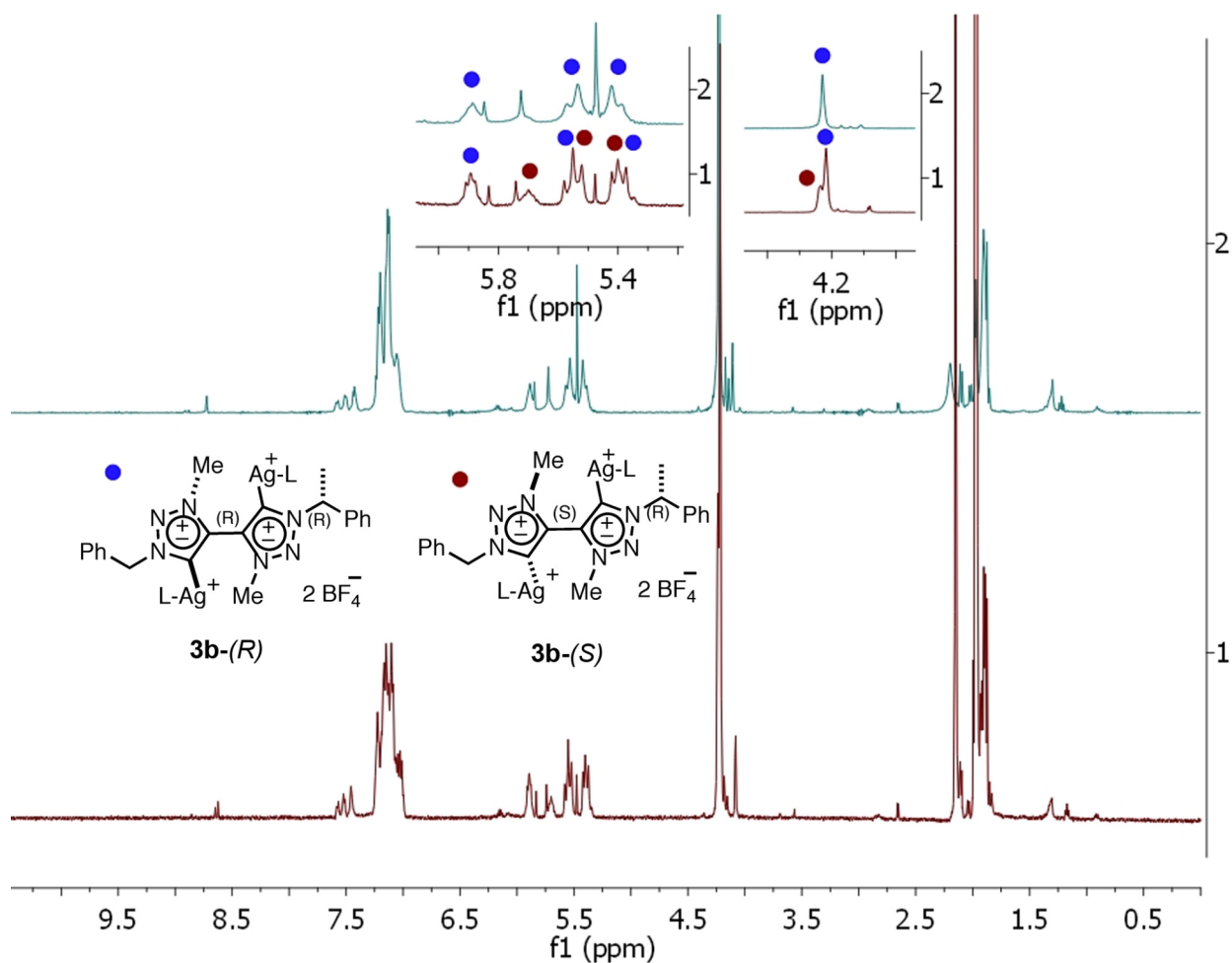


Figure S4. ¹H-NMR Spectra (500MHz, CD₃CN) of a mixture of the diastereomers **3b**-(*R*) and **3b**-(*S*) (spectrum 1) and thermodynamically equilibrated isomer **3b**-(*R*) (spectrum 2) [M= Ag; L = MeCN] including insets of the benzylic protons and N-Me protons.

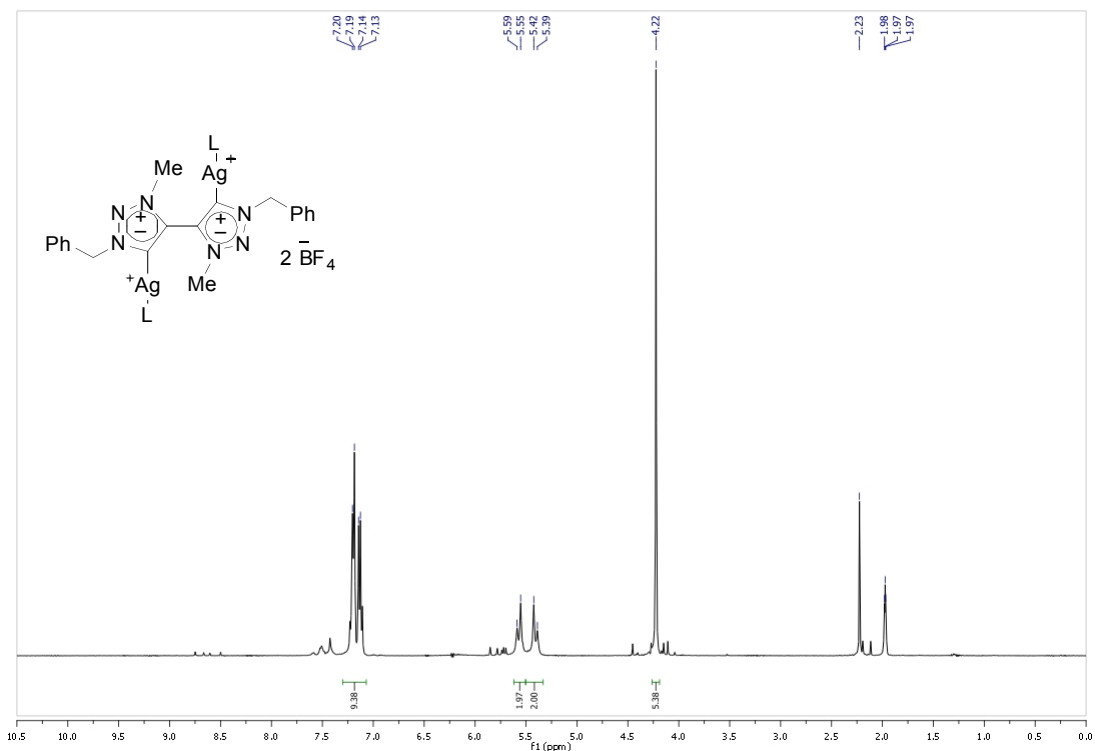


Figure S5. ¹H-NMR Spectrum (500MHz, CD₃CN) of compound **3a** [M= Ag]

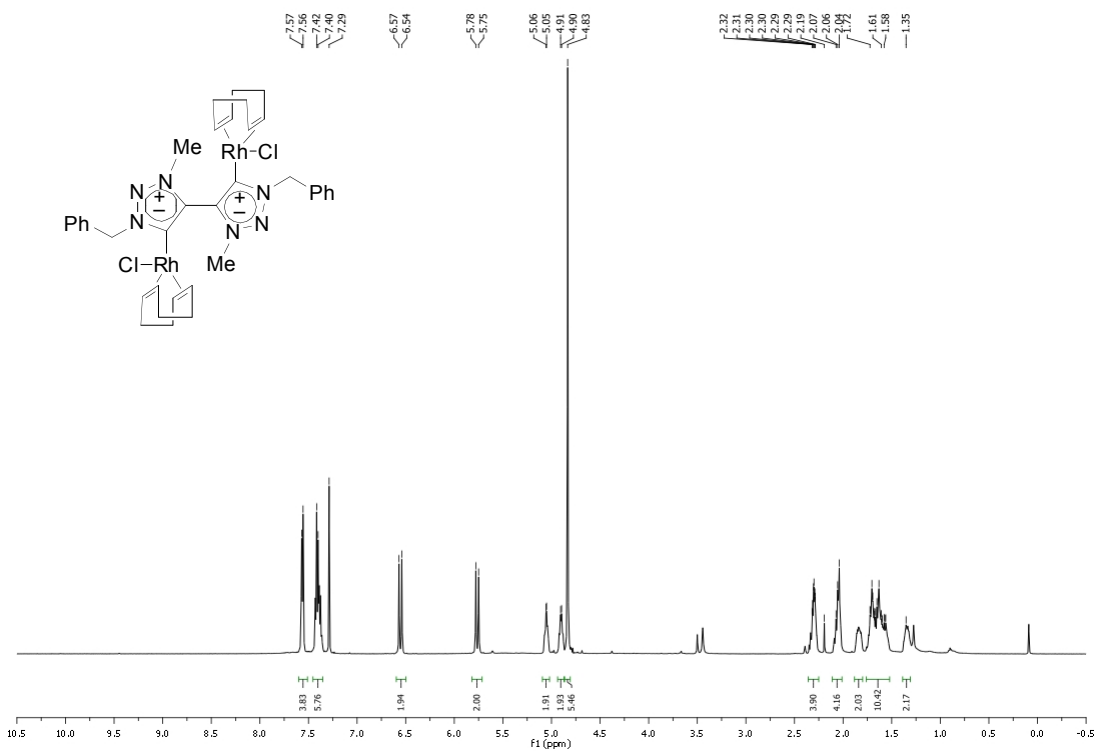


Figure S6. ¹H-NMR Spectrum (500MHz, CDCl₃) of compound **3a** [M= Rh(cod)Cl]

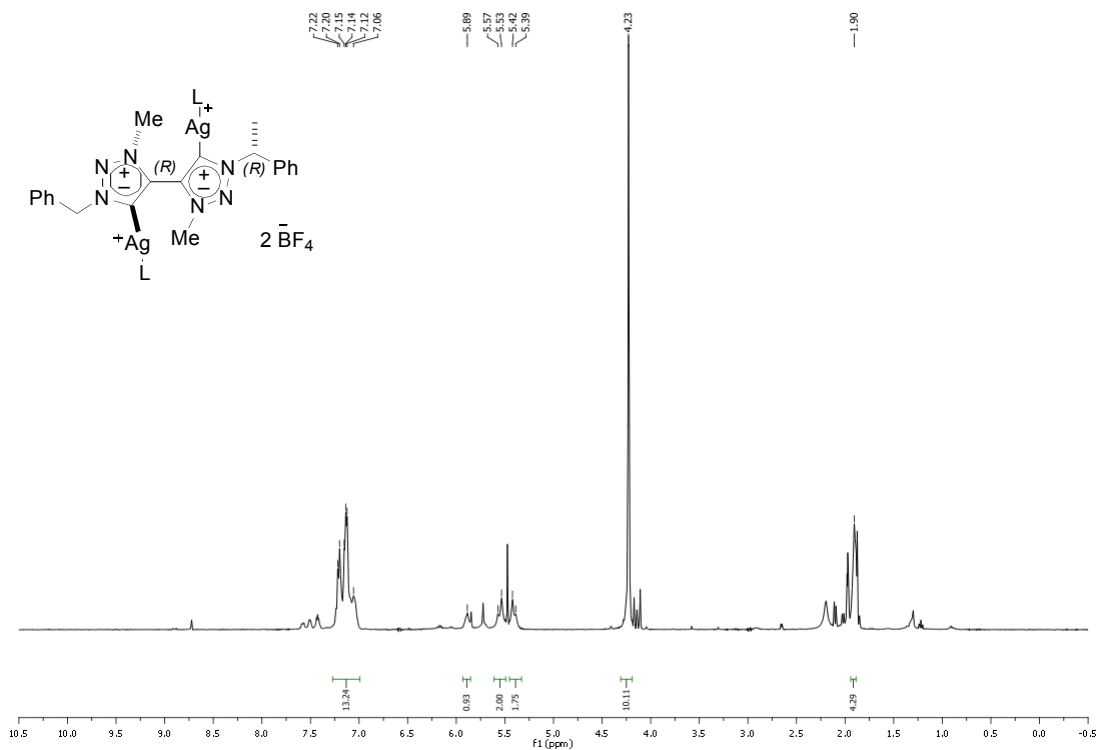


Figure S7. ¹H-NMR Spectrum (500MHz, CD₃CN) of compound **3b** [M= Ag]

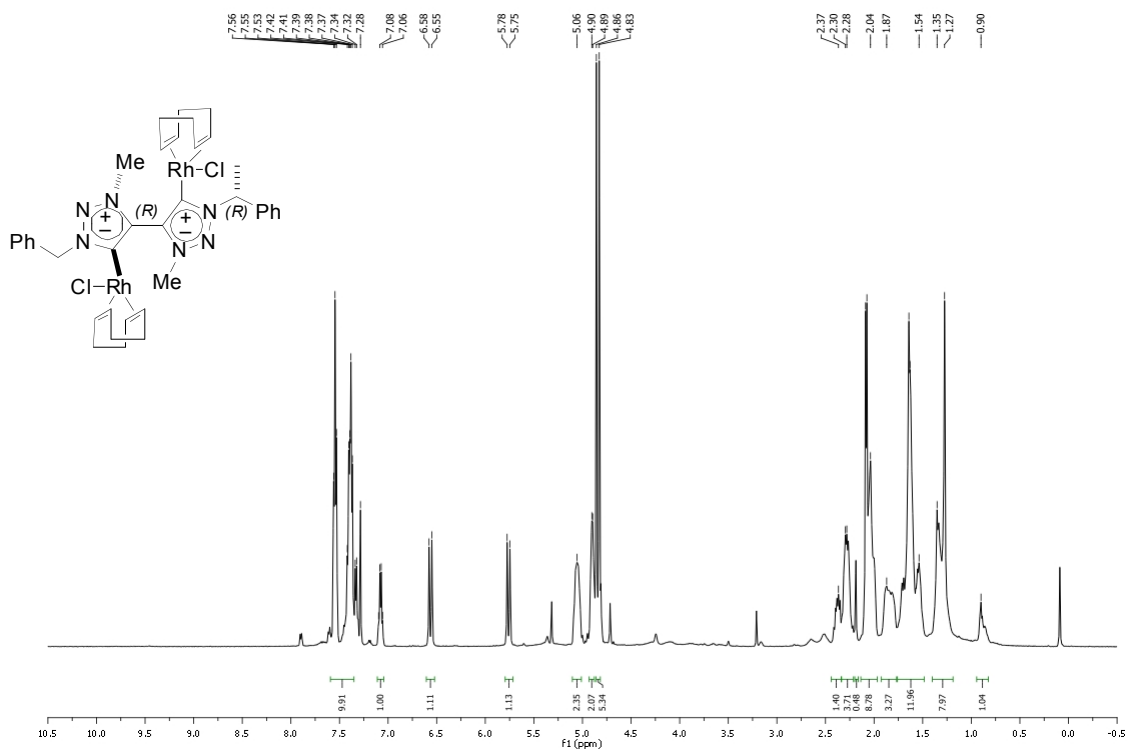


Figure S8. ¹H-NMR Spectrum (500MHz, CDCl₃) of compound **3b** [M= Rh(cod)Cl]

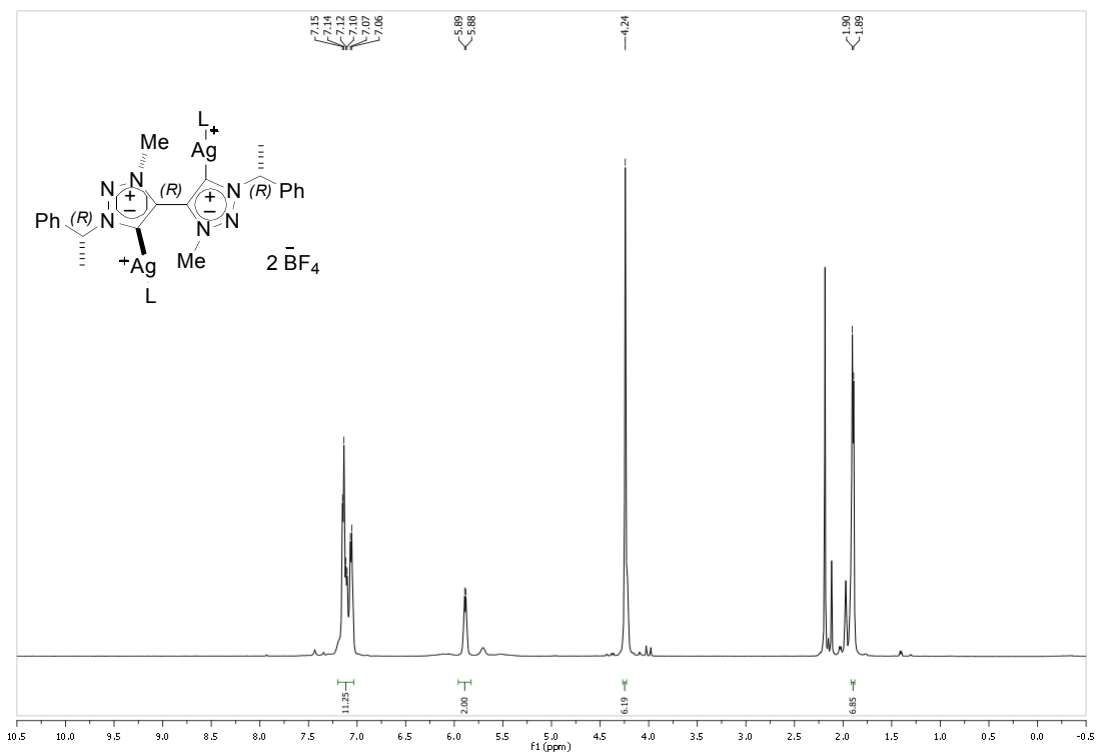


Figure S9. ¹H-NMR Spectrum (500MHz, CD₃CN) of compound **3c** [M= Ag]

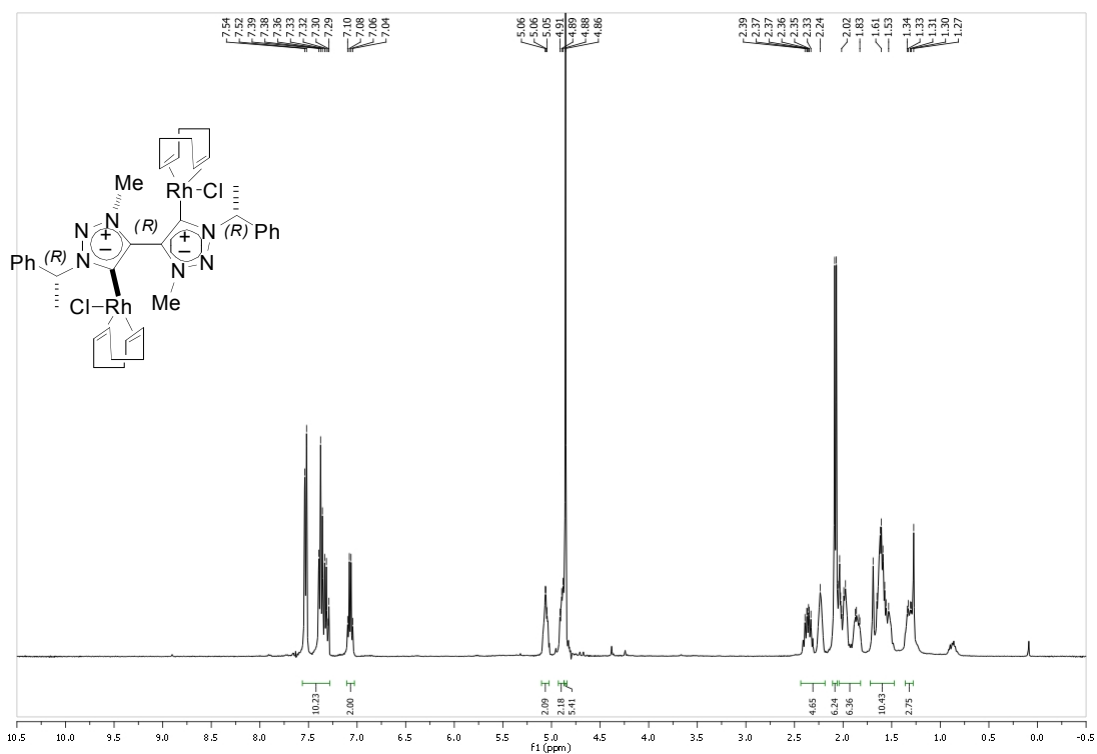


Figure S10. ¹H-NMR Spectrum (500MHz, CDCl₃) of compound **3c** [M= Rh(cod)Cl]

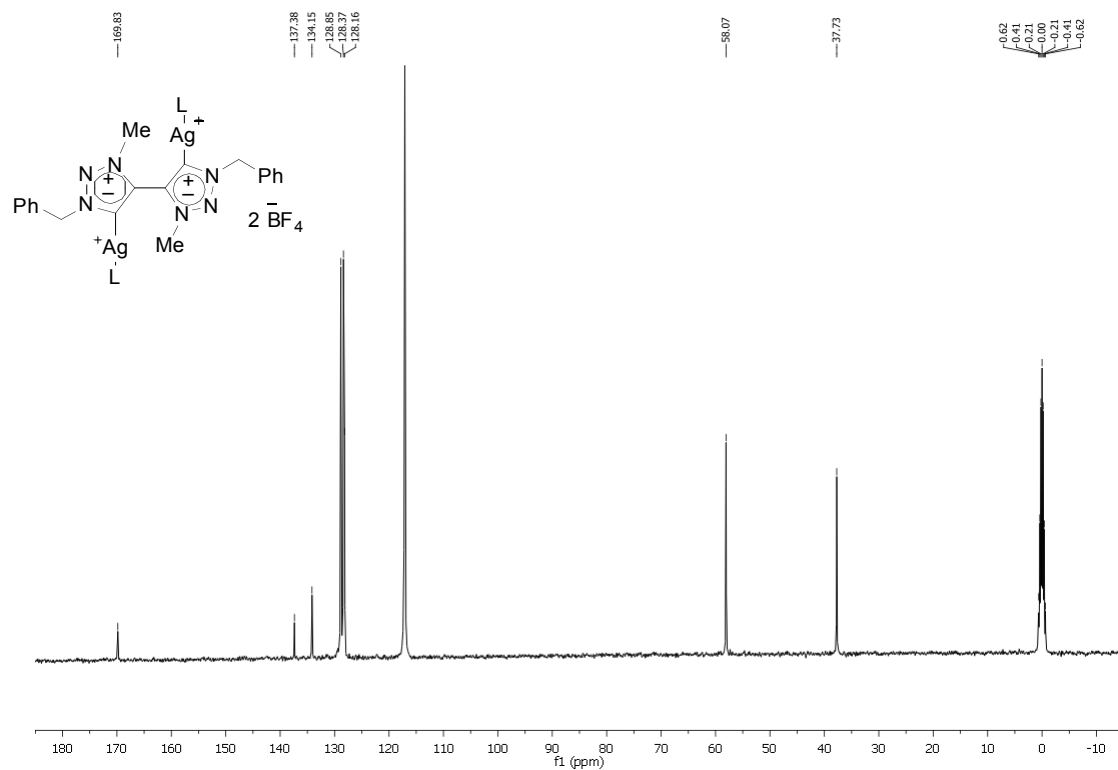


Figure S11. ¹³C-NMR Spectrum (125MHz, CD₃CN) of compound **3a** [M= Ag]

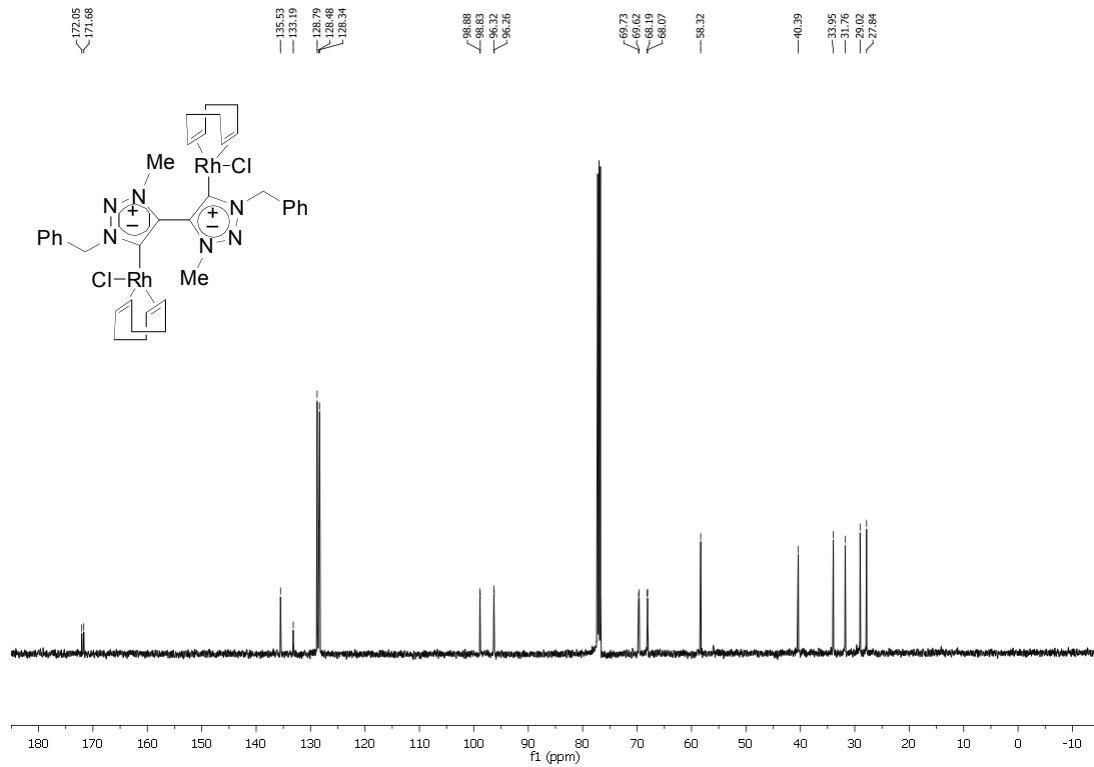


Figure S12. ¹³C-NMR Spectrum (125MHz, CDCl₃) of compound **3a** [M= Rh(cod)Cl]

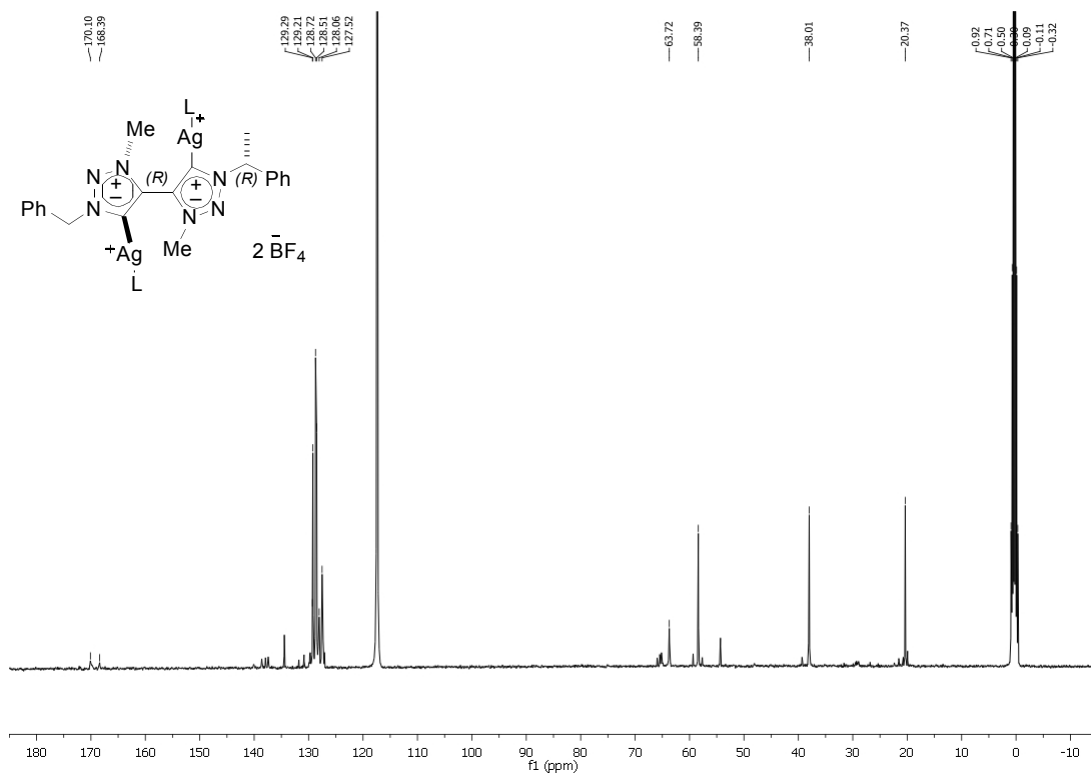


Figure S13. ¹³C-NMR Spectrum (125MHz, CD₃CN) of compound **3b** [M= Ag]

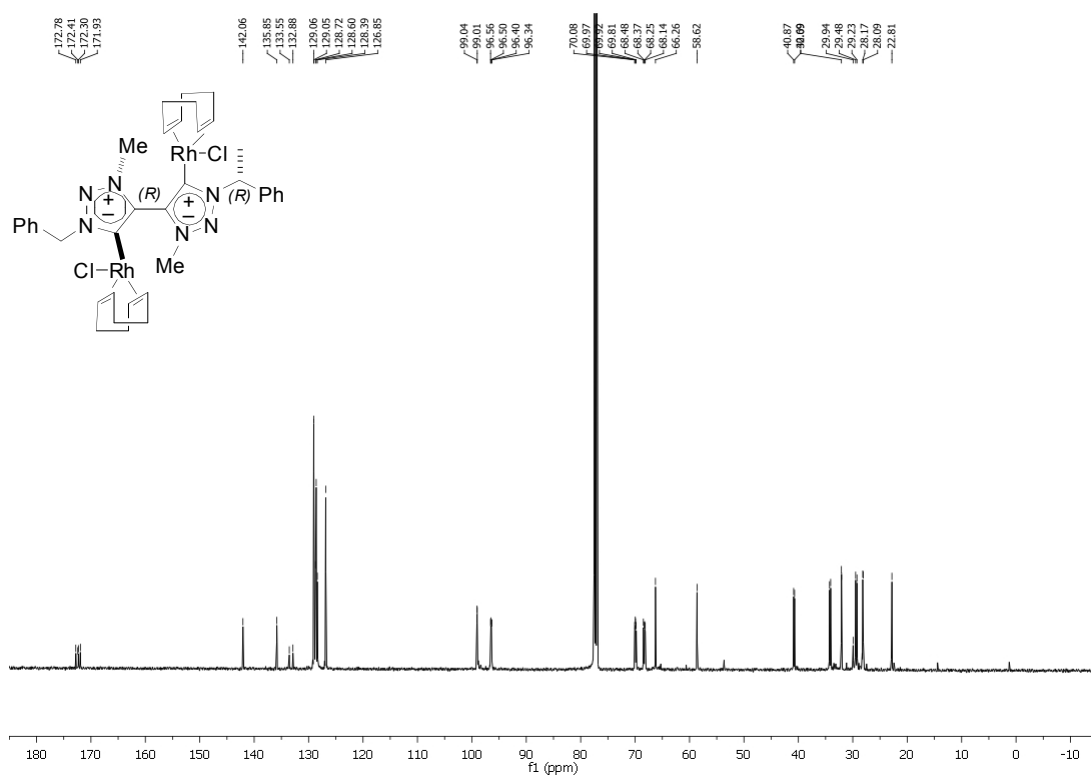


Figure S14. ¹³C-NMR Spectrum (125MHz, CDCl₃) of compound **3b** [M= Rh(cod)Cl]

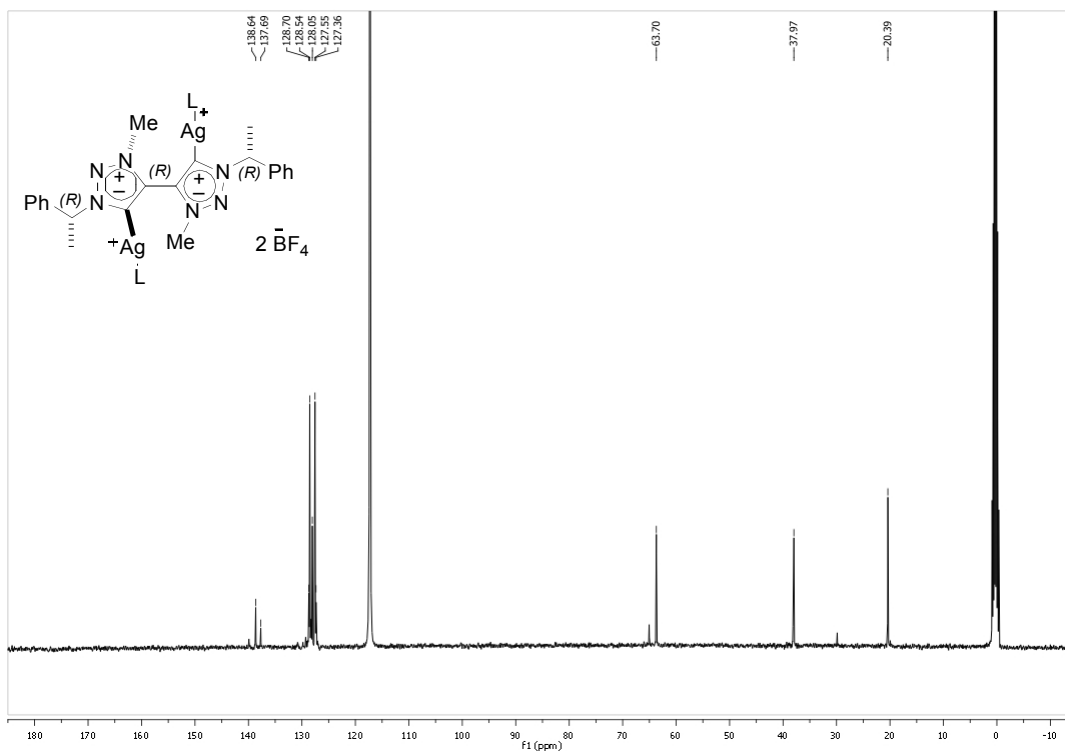


Figure S15. ^{13}C -NMR Spectrum (125MHz, CD_3CN) of compound **3c** [M= Ag]

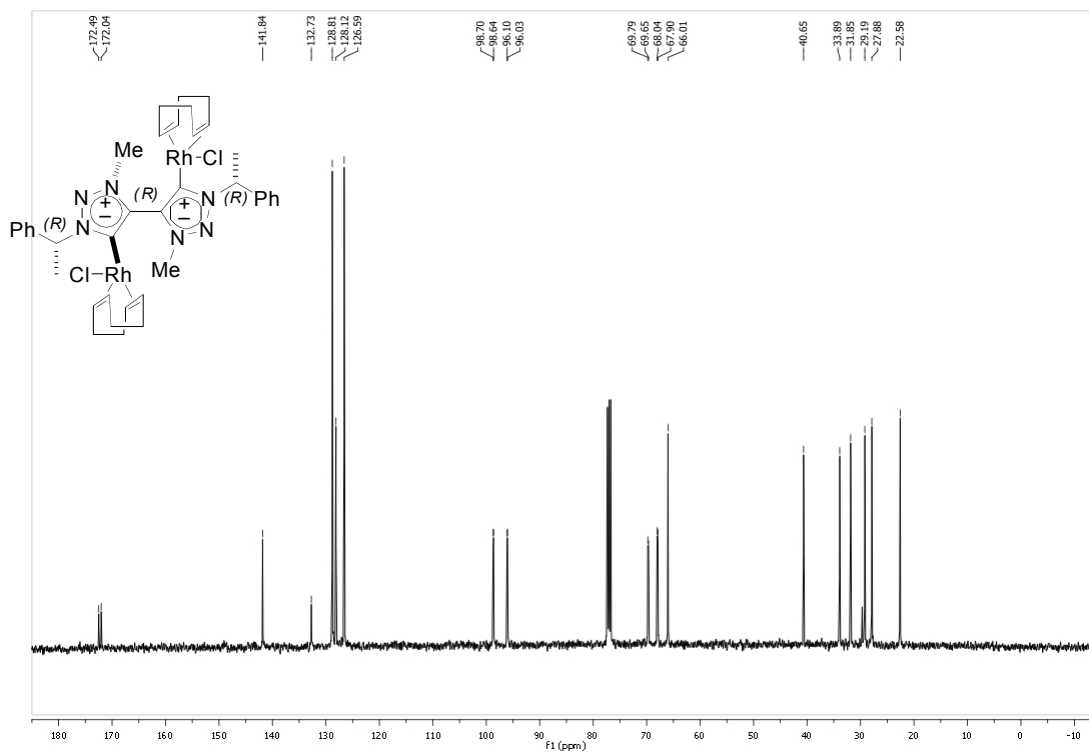


Figure S16. ^{13}C -NMR Spectrum (125MHz, CDCl_3) of compound **3c** [M= Rh(cod)Cl]

3. Proton Affinity (PA1) Calculations for Mesoionic Carbenes 5-7

3.1. Computational Methods: Geometry optimizations without symmetry constraints were carried out using the Gaussian09⁷ optimizer energies and gradients at the BP86⁸/def2-SVP⁹ level of theory (BP-I). Stationary points were characterized as minima and thermodynamic corrections were derived by calculating the Hessian matrix analytically at such level of theory. Kohn–Sham orbitals were also taken from these calculations. The standard state for all thermodynamic data is 298.15 K and 1 atm. Single-point energies have been calculated with BP86 and MP2 using the def2-TZVPP¹⁰ basis set (BP-II, MP2-II). The NBO¹¹ analyses were carried out with the internal module of Gaussian 09 at BP-II and without using the resolution of the identity approximation.

The PA1 protonation affinities (in kcal.mol⁻¹) and HOMO/LUMO orbital energies (in Hartrees) computed for carbene structures **5-7** are collected in Figure (S17).

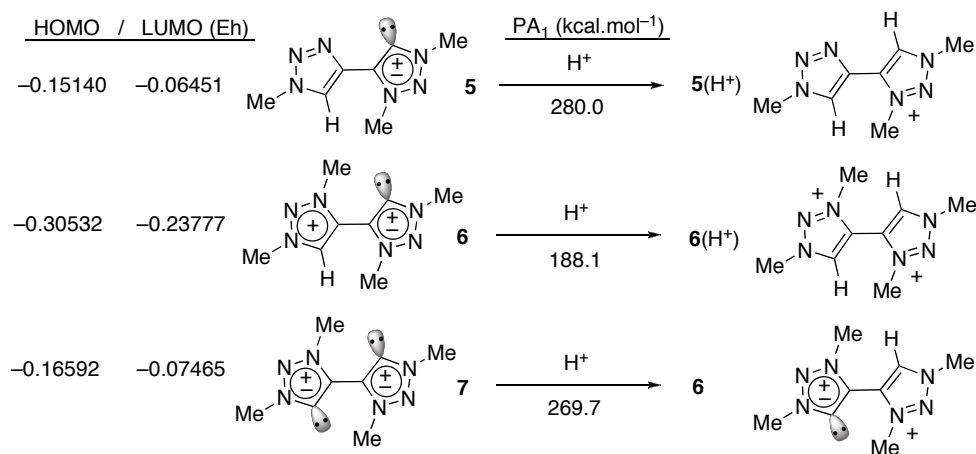


Figure S17. Protonation reactions of 4,4'-bis(1,2,3-triazole)-5-ylidenes **5-7**

⁷ Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

⁸ (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822-8824.

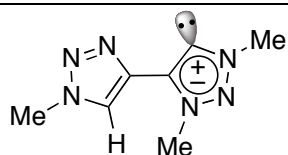
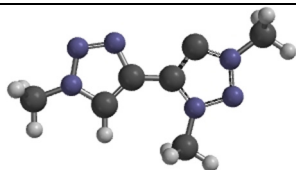
⁹ Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

¹⁰ Weigend, F.; *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.

¹¹ Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899-926.

3.2. Cartesian coordinates for structures 5-7 and protonated analogs 5(H⁺)-6(H⁺)

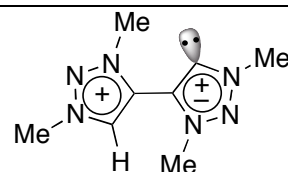
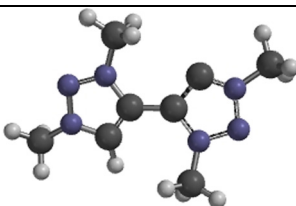
5



C	-0.67227	-0.19503	0.00001
C	0.78375	-0.31235	-0.00004
C	1.80963	0.64558	0.00009
N	1.38706	-1.55647	-0.00006
H	1.83042	1.73835	0.00026
C	-1.63080	-1.24038	0.00008
N	2.68351	-1.41649	-0.00037
N	2.96262	-0.08835	-0.00000
C	4.34436	0.36579	0.00008
N	-2.66380	0.85847	0.00008
N	-2.78169	-0.48544	0.00007
C	-4.13722	-1.02907	0.00012
H	4.36654	1.47108	0.00040
H	4.86811	-0.01110	-0.90073
H	4.86818	-0.01162	0.90064
H	-4.27935	-1.66012	0.89821
H	-4.27926	-1.66048	-0.89772
H	-4.86257	-0.19450	-0.00007
N	-1.34658	1.02558	-0.00001
C	-0.83833	2.38975	-0.00010
H	-0.22480	2.57374	0.90493
H	-1.70511	3.07418	-0.00015
H	-0.22479	2.57362	-0.90514

E(RB-P86) = -600.715218588

6

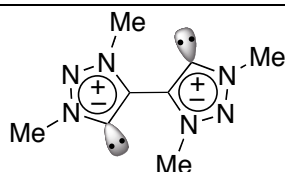
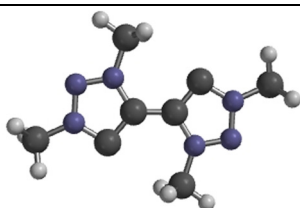


C	0.75177	0.04453	-0.00005
C	-0.69533	-0.01218	-0.00006
C	-1.69861	0.96699	-0.00020
H	-1.65599	2.05900	-0.00029
C	1.64106	-1.05259	-0.00002
N	-2.72015	-1.01904	-0.00009
N	-2.88583	0.28990	-0.00022
C	-4.24323	0.84668	0.00034
N	2.78360	0.96558	0.00004
N	2.83998	-0.37547	0.00003
C	4.16880	-0.99539	0.00011
H	-4.38946	1.46702	-0.90447
H	-4.39215	1.45906	0.91015

H	-4.95069	-0.00085	-0.00440
H	4.27187	-1.62924	-0.90042
H	4.27185	-1.62906	0.90077
H	4.93458	-0.19948	0.00006
N	1.49433	1.23250	-0.00001
C	1.07974	2.63446	-0.00003
H	0.48996	2.85986	-0.91075
H	1.99386	3.25418	0.00000
H	0.48988	2.85987	0.91064
N	-1.40735	-1.20805	-0.00000
C	-0.91119	-2.59056	-0.00001
H	-0.27634	-2.75230	0.88982
H	-0.27663	-2.75241	-0.89003
H	-1.80087	-3.24525	0.00016

E(RB-P86) = -640.393911372

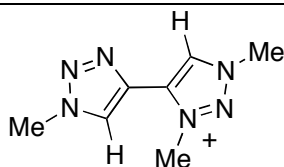
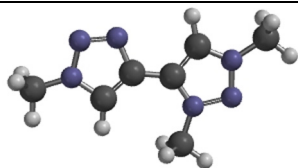
7



C	-1.65699	-1.05677	0.00995
C	-0.73061	0.01897	0.00097
N	-2.75769	0.98898	0.00401
N	-2.83741	-0.35460	0.01208
C	-4.17627	-0.93617	-0.00848
H	-4.07022	-2.00953	0.22532
H	-4.63513	-0.81789	-1.01119
H	-4.81790	-0.43738	0.74352
C	0.73061	-0.01894	-0.00104
C	1.65699	1.05677	-0.01010
N	2.75768	-0.98899	-0.00396
N	2.83741	0.35459	-0.01217
N	-1.45277	1.21147	-0.00176
C	-0.98636	2.60001	-0.00066
H	-1.36063	3.11049	0.90833
H	-1.37830	3.11711	-0.89827
H	0.12674	2.56883	-0.01064
C	4.17628	0.93613	0.00837
H	4.63523	0.81770	1.01102
H	4.07021	2.00952	-0.22528
H	4.81784	0.43746	-0.74376
N	1.45278	-1.21146	0.00183
C	0.98635	-2.59999	0.00087
H	1.37815	-3.11698	0.89860
H	1.36075	-3.11059	-0.90799
H	-0.12675	-2.56879	0.01070

E(RB-P86) = -639.95882817

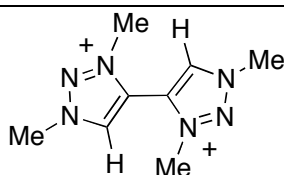
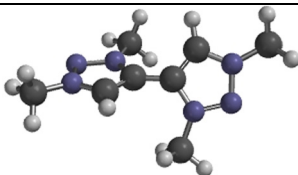
5(H⁺)



C	0.61300	-0.07241	-0.00001
C	-0.82853	-0.20530	-0.00002
C	-1.89893	0.70044	-0.00012
N	-1.34966	-1.48263	-0.00017
H	-1.97364	1.79215	-0.00023
C	1.55640	-1.10418	-0.00005
H	1.41202	-2.18974	-0.00006
N	-2.64671	-1.41444	0.00037
N	-2.99853	-0.09935	-0.00001
C	-4.41284	0.27182	-0.00001
N	2.68125	0.83131	-0.00012
N	2.77400	-0.48803	-0.00002
C	4.10091	-1.11723	-0.00003
H	-4.49866	1.37310	-0.00026
H	-4.90204	-0.14251	0.90235
H	-4.90215	-0.14292	-0.90213
H	4.21050	-1.74202	-0.90687
H	4.21042	-1.74223	0.90667
H	4.85466	-0.31070	0.00009
N	1.37270	1.08013	0.00004
C	0.92001	2.47114	0.00014
H	0.31959	2.66828	-0.90936
H	1.81808	3.11372	0.00013
H	0.31966	2.66819	0.90970

E(RB-P86) = -601.167982597

6(H⁺)



C	0.73587	0.01967	-0.15211
C	-0.73588	-0.01968	-0.15209
C	-1.67006	0.78753	-0.79841
H	-1.54821	1.65603	-1.45795
C	1.67004	-0.78760	-0.79839
H	1.54817	-1.65617	-1.45783
N	-2.78952	-0.78505	0.32319
N	-2.89191	0.27063	-0.46815
C	-4.22765	0.74704	-0.87898
N	2.78952	0.78511	0.32300
N	2.89189	-0.27065	-0.46823

C	4.22763	-0.74724	-0.87887
H	-4.27915	0.77006	-1.98426
H	-4.39762	1.75879	-0.46277
H	-4.97183	0.03770	-0.47533
H	4.27839	-0.77269	-1.98412
H	4.39844	-1.75798	-0.46052
H	4.97170	-0.03661	-0.47728
N	1.49823	0.96663	0.51852
C	1.05705	2.10245	1.34723
H	0.74440	2.94202	0.69562
H	1.91732	2.41653	1.96586
H	0.22149	1.78066	1.99576
N	-1.49821	-0.96656	0.51867
C	-1.05701	-2.10226	1.34754
H	-0.74436	-2.94191	0.69604
H	-1.91727	-2.41627	1.96623
H	-0.22145	-1.78037	1.99601

E(RB-P86) = -640.694415875

4. Cyclic Voltammetry

4.1. General: Electrochemical experiments were performed with a multi-channel potentiostat (VMP3, Bio-Logic-Science Instruments, France) using a conventional three-electrode electrolytic cell at room temperature. To minimize contamination, a double-junction system consisting of a Ag/AgCl reference electrode separated from the measured solution by a second solution (supporting electrolyte) was selected. A Pt wire was used as counter electrode, separated from the bulk solution by a porous frit. All potentials were reported against the ferrocene/ferrocenium (Fc/Fc⁺) redox couple ($E^\circ = 0.508$ V vs Ag/AgCl).

The working electrode consisted on a rod of glassy carbon (SIGRADUR® G, HTW, 5 mm diameter) with 0.2 cm² of exposed geometric area (lower surface of the glassy carbon rod). The working electrode was polished, sonicated, rinsed with ethanol and dried prior to each experiment. All glass material was washed in piranha solution (3:1 H₂SO₄:H₂O₂) to remove organic residues and dried in an oven (90°C, 1 hour) before each set of experiments.

The supporting electrolyte was a N,N-dimethylformamide (DMF, Sigma Aldrich) solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAFP, Fluka). The DMF used in the experiments was of Biotech grade, purchased in sure-sealed containers under nitrogen. The TBAFP was dried at 120°C for 12 hours before use. The electrolytes were prepared in a controlled environment (e.g. glove box), purged with nitrogen for 30 min previous to the onset of

the experiment and maintained under a positive pressure of nitrogen throughout the entire electrochemical test.

4.2. Voltammograms of 3-methyl-1,2,3-triazolium salts (additional data): The cyclic voltammetry analysis of monoheterocyclic triazolium compounds **11a-c** (Figure S18) was conducted to compare their redox behaviour to the 4,4'-bis-(1,2,3-triazolium) salts **4a** and **9a** (Figure 3, main text). Compounds **11a-c** showed very similar and well defined cathodic carbene (**1a-1c**) formation peaks between -1.58 V and -1.61 V, irrespective of the electrodonating or electron-withdrawing nature of the Ar substituents. Triazole **10a** remained unchanged within the potential interval tested.

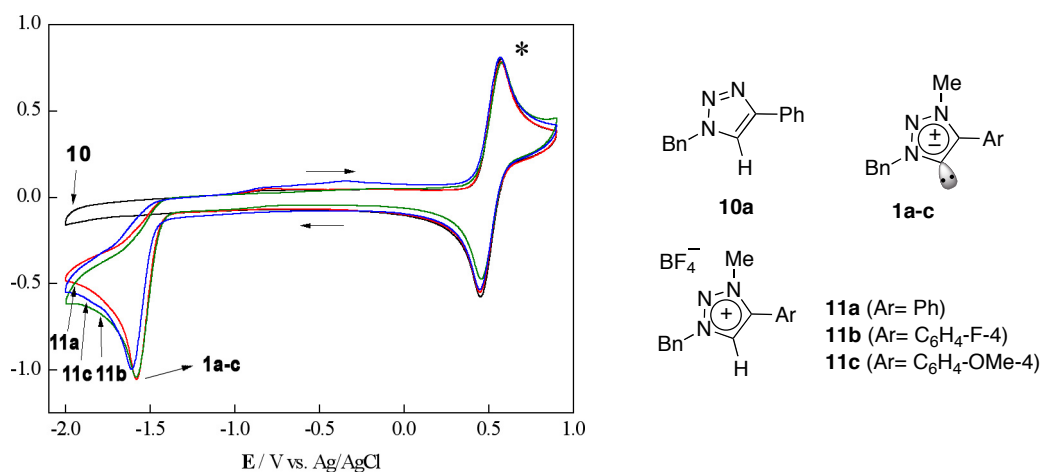


Figure S18. Cyclic voltammetry analysis of triazolium tetrafluoroborates **11a-c**

Compounds **10a**¹² and **11a**¹³ were previously known. Novel triazolium tetrafluoroborates **11b-c** were prepared from their parent triazoles **10b**¹⁴ and **10c**¹⁵ following the General Procedure 1.2.2.

Compound 11b: Yield = 85%; M.p. = 102.2-103.0°C; IR (cm⁻¹): 3066, 2929, 1500 (trz), 1049 (BF₄); ¹H NMR (500 MHz, CDCl₃) δ 8.50 (s, 1H), 7.68 – 7.36 (m, 7H), 7.23 – 7.13 (m, 2H), 5.72 (s, 2H), 4.20 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 164.4 (d, *J* = 254.0), 142.5, 131.9 (d, *J* =

¹² Chan, T. R.; Hilgraf, R.; Sharpless, K. B.; Fokin, V. V. *Org. Lett.*, **2004**, *6*, 2853-2855.

¹³ Kilpin, K. J.; Paul, U. S. D.; Lee, A.-L.; Crowley, J. D. *Chem. Commun.*, **2011**, *47*, 328-330.

¹⁴ Park I. S.; Kwon, M. S.; Kim, Youngkwon; Lee, J. S.; Park, J. *Org. Lett.*, **2008**, *10*, 497-500.

¹⁵ Asano, K.; Matsubara, S. *Org. Lett.*, **2010**, *12*, 4988-4991.

9.0), 131.1, 129.8, 129.6, 129.34, 128.2, 118.0, 116.9 (d, $J = 22.3$), 57.4, 38.4. HRMS (ESI+): m/z [M]⁺ calcd for C₁₆H₁₅N₃F⁺: 268.1250; found 268.1245.

Compound 11c: Yield= 70%; M.p. = 144.4-145.3°C. IR (cm⁻¹): 3133, 1502 (triz), 1014 (BF₄). ¹H NMR (500 MHz, CDCl₃) δ 8.53 (s, 1H), 7.64 – 7.40 (m, 7H), 7.03 (d, $J = 8.8$, 2H), 5.77 (s, 2H), 4.23 (s, 3H), 1.62 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 162.29, 143.61, 131.29, 130.96, 129.97, 129.74, 129.49, 127.97, 115.20, 113.62, 57.63, 55.53, 38.31. HRMS (ESI+): m/z [M]⁺ calcd for C₁₇H₁₈N₃O⁺: 280.1450; found 280.1451.

5. X-Ray Analysis

5.1. Crystal structure determination for 3a-c: Crystals were grown by slow vapor diffusion of pentane into a solution of **3a-c** in CH₂Cl₂ at room temperature. The quality of the crystals of compounds **3a**·CH₂Cl₂, **3b-c** was checked under the polarizing microscope and a fragment of adequate dimensions was mounted on a Mitegen MicromeshTM using inert oil. Data collection for sample **3a**·CH₂Cl₂ was carried out on a Oxford Diffraction (now Agilent) Xcalibur 2 diffractometer equipped with a Sapphire2 CCD area detector at 50mm from the crystal, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å, 0.5mm collimator); and for **3b-c**, on an Agilent Supernova diffractometer equipped with an Atlas CCD area detector at 55mm from the crystal, using a microfous Cu $K\alpha$ source ($\lambda = 1.54148$ Å, 0.25mm FWHM). All data collections were performed at 100(1)K using an Oxford Cryosystems Cryostream 700 cooler.

Data reduction was performed with CrysAlisPro¹⁶. The intensities were corrected for Lorentz and polarization effects; and for absorption, using an analytical numeric absorption correction with a multifaceted crystal model.¹⁷ The structures were solved using the charge-flipping

¹⁶ Oxford Diffraction (2011). *CrysAlisPro software*, Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

¹⁷ Clark, R. C.; Reid, J. S. *Acta Cryst. A* **1995**, *51*, 887-897.

algorithm as implemented in Superflip,¹⁸ which revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the positions indicated by a difference electron density map, and were placed in geometrically calculated positions and refined using a riding model. The refinement of the structures was carried out on F^2 against all reflections, by using full-matrix least-squares procedures with the SHELXL97¹⁹ program. The Flack parameter values for compounds **3b** and **3c**, -0.012(4) and -0.035(7) respectively, indicate that the absolute structure has been determined correctly.²⁰

The $-\text{CH}_2-\text{CH}_2-$ groups of one of the cyclooctadiene ligands in compound **3a**· CH_2Cl_2 are disordered over two positions with occupancy factors in the approximate ratio 70:30, so that the cod ligand displays two different conformations. In the crystal structure of compound **3b** there are two molecules in the asymmetric unit ($Z'=2$). Both of them are disordered between two molecular orientations which can be regarded as being related by rotation about the pseudo 2-fold axis passing through the midpoint of the C4–C4' chiral axis. Both molecular orientations have about equal populations, with the Bn group of one orientation and the (*R*)-CHMePh of the other occupying the same sites. This disorder affects the intra- and intermolecular interactions, extends to whole molecules, and makes all thermal ellipsoids (ADPs) larger and more elongated than expected, mainly those of the phenyl groups.

¹⁸ Palatinus L.; Chapuis G. *J. Appl. Cryst.* **2007**, *40*, 786-790.

¹⁹ (a) Sheldrick, G.M. SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997. (b) Sheldrick, G. M. *Acta Cryst. A* **2008**, *64*, 112-122.

²⁰ (a) Flack, H. D. *Acta Cryst. A*, **1983**, *39*, 876-881. (b) Flack, H.D.; Bernardinelli, G. *Acta Cryst. A* **1999**, *55*, 908-915.; (c) Flack, H.D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, *33*, 1143-1148.

Table S1. Crystal data and structure refinement.

	3a·CH₂Cl₂	3b	3c
CCDC deposit number	851376	851377	851378
Empirical formula	C ₃₆ H ₄₄ Cl ₂ N ₆ Rh ₂ ·CH ₂ Cl ₂	C ₃₇ H ₄₆ Cl ₂ N ₆ Rh ₂	C ₃₈ H ₄₈ Cl ₂ N ₆ Rh ₂
Formula weight [g mol ⁻¹]	922.42	851.52	865.54
Temperature [K]	100(1)	100(1)	100(1)
Wavelength [Å]	0.71073	1.54184	1.54184
Crystal colour, habit	yellow, prism	yellow, prism	yellow, prism
Crystal dimensions [mm]	0.32×0.24×0.23	0.25×0.21×0.15	0.22×0.18×0.17
Crystal system	triclinic	orthorhombic	orthorhombic
Space group	<i>P</i> -1	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
<i>a</i> [Å]	11.2161(2)	11.5888(1)	12.2404(1)
<i>b</i> [Å]	11.3765(2)	20.8645(2)	16.9563(1)
<i>c</i> [Å]	16.4230(4)	29.5473(3)	17.6791(1)
α [°]	80.240(4)	90	90
β [°]	79.998(2)	90	90
γ [°]	65.672(2)	90	90
<i>V</i> [Å ³]	1869.23(7)	7144.38(12)	3669.33(4)
<i>Z</i> , <i>Z'</i>	2, 1	8, 2	4, 1
<i>F</i> (000)	936	3472	1768
<i>D_x</i> [g cm ⁻³]	1.639	1.583	1.567
μ [mm ⁻¹]	1.205	9.123	8.892
Data collection 2θ range [°]	1.98–30.5	2.59–75.0	3.61–75.0
(<i>hkl</i>) _{min} ,(<i>hkl</i>) _{max}	(-16 -16 -23),(16 16 23)	(-14 -23 -36),(14 26 36)	(-11 -20 -22),(15 21 21)
Total reflections measured	41426	45967	26162
Symm. independent reflections, <i>R</i> _{int}	11403, 0.033	14537, 0.043	7495, 0.024
Reflections with <i>I</i> > 2 σ (<i>I</i>)	9515	13502	7448
Parameters refined, restraints	481, 130	876, 24	438, 0
Final <i>R</i> (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>), all data]	0.0261, 0.0346	0.0379, 0.0425	0.0167, 0.0168
Final <i>wR</i> (<i>F</i> ²) [<i>I</i> > 2 σ (<i>I</i>), all data]	0.0666, 0.0690	0.0797, 0.0828	0.0421, 0.0422
Goodness of fit	1.039	1.033	1.036
Final (Δ/σ) _{max} ,(Δ/σ) _{mean}	0.001, 0.000	0.001, 0.000	0.002, 0.000
$\Delta\rho$ (max, min) [e Å ⁻³]	0.83, -0.67	1.03, -1.09	0.39, -0.38
Flack parameter	–	-0.035(7)	-0.012(4)
$\alpha d(C-C)$ [Å]	0.0033	0.0089	0.0031

5.2. ORTEP plots of the crystal structures of compounds $3a \cdot CH_2Cl_2$, $3b-c$:

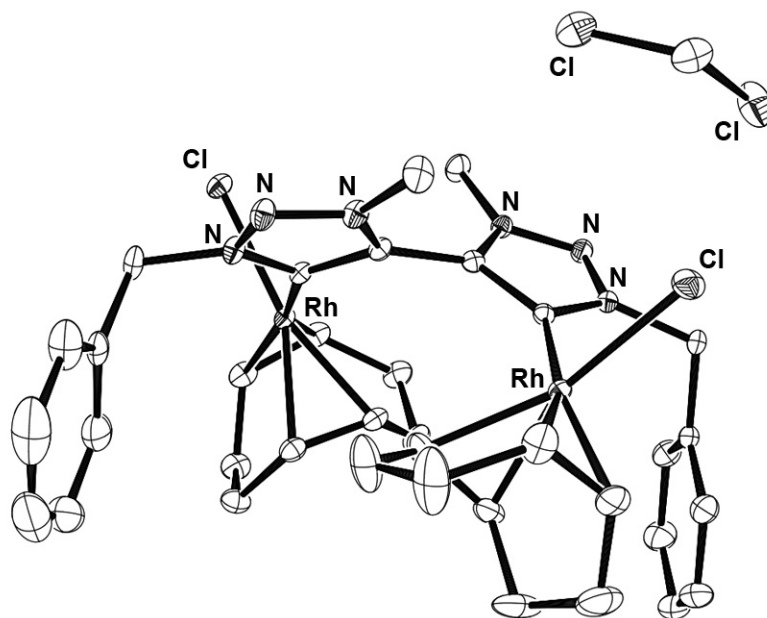


Figure S19. ORTEP plot of $3a \cdot CH_2Cl_2$.

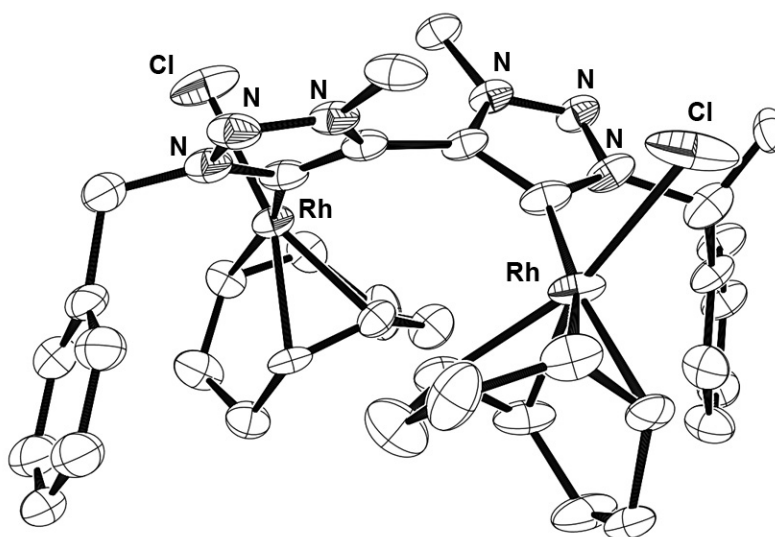


Figure S20. ORTEP plot of $3b$.

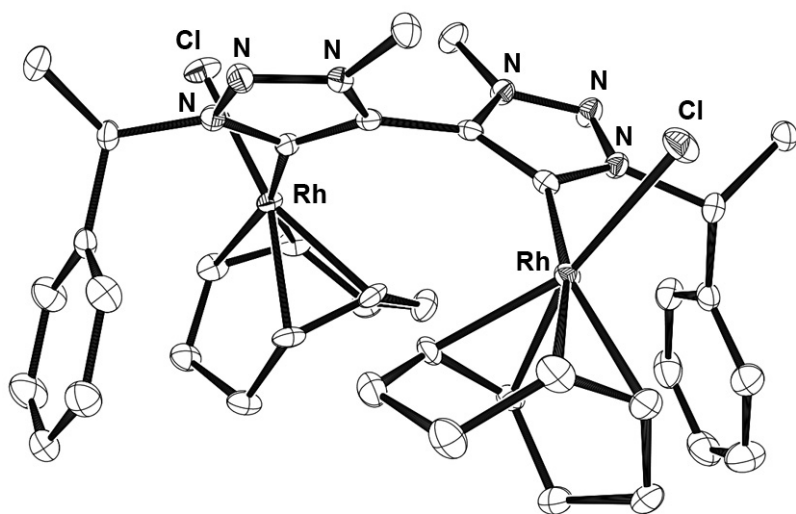


Figure S21. ORTEP plot of **3c**.