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# [(Arene)Rh(COD)]<sup>+</sup> Complexes as Catalysts for [5 + 2] Cycloaddition Reactions

Paul A. Wender\* and Travis J. Williams

**General methods.** Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen from a manifold, unless otherwise indicated. Similarly sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Reactions were run using Teflon-coated magnetic stir bars. Elevated temperatures were maintained in oil baths. Organic solutions were concentrated using a Buchi rotary evaporator with a desktop vacuum pump. Thin layer chromatography plates were visualized by ultraviolet light and treatment with acidic *p*-anisaldehyde stain followed by gentle heating. Chromatographic purification of products was accomplished by flash chromatography, as described by Still and co-workers.<sup>1</sup> Silica gel 60, 230-400 mesh was purchased from EM Science.

NMR spectra were measured on a Varian INOVA 500 (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz) or Varian Gem-300 (<sup>1</sup>H at 300 MHz, <sup>13</sup>C at 75 MHz) magnetic resonance spectrometer. Data for <sup>1</sup>H NMR spectra are reported as follows: chemical shift ( ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for <sup>13</sup>C are reported in terms of chemical shift and quantity of carbons. Infrared spectra were recorded on a Perkin-Elmer Spectrum BX Fourier transform spectrometer (IR) and are reported as follows: wavenumbers (cm<sup>-1</sup>), description (w = weak, m = medium, s = strong, b = broad). Low-resolution mass spectra (LRMS) were recorded with a Hewlett-Packard model 6890 gas chromatograph with model 5973 mass-selective detector. High-resolution mass spectra (HRMS) were recorded at the NIH regional mass spectrometry facility at the University of California, San Francisco. Reported mass values are with error limits of ±1 millimass unit. Elemental analyses (%C, %H, %F, %N, %O, %S) were determined by Desert Analytics, Tucson, Arizona (USA). Reported atomic percentages are within error limits of ±0.4%. X-ray crystal data collection was done at the University of California, Berkeley. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-191383 (**1**), CCDC-191384 (**7**), CCDC-191385 (**22**), and CCDC-191386 (**24**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-366-033; email deposit@ccdc.cam.ac.uk).

## Catalyst Complex 1:

Chloro(COD)rhodium(I) dimer (98.4 mg, 0.200 mmol) and silver hexafluoroantimonate (137 mg, 0.400 mmol) were weighed out in an oven-dried, 25 mL, round-bottom flask with stir bar. To this was added freshly distilled acetone (15 mL), and the resulting suspension was stirred for 30 minutes while a white precipitate formed. This material was then removed by filtration through a Shlenk filter into another oven-dried, 25 mL, round-bottom flask with stir bar containing naphthalene (102 mg, 0.800 mmol). The resulting solution was stirred for an additional 30 minutes and concentrated by rotary evaporation. The residue was dispersed in diethyl ether to leave a granular, yellow powder that was collected over fine-grain filter paper. The concentration, dispersion, filtration process was repeated twice more before the material was collected to yield 162 mg (70%) of [(C<sub>10</sub>H<sub>8</sub>)Rh(COD)]<sup>+</sup> SbF<sub>6</sub><sup>-</sup> as a granular, yellow powder.

$^1\text{H}$  NMR (300 MHz,  $[\text{D}_2]$ dichloromethane, TMS):  $\delta$  = 7.97- 7.93 (m, 2H), 7.90- 7.86 (m, 2H), 7.33- 7.30 (m, 2H), 6.58- 6.55 (m, 2H), 4.65 (s, 4H), 2.04- 1.94 (m, 8H).  $^{13}\text{C}$  NMR (75 MHz,  $[\text{D}_2]$ dichloromethane):  $\delta$  = 132.3 (2C), 126.4 (2C), 116.1 (2C), 105.1 (2C), 94.92 (2C), 81.45 (2C), 81.28 (2C), 30.33 (4C). IR (neat)  $\nu$  = 2939.7 (m), 2877.1 (m), 2831.7 (m), 1493.6 (w), 1432.7 (w), 1374.1 (w), 1331.8 (w), 1260.1 (w), 961.01 (w), 878.56 (w), 837.70 (m), 820.66 (w), 794.56 (s), 761.83 (m)  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{18}\text{H}_{20}\text{F}_6\text{RhSb}$ : 37.60% C; 3.51% H; 19.82% F. Found: 37.49% C; 3.37% H; 19.56% F.

X-ray crystallographic analysis: The largest residual peaks on the final difference Fourier map are located in the vicinity of the  $\text{SbF}_6^-$  anion, and these together with the elongated fluorine thermal ellipsoids indicate that this ion is likely disordered. However, attempts to resolve this disorder did not improve the refinement. The two perfectly-eclipsed, non-ligated, “*exo*-oriented” carbon atom pairs of the COD ligand that straddle the mirror plane also exhibit significantly elongated thermal ellipsoids and somewhat shorter carbon-carbon bond distances (1.42 Å) than are commonly observed for  $sp^3$ -hybridized carbons. Although the methylene protons could not be definitively located in difference Fourier electron density maps, integrated solution  $^1\text{H}$  NMR spectra of redissolved crystals confirmed their presence in stoichiometric quantity, ruling out partial substitution of 1,3,5,7-cyclooctatetraene pursuant to some Rh-catalyzed internal dehydrogenation. A recently reported structure containing an isoelectronic and crystallographically unique  $\text{Ru}(0)(\text{COD})(\text{naphthalene})$  moiety (as cited in the main text) exhibits maximum  $sp^3$  dihedrals of *ca.*  $2^\circ$  in the COD ligand. Attempts to model the symmetry-related carbons as conformationally disordered (*i.e.*, slightly staggered) methylene pairs at more reasonable  $sp^3$  bond distances (1.50 Å) did not improve refinement and were therefore abandoned; however, static or dynamic disorder (distributed symmetrically with respect to the mirror plane) likely provides the best explanation for the short averaged  $sp^3$  C-C bond distances in the final model.

### Cycloadduct **3**:

Freshly prepared and purified yne-vinylcyclopropane substrate **2**<sup>5</sup> (8.3 mg, 31  $\mu\text{mol}$ ) was weighed out in an oven-dried 4 mL vial equipped with a stir bar. 1,2-Dichloroethane (207  $\mu\text{L}$ , 0.15M) and catalyst complex **1** (360  $\mu\text{g}$ , 620 nmol) were then added, the vial was sealed with teflon tape, and the reaction was stirred at room temperature for 15 minutes before it was concentrated by rotary evaporation and purified by flash column chromatography, eluting with 5% ether in petroleum ether. Product-containing fractions were identified and concentrated by rotary evaporation to yield product **3**, 8.3 mg (>99%) as a colorless oil. Data is consistent with a known compound.<sup>5</sup>

Substrates **4**, **6**, **8**, and **18** were prepared from known synthetic intermediates<sup>2,3,5</sup> according to a known procedure used to make analogous yne-dienes<sup>4</sup>. The general procedure is as follows:

*N-tert*Butoxytoluenesulfonamide (1 equiv.) is weighed out in an oven-dried round-bottom flask with stir bar. Tetrahydrofuran (15 mL/ g sulfonamide) and triphenyl phosphine (1.5 equiv.) are then added, the flask is topped with a septum, flushed with nitrogen, and cooled to 0 °C. Propargyl alcohol or allyl alcohol (1.1 equiv.) and diisopropylazodicarboxylate (1.5 equiv.) are then added drop wise and the reaction is stirred overnight. The crude product is then concentrated by rotary evaporation and purified by flash column chromatography.

The resulting sulfonamide is then dissolved in dichloromethane (15 mL/ g sulfonamide) in a round-bottom flask with stir bar. Trifluoroacetic acid (6 equiv.) is then added drop wise and the reaction is stirred overnight. Water (1 mL/ 3 mL dichloromethane) and saturated aqueous

sodium bicarbonate (until gas evolution ceases) are then added and the organic layer is extracted. The aqueous layer is then extracted with diethyl ether (1 mL/ 1 mL dichloromethane) and the combined organic fraction are concentrated by rotary evaporation and crystallized/ triturated from pentane.

The resulting sulfonamide is weighed out in an oven-dried round-bottom flask with stir bar. Tetrahydrofuran (15 mL/ g sulfonamide) and triphenyl phosphine (1.3 equiv.) are then added, the flask is topped with a septum, flushed with nitrogen, and cooled to 0 °C. Vinylcyclopropane alcohol (1.1 equiv.) is then cannulated drop wise from a concentrated solution in THF. Diisopropylazodicarboxylate (1.3 equiv.) is then added drop wise and the reaction is stirred overnight. The crude product is then concentrated by rotary evaporation and purified by flash column chromatography. When applicable the product is crystallized or triturated from pentane.

#### Yne-vinylcyclopropane **4**:

Isolated as a white solid, m.p. 53.0- 54.5 °C. <sup>1</sup>H NMR (300 MHz, [D]chloroform, TMS):  $\delta$  = 7.72 (d, <sup>3</sup>J (H,H) = 8.3 Hz, 2H), 7.27 (d, <sup>3</sup>J (H,H) = 8.5 Hz, 2H), 5.42- 5.23 (m, 1H), 5.20- 5.15 (m, 1H), 4.00 (q, <sup>5</sup>J (H,H) = 2.4 Hz, 2H), 3.71 (d, <sup>3</sup>J (H,H) = 6.8 Hz, 2H), 2.42 (s, 3H), 1.53 (t, <sup>5</sup>J (H,H) = 2.3 Hz, 3H), 1.40- 1.34 (m, 1H), 0.733- 0.670 (m, 2H), 0.368- 0.317 (m, 2H). <sup>13</sup>C-NMR (75 MHz, [D]chloroform):  $\delta$  = 143.0, 140.2, 129.1 (2C), 127.9 (2C), 120.9, 100.2, ~77 (2C), 48.15, 35.94, 21.47, 13.34, 6.779 (2C), 3.223. IR (neat)  $\nu$  = 3005.2 (w), 2920.4 (w), 2857.0 (w), 1598.1 (w), 1442.2 (w), 1347.3 (s), 1160.9 (s), 1093.3 (m), 964.46 (m), 904.31 (m), 813.89 (m), 737.15 (m), 656.58 (m) cm<sup>-1</sup>. HRMS for C<sub>17</sub>H<sub>21</sub>NO<sub>2</sub>S (M-H<sup>+</sup>) calcd: 302.12148 g/mol, found: 302.12071 g/mol.

#### Cycloadduct **5**:

Freshly prepared and crystallized substrate **4** (42.1 mg, 139  $\mu$ mol) was weighed out in an oven-dried 4 mL vial equipped with a stir bar and sealed with a septum. 1,2-Dichloroethane (695  $\mu$ L, 0.20 M) and catalyst complex **1** (4.00 mg, 6.94  $\mu$ mol, added in 4 aliquots dispersed in 30  $\mu$ L DCE and spaced 15 min apart) were then added, and the reaction was stirred at 60 °C for 60 minutes (total time from first aliquot). The crude reaction mixture was concentrated by rotary evaporation and purified by flash column chromatography, eluting with 8% ether in pentane. Product-containing fractions were identified and concentrated by rotary evaporation to yield product **11**, 28.9 mg (91%) as a white solid.

m.p. 77.5- 80.5 °C. <sup>1</sup>H NMR (300 MHz, [D]chloroform, TMS):  $\delta$  = 7.73 (d, <sup>3</sup>J (H,H) = 8.3 Hz, 2H), 7.33 (d, <sup>3</sup>J (H,H) = 8.3 Hz, 2H), 5.69- 5.62 (m, 1H), 5.33 (d, <sup>3</sup>J (H,H) = 10.5 Hz, 1H), 3.97 (d, <sup>2</sup>J (H,H) = 13.2 Hz, 1H), 3.71- 3.75 (m, 2H), 3.48 (d, <sup>2</sup>J (H,H) = 13.2 Hz, 1H), 2.68- 2.59 (m, 1H), 2.46- 2.38 (m, 1H), 2.43 (s, 3H), 2.29- 2.22 (m, 1H), 2.08- 2.05 (m, 1H), 1.90- 1.82 (m, 1H), 1.570 (s, 3H). <sup>13</sup>C NMR (75 MHz, [D]chloroform):  $\delta$  = 143.7, 131.8, 131.7, 131.0, 129.7, 129.6 (2C), 128.9, 128.1 (2C), 54.74, 51.70, 39.98, 32.02, 25.70, 21.52, 21.15. IR (neat)  $\nu$  = 2921.0 (m), 2851.3 (m), 1598.0 (w), 1447.4 (w), 1346.8 (s), 1163.2 (s), 1094.2 (s), 1036.2 (m), 816.59 (m), 735.60 (m), 665.19 (s) cm<sup>-1</sup>. HRMS for C<sub>17</sub>H<sub>21</sub>NO<sub>2</sub>S calcd: 303.12930 g/mol, found: 303.12993 g/mol.

#### Yne-vinylcyclopropane **6**:

Isolated as a white solid, m.p. 56.5- 58.0 °C. <sup>1</sup>H NMR (300 MHz, [D]chloroform, TMS):  $\delta$  = 7.72 (d, <sup>3</sup>J (H,H) = 8.3 Hz, 2H), 7.28 (d, <sup>3</sup>J (H,H) = 8.1 Hz, 2H), 5.42- 5.39 (m, 1H), 5.25- 5.16 (m, 1H), 4.08 (d, <sup>4</sup>J (H,H) = 2.2, 2H), 3.74 (d, <sup>3</sup>J (H,H) = 6.8 Hz, 2H), 2.42 (s, 3H), 1.97 (t, <sup>4</sup>J (H,H) = 2.3 Hz, 1H), 1.41- 1.35 (m, 1H), 0.741- 0.679 (m, 2H), 0.374- 0.323 (m, 2H). <sup>13</sup>C

NMR (75 MHz, [D]chloroform):  $\delta$  = 143.4, 140.8, 136.1, 129.4 (2C), 127.8 (2C), 120.4, 77.21, 73.47, 48.17, 35.37, 21.54, 13.38, 6.847 (2C). IR (neat)  $\nu$  = 3291.3 (m), 3082.5 (w), 3005.3 (w), 2923.8 (w), 2862.3 (w), 2118.6 (w), 1664.9 (w), 1597.9 (w), 1494.3 (w), 1348.0 (s), 1161.0 (s), 1093.8 (m), 966.28 (m), 898.91 (m), 813.94 (m), 741.04 (m), 659.21 (m)  $\text{cm}^{-1}$ . HRMS for  $\text{C}_{16}\text{H}_{19}\text{NO}_2\text{S}$  ( $\text{M-H}^+$ ) calcd: 288.10583 g/mol, found: 288.10642 g/mol. Anal. calcd for  $\text{C}_{16}\text{H}_{19}\text{NO}_2\text{S}$ : 66.40% C; 6.62% H; 4.84% N; 10.90% S. Found: 66.65% C; 6.60% H; 4.89% N; 10.90% S.

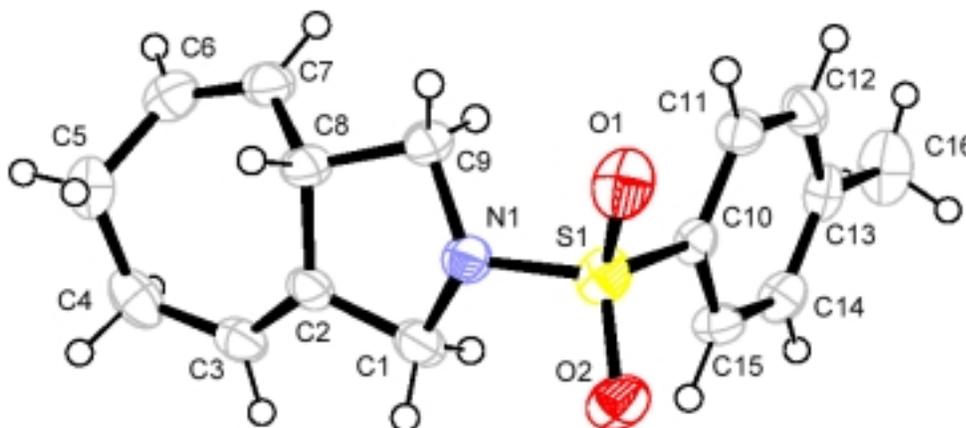
#### Cycloadduct **7**:

Freshly prepared and crystallized substrate **6** (38.2 mg, 132  $\mu\text{mol}$ ) was weighed out in an oven-dried 8 mL vial equipped with a stir bar. 1,2-Dichloroethane (4.40 mL, 0.03 M) and catalyst complex **1** (3.79 mg, 6.60  $\mu\text{mol}$ ) were then added, the vial was sealed with teflon tape, and the reaction was stirred at 60  $^\circ\text{C}$  for 60 minutes before it was concentrated by rotary evaporation and purified by flash column chromatography, eluting with 10% ether in pentane. Product-containing fractions were identified and concentrated by rotary evaporation to yield product **7**, 34.8 mg (91%) as a white powder.

Preparative scale procedure: Freshly prepared and crystallized substrate **6** (1.00 g, 3.46 mmol) was weighed out in an oven-dried 25 mL flask equipped with a stir bar. Dichloroethane (17.3 mL, 0.20 M) and catalyst complex **1** (99.3 mg, 173  $\mu\text{mol}$ , added in 4 aliquots dispersed in 1.25 mL DCE and spaced 15 min apart) were then added as the reaction was stirred at room temperature for a total 55 minutes. The crude product was concentrated and purified by flash column chromatography, eluting with 10% ether in pentane. Product-containing fractions were concentrated and recrystallized to yield product **7**, 900.3 mg (90%) as a white solid.

m.p. 90.0- 90.5  $^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz, [D]chloroform, TMS):  $\delta$  = 7.69 (d,  $^3J(\text{H,H})$  = 8.30 Hz, 2H), 7.32 (d,  $^3J(\text{H,H})$  = 8.3 Hz, 2H), 5.78- 5.70 (m, 1H), 5.57- 5.56 (m, 1H), 5.38 (d,  $^3J(\text{H,H})$  = 10.7 Hz, 1H), 3.97 (d,  $^2J(\text{H,H})$  = 13.2 Hz, 1H), 3.79- 3.72 (m, 2H), 3.54 (d,  $^2J(\text{H,H})$  = 13.4 Hz, 1H), 2.70 (dd,  $^3J(\text{H,H})$  = 12.9 Hz,  $^3J(\text{H,H})$  = 13.4 Hz, 1H), 2.43 (s, 3H), 2.38- 2.22 (m, 2H), 2.07- 2.00 (m, 2H); assigned with a 2D-COSY experiment.  $^{13}\text{C}$  NMR (75 MHz, [D]chloroform):  $\delta$  = 143.7, 138.2, 132.0, 131.8, 129.6 (2C), 128.9, 128.0 (2C), 122.4, 54.43, 53.09, 40.24, 25.97, 25.45, 21.54. IR (neat)  $\nu$  = 3023.8 (m), 2905.3 (m), 2848.2 (m), 1597.6 (m), 1493.3 (w), 1473.8 (w), 1449.5 (w), 1429.5 (w), 1346.4 (s), 1263 (w), 1212.2 (w), 1164.8 (s), 1093.9 (m), 1044.0 (m), 815.42 (m), 709.39 (w), 662.39 (s)  $\text{cm}^{-1}$ . HRMS for  $\text{C}_{16}\text{H}_{19}\text{NO}_2\text{S}$  calcd: 289.11365 g/mol, found: 289.11402 g/mol. Anal. calcd for  $\text{C}_{16}\text{H}_{19}\text{NO}_2\text{S}$ : 66.40% C; 6.62% H; 4.84% N; 11.06% O. Found: 66.61% C; 6.47% H; 4.90% N; 10.91% O.

X-ray analysis of a single crystal of **7** afforded the ORTEP diagram shown in Figure 1.



**Figure 1.** ORTEP diagram for cycloadduct **7**. Ellipsoids illustrated at 50% probability level.

### Yne-cyclopropane **8**:

Isolated as a white solid, m.p. 40.0- 41.5 °C. <sup>1</sup>H NMR (300 MHz, [D]chloroform, TMS): δ = 7.73 (d, <sup>3</sup>J (H,H) = 8.1 Hz, 2H), 7.28 (d, <sup>3</sup>J (H,H) = 8.3 Hz, 2H), 5.12 (t, <sup>3</sup>J (H,H) = 7.3 Hz, 1H), 4.06 (d, <sup>4</sup>J (H,H) = 2.4 Hz, 2H), 3.83 (d, <sup>3</sup>J (H,H) = 7.3 Hz, 2H), 2.42 (s, 3H), 1.98 (t, <sup>4</sup>J (H,H) = 2.1 Hz, 1H), 1.55 (s, 3H), 1.39- 1.34 (m, 1H), 0.614- 0.551 (m, 2H), 0.460- 0.406 (m, 2H). <sup>13</sup>C NMR (75 MHz, [D]chloroform): δ = 143.4, 143.2, 136.2, 129.4 (2C), 127.8 (2C), 115.8, ~77, 73.33, 43.80, 35.40, 21.52, 18.79, 13.95, 4.760 (2C). IR (neat) ν = 3290.6 (m), 3083.9 (w), 3005.2 (w), 2923.5 (w), 2871.3 (w), 2118.4 (w), 1654.7 (w), 1597.9 (w), 1494.26 (w), 1447.6 (w), 1346.9 (s), 1161.1 (s), 1093.5 (m), 899.03 (m), 815.08 (m), 750.02 (m), 722.66 (m), 659.49 (s) cm<sup>-1</sup>. HRMS for C<sub>17</sub>H<sub>21</sub>NO<sub>2</sub>S (M-H<sup>+</sup>) calcd: 302.12148 g/mol, found: 302.12082 g/mol.

### Cycloadduct **9**:

Substrate **8** was weighed out (23.7 mg, 78.1 μmol) in an oven-dried 8 mL vial equipped with a stir bar. 1,2-Dichloroethane (2.6 mL, 0.03 M) and catalyst complex **1** (2.2 mg, 3.9 μmol) was then added, the vial was flushed with nitrogen, sealed with teflon tape, and the reaction was stirred at room temperature for 60 min. The crude reaction mix was then concentrated by rotary evaporation and purified by flash column chromatography, eluting with 8% ether in petroleum ether. Product-containing fractions were identified and concentrated by rotary evaporation to yield product **9**, 22.1 mg (93.2%) as a white solid.

Mp 69.0– 72.0 °C. <sup>1</sup>H NMR (300 MHz, [D]chloroform, TMS): δ = 7.70 (d, <sup>3</sup>J (H,H) = 8.3 Hz, 2H), 7.34 (d, <sup>3</sup>J (H,H) = 8.3 Hz, 2H), 5.56 (m, 2H), 3.94- 3.90 (m, 1H), 3.79- 7.78 (m, 1H), 3.72- 3.66 (m, 1H), 3.44- 3.52 (m, 1H), 2.89 (dd <sup>3</sup>J (H,H) = 9.4 Hz, <sup>3</sup>J (H,H) = 9.4 Hz, 1H), 2.44 (s, 3H), 2.33 (m, 1H), 2.13 (m, 1H), 2.00- 1.98 (m, 2H), 1.65 (s, 3H). <sup>13</sup>C NMR (75 MHz, [D]chloroform): δ = 143.7, 136.3, 135.6, 131.9, 129.6 (2C), 128.0 (2C), 127.1, 122.9, 53.30, 52.10, 43.41, 25.73, 25.47, 22.23, 21.54. IR (neat) ν = 2922.3 (m), 2852.2 (m), 1597.8 (w), 1450.3 (m), 1347.3 (s), 1163.8 (s), 1093.1 (s), 1043.2 (m), 911.83 (w), 816.37 (m), 735.49 (w), 708.94 (w), 666.97 (s), 610.13 (w) cm<sup>-1</sup>. HRMS for C<sub>17</sub>H<sub>21</sub>NO<sub>2</sub>S calcd: 303.12930 g/mol, found: 303.12949 g/mol.

### Cycloadduct **11**:

Substrate **10**<sup>5</sup> (19.2 mg, 118 μmol) was weighed out in an oven-dried 4 mL vial equipped with a stir bar. 1,2-Dichloroethane (787 μL, 0.15 M) and catalyst complex **1** (1.36 mg, 2.36 μmol) were added, the vial was flushed with nitrogen, and the reaction was stirred at room temperature for 16 min. The crude reaction mix was concentrated by rotary evaporation and purified by flash column chromatography, eluting with 10% ether in petroleum ether. Product-containing fractions were identified and concentrated by rotary evaporation to yield product **11**, 21.9 mg (96.4%) as a colorless oil. Data was found to be consistent with a known compound.<sup>5</sup>

### Cycloadduct **13**:

Substrate **10**<sup>2</sup> (28.4 mg, 136 μmol) was weighed out in an oven-dried 4 mL vial equipped with a stir bar. 1,2-Dichloroethane (1.26 mL, 0.11 M) and catalyst complex **1** (1.56 mg, 2.13 μmol) were added, the vial was flushed with nitrogen, and the reaction was stirred at room temperature for 10 min. The crude reaction mix was concentrated by rotary evaporation and purified by flash column chromatography, eluting with 10% ether in petroleum ether. Product-containing fractions were identified and concentrated by rotary evaporation to yield product **11**, 28.0 mg (98.6%) as a colorless oil. Data was found to be consistent with a known compound.<sup>2</sup>

#### Cycloadduct **15**:

Ene-vinylcyclopropane substrate **14**<sup>3</sup> (19.2 mg, 76.1 μmol) was weighed out in an oven-dried 10 mL flask equipped with a stir bar. 1,2-Dichloroethane (1.5 mL, 0.05 M) and catalyst complex **1** (2.08 mg, 3.80 μmol) were added, the flask was flushed with nitrogen, and the reaction was stirred at 60 °C for 6 hours. The crude reaction mix was concentrated by rotary evaporation and purified by flash column chromatography, eluting with 8% ether in petroleum ether. Product-containing fractions were identified and concentrated by rotary evaporation to yield product **15**, 18.5 mg (96.4%) as a colorless oil. Data was found to be consistent with a known compound.<sup>3</sup>

#### Cycloadduct **17**:

Ene-vinylcyclopropane substrate **16**<sup>2</sup> (10.3 mg, 38.7 μmol) was weighed out in an oven-dried 4 mL vial equipped with a stir bar. 1,2-Dichloroethane (750 μL, 0.05M) and catalyst complex **1** (1.1 mg, 1.9 μmol) were added, the vial was flushed with nitrogen, sealed with teflon tape, and the reaction was stirred at 60 °C for 6.5 hours. The crude reaction mix was concentrated by rotary evaporation and purified by flash column chromatography, eluting with 8% ether in pentane. Product-containing fractions were identified and concentrated by rotary evaporation to yield product **17**, 9.3 mg (90%) as a colorless oil. Data was found to be consistent with a known compound.<sup>2</sup>

#### Ene-vinylcyclopropane **18**:

Isolated as a colorless oil. <sup>1</sup>H NMR (300 MHz, [D]chloroform, TMS): δ = 7.79 (d, <sup>3</sup>J (H,H) = 8.3 Hz, 2H), 7.29 (d, <sup>3</sup>J (H,H) = 8.5 Hz, 2H), 5.71- 5.58 (m, 1H), 5.19- 5.10 (m, 2H), 4.97 (t, <sup>3</sup>J (H,H) = 7.1 Hz, 1H), 3.81 (d, <sup>3</sup>J (H,H) = 7.1 Hz, 2H), 3.76 (d, <sup>3</sup>J (H,H) = 6.2 Hz, 2H), 2.43 (s, 3H), 1.47 (s, 3H), 1.32- 1.23 (m, 1H), 0.578- 0.503, (m, 2H), 0.370- 0.318 (m, 2H). <sup>13</sup>C NMR (75 MHz, [D]chloroform): δ = 140.9, 137.7, 133.2, 129.6 (2C), 127.2 (2C), 119.5, 118.4, 116.7, 49.27, 43.30, 21.49, 18.62, 14.16, 4.566 (2C). IR (neat) ν = 3082.8 (m), 3006.5 (m), 2922.3 (m), 2866.5 (m), 1656.3 (w), 1644.0 (w), 1598.2 (m), 1494.8 (m), 1443.1 (m), 1342.5 (s), 1158.8 (s), 1092.1 (s), 1048.3 (m), 1018.3 (m), 990.00 (m), 928.41 (s), 908.68 (s), 815.58 (s), 757.26 (s), 726.32 (m), 661.13 (s) cm<sup>-1</sup>. HRMS for C<sub>17</sub>H<sub>23</sub>NO<sub>2</sub>S calcd: 305.14495 g/mol, found: 305.14516 g/mol. Anal. calcd for C<sub>17</sub>H<sub>23</sub>NO<sub>2</sub>S: 66.85% C; 7.51% H; 4.59% N; 10.43% S. Found: 66.61% C; 7.51% H; 4.62% N; 10.48% S.

#### Cycloadduct **19**:

Substrate **18** was weighed out (25.9 mg, 84.8 μmol) in an oven-dried 8 mL vial equipped with a stir bar. 1,2-Dichloroethane (2.83 mL, 0.03 M) and catalyst complex **1** (2.4 mg, 4.2 μmol) were then added, the vial was flushed with nitrogen, sealed with teflon tape, and the reaction was stirred at 60 °C for 19 h. The crude reaction mix was then concentrated by rotary evaporation and purified by flash column chromatography, eluting with 8% ether in petroleum ether. Product-containing fractions were identified and concentrated by rotary evaporation to yield product **19**, 19.6 mg (76%) as a colorless oil.

<sup>1</sup>H NMR (300 MHz, [D]chloroform, TMS): δ = 7.72 (d, <sup>3</sup>J (H,H) = 8.1, 2H), 7.32 (d, <sup>3</sup>J (H,H) = 8.1, 2H), 5.48 (dd, <sup>3</sup>J (H,H) = 5.7 Hz, <sup>3</sup>J (H,H) = 5.7 Hz, 1H), 3.58 (dd, <sup>2</sup>J (H,H) = 9.28 Hz, <sup>3</sup>J (H,H) = 7.81 Hz, 1H), 3.41 (dd, <sup>2</sup>J (H,H) = 8.9 Hz, <sup>3</sup>J (H,H) = 6.23 Hz, 1H), 3.05- 2.98 (m, 2H), 2.69- 2.61 (m, 1H), 2.44 (s, 3H), 2.21- 2.10 (m, 2H), 1.85- 1.75 (m, 1H), 1.64 (s, 3H), 1.63- 1.44 (m, 2H), 1.34- 1.18 (m, 2H). <sup>13</sup>C NMR (75 MHz, [D]chloroform): δ = 143.3, 134.0, 132.9, 129.6 (2C), 127.5 (2C), 126.2, 55.76, 50.06, 47.31, 39.79, 30.50, 27.56, 25.92, 25.06,

21.57. IR (neat)  $\nu = 2924.9$  (m), 2858.3 (w), 1597.9 (w), 1479.9 (w), 1448.7 (w), 1345.3 (s), 1160.7 (s), 1093.6 (m), 1047.3 (w), 1016.7 (w), 816.32 (m), 709.22 (w), 668.66 (s)  $\text{cm}^{-1}$ . HRMS for  $\text{C}_{17}\text{H}_{23}\text{NO}_2\text{S}$  calcd: 305.14495 g/mol, found: 305.145742 g/mol. Anal. calcd for  $\text{C}_{17}\text{H}_{23}\text{NO}_2\text{S}$ : 67.29% C; 6.98% H; 4.62% N; 10.57% O. Found: 67.45% C; 7.11% H; 4.55% N; 10.80% O.

#### Cycloadduct **21a**:

Substrate **20**<sup>3</sup> was weighed out (32.9 mg, 124  $\mu\text{mol}$ ) in an oven-dried 8 mL vial equipped with a stir bar. 1,2-Dichloroethane (4.13 mL, 0.03 M) and catalyst complex **1** (7.1 mg, 12  $\mu\text{mol}$ ) were then added, the vial was flushed with nitrogen, sealed with teflon tape, and the reaction was stirred at 70 °C for 10 h. The crude reaction mix was then concentrated by rotary evaporation and purified by flash column chromatography, eluting with 3% ether in petroleum ether. Product-containing fractions were identified and concentrated by rotary evaporation to yield product **21a**, 24.6 mg (75%) as a colorless oil. (**21b** is a known compound.<sup>3</sup>)

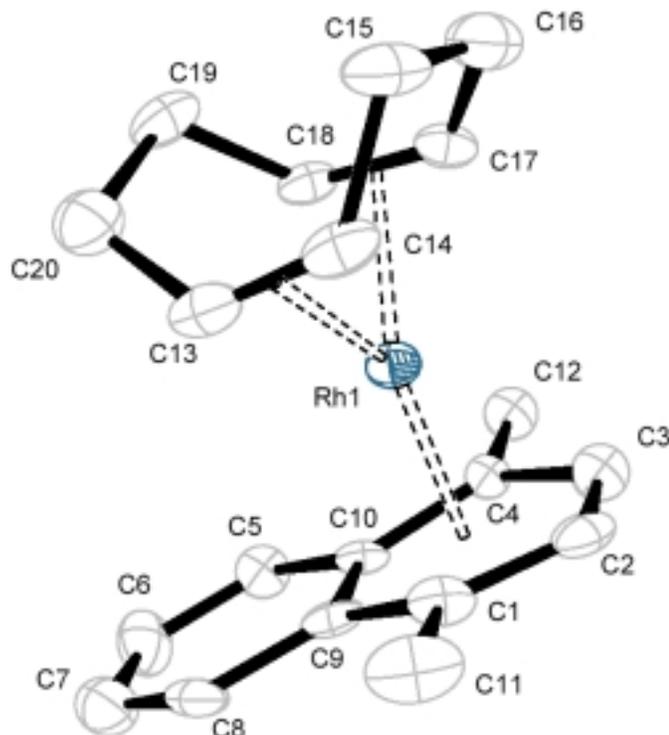
<sup>1</sup>H NMR (500 MHz, [D]chloroform):  $\delta = 5.46$ - 5.43 (m, 1H), 3.71 (s, 3H), 3.72 (s, 3H), 2.75- 2.70 (m, 1H), 2.54 (dd, <sup>2</sup>J (H,H) = 13.1 Hz, <sup>3</sup>J (H,H) = 7.2 Hz, 1H), 2.44 (dd, <sup>2</sup>J (H,H) = 13.5 Hz, <sup>3</sup>J (H,H) = 7.3 Hz, 1H), 2.18- 2.09 (m, 2H), 2.12 (dd, <sup>2</sup>J (H,H) = 12.9 Hz, <sup>3</sup>J (H,H) = 12.9 Hz, 1H), 1.94 (dd, <sup>2</sup>J (H,H) = 13.6 Hz, <sup>3</sup>J (H,H) = 5.2 Hz, 1H), 1.91- 1.88 (m, 1H), 1.72 (s, 3H), 1.71- 1.53 (m, 2H), 1.48- 1.41 (m, 1H), 1.38- 1.33 (m, 1H); assigned by 2D-COSY and HSQC experiments. <sup>13</sup>C NMR (75 MHz, [D]chloroform):  $\delta = 172.9$  (2C), 136.1, 123.9, 58.33, 52.66 (2C), 46.74, 41.95, 39.59, 37.73, 31.10, 26.94, 25.47, 24.85. IR (neat)  $\nu = 2952.0$  (m), 2923.6 (m), 2855.1 (m), 1735.8 (s), 1435.3 (m), 1263.9 (s), 1249.2 (s), 1196.4 (m), 1168.1 (m), 1072.4 (w)  $\text{cm}^{-1}$ . LRMS for  $\text{C}_{15}\text{H}_{22}\text{O}_4$  calcd: 266.15181 g/mol, found 266.1 g/mol. Anal. calcd for  $\text{C}_{13}\text{H}_{22}\text{O}$ : 67.64% C; 8.33% H; 24.03% O. Found: 68.04% C; 8.68% H.

#### $[(\eta^6\text{-}(1,4\text{-dimethylnaphthalene)}\text{Rh}(\text{COD}))^+ \text{SbF}_6^- \text{22}$ :

Chloro(COD)rhodium(I) dimer (49.2 mg, 0.100 mmol) and silver hexafluoroantimonate (68.7 mg, 0.200 mmol) were weighed out in an oven-dried, 25 mL, round-bottom flask with stir bar. To this was added freshly distilled acetone (8 mL), and the resulting suspension was stirred for 30 minutes while a white precipitate formed. This material was filtered through a Shlenk filter into another oven-dried, 25 mL, round-bottom flask with stir bar containing 1,4-dimethylnaphthalene (62.5 mg, 61.5  $\mu\text{L}$ , 0.400 mmol). The resulting solution was stirred for an additional 20 minutes and concentrated by rotary evaporation. The resulting residue was dispersed in diethyl ether to leave granular, yellow powder that was collected over fine-grain #40 filter paper to yield 81.3 mg (67.4%).

<sup>1</sup>H NMR (300 MHz, [D<sub>2</sub>]dichloromethane):  $\delta = 8.03$ - 7.95 (m, 4H), 7.08 (s, 2H), 4.15 (s, 4H), 2.32 (s, 6H), 2.12- 1.95 (m, 8H). <sup>13</sup>C NMR (75 MHz, [D<sub>2</sub>]dichloromethane):  $\delta = 132.5$  (2C), 124.2 (2C), 116.1 (2C), 106.3 (4C), 82.91 (2C), 28.73 (2C), 30.91 (4C), 17.04 (2C). IR (neat)  $\nu = 2928.6$  (m), 2882.2 (m), 2939.7 (w), 1643.1 (m), 1503.9 (w), 1463.5 (w), 1443.3 (w), 1387.5 (m), 1331.9 (w), 1204.7 (w), 1032.2 (w), 876.41 (w), 821.56 (w), 759.49 (m), 657.45 (s)  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{20}\text{H}_{24}\text{F}_6\text{RhSb}$ : 39.83% C; 4.01% H; 18.90% F; 17.06% Rh; 20.19% Sb. Found: 39.83% C; 4.26% H; 19.12% F.

X-ray analysis of a single crystal of **22** afforded the ORTEP diagram shown in Figure 2.



**Figure 2.** ORTEP diagram for  $[(\eta^6\text{-}(1,4\text{-dimethylnaphthalene})\text{Rh}(1,5\text{-cyclooctadiene}))]^+ \text{SbF}_6^-$ . Ellipsoids illustrated at 50% probability level.

$[(\eta^6\text{-C}_6\text{H}_6)\text{Rh}(\text{COD})]^+ \text{SbF}_6^-$  **23**:

Chloro(COD)rhodium(I) dimer (98.4 mg, 0.200 mmol) and silver hexafluoroantimonate (137.4 mg, 0.400 mmol) were weighed out in an oven-dried, 25 mL, round-bottom flask with stir bar. To this was added freshly distilled acetone (15 mL), and the resulting suspension was stirred for 30 minutes while a white precipitate formed. This material was filtered through a Shlenk filter into another oven-dried, 25 mL, round-bottom flask with stir bar containing benzene (62.5 mg, 74.5  $\mu\text{L}$ , 0.800 mmol). The resulting solution was stirred for an additional 20 minutes and concentrated by rotary evaporation. The resulting residue was dispersed in diethyl ether and benzene to leave granular, yellow powder that was collected over fine-grain #40 filter paper to yield 137.2 mg (65%).

$^1\text{H}$  NMR (300 MHz,  $[\text{D}_2]$ dichloromethane):  $\delta$  = 6.81 (s, 6H), 5.32 (s, 4H), 2.40- 2.36 (m, 4H), 2.14- 2.12 (m, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $[\text{D}_2]$ dichloromethane):  $\delta$  = 104.7 (6C), 78.15 (2C), 77.98 (2C), 30.77 (4C). IR (KBr):  $\nu$  = 3097.9 (m), 2956.6 (m), 2889.6 (m), 2843.4 (m), 1686.1 (w, b), 1465.1 (m), 1444.5 (m), 1337.4 (w), 1309.5 (w), 1261.6 (w), 1164.0 (w), 1078.4 (w), 1011.0 (w), 891.75 (w), 826.61 (w), 787.62 (s), 656.79 (s)  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{14}\text{H}_{18}\text{F}_6\text{RhSb}$ : 32.03% C; 3.46% H; 21.71% F; 19.60% Rh; 23.19% Sb. Found: 31.82% C; 3.35% H; 22.07% F.

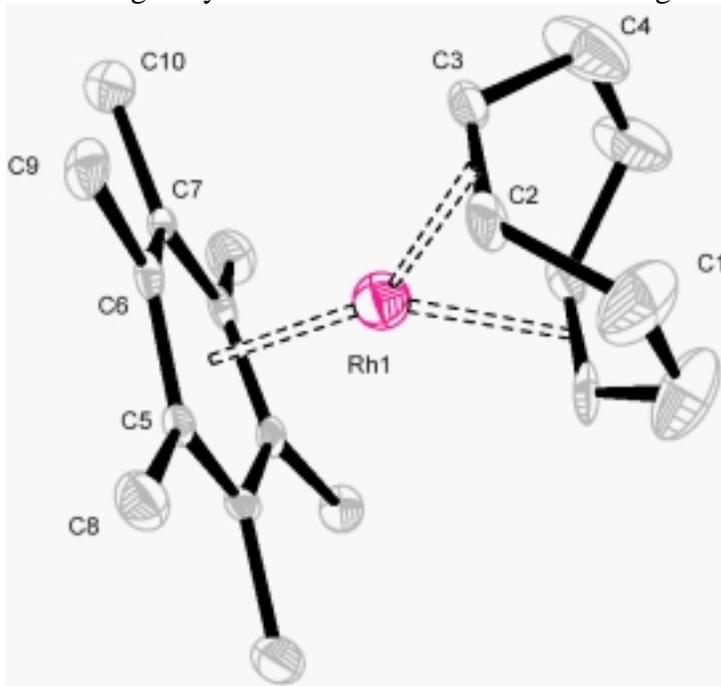
$[(\eta^6\text{-C}_{12}\text{H}_{18})\text{Rh}(\text{COD})]^+ \text{SbF}_6^-$ , **24**:

Chloro(COD)rhodium(I) dimer (98.4 mg, 0.200 mmol) and silver hexafluoroantimonate (137 mg, 0.400 mmol) were weighed out in an oven-dried, 25 mL, round-bottom flask with stir bar. To this was added freshly distilled acetone (15 mL) and the resulting suspension was stirred for 30 minutes while a canary-yellow precipitate formed. This material was then removed by filtration through a shlenk filter into another oven-dried, 25 mL, round-bottom flask with stir bar

containing hexamethylbenzene (130 mg, 0.800 mmol). The resulting solution was stirred for an additional 30 minutes and concentrated by rotary evaporation. The residue was dispersed in diethyl ether to leave a crystalline, yellow powder that was collected over fine-grain filter paper to yield 216 mg (87%) of  $[(\eta^6\text{-C}_{12}\text{H}_{18})\text{Rh}(\text{COD})]^+ \text{SbF}_6^-$  as yellow crystals.

$^1\text{H}$  NMR (300 MHz,  $[\text{D}]\text{chloroform}$ ):  $\delta$  = 3.68 (s, 4H), 2.35- 2.09 (m, 8H), 2.25 (s, 18H).  $^{13}\text{C}$  NMR (75 MHz,  $[\text{D}]\text{chloroform}$ ):  $\delta$  = 115.5 (6C), 82.75 (2C), 82.57 (2C), 31.47 (6C), 15.84 (4C). IR (neat):  $\nu$  = 2954.5 (m), 2924.5 (m), 2880.0 (w), 2847.3 (w), 1451.6 (m), 1433.4 (m), 1386.3 (m), 1330.1 (w), 1305.6 (w), 1288.6 (w), 1177.9 (w), 1157.9 (w), 1067.1 (m), 1004.5 (m), 877.79 (w), 825.69 (w), 654.57 (s)  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{20}\text{H}_{30}\text{F}_6\text{RhSb}$ : 39.44% C; 4.96% H; 18.71% F. Found: 39.05% C; 4.87% H; 19.02% F.

X-ray analysis of a single crystal of **24** afforded the ORTEP diagram shown in Figure 3.



**Figure 3.** ORTEP diagram for  $[(\eta^6\text{-C}_6(\text{CH}_3)_6)\text{Rh}(1,5\text{-cyclooctadiene})]^+ \text{SbF}_6^-$ . Ellipsoids illustrated at 50% probability level.

General Procedure for the reaction of 2,3-dimethyl-1,3-butadiene and propargyl methyl ether:

In an oven-dried, 10 mL, round-bottom flask, catalyst complex **1** (8.61 mg, 0.0150 mmol) was weighed out. To this were added dichloromethane (6 mL), 2,3-dimethyl-1,3-butadiene (370 mg, 509  $\mu\text{L}$ , 4.50 mmol), and propargyl methyl ether (107 mg, 128  $\mu\text{L}$ , 1.50 mmol). This yellow solution was allowed to stir at room temperature for 90 minutes then was concentrated by rotary evaporation, and the residue was purified by flash column chromatography eluting with 2% ether in pentane. Product-containing fractions were identified and concentrated by rotary evaporation to leave product **3**, 234 mg (> 99%).  $^1\text{H}$  NMR (300 MHz,  $[\text{D}]\text{chloroform}$ ):  $\delta$  = 5.67 (m, 1H), 3.82 (s, 2H), 3.26 (s, 3H), 2.64- 2.58 (m, 4H), 1.66- 1.64 (m, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $[\text{D}]\text{chloroform}$ ):  $\delta$  = 132.4, 122.9, 122.6, 122.5, 76.56, 57.52, 33.56, 33.45, 18.46, 18.21. IR (neat)  $\nu$  = 2981.4 (m), 2917.9 (s), 2871.6 (s), 2815.2 (s), 1448.7 (m), 1379.1 (m), 1184.2 (m), 1110.0 (s), 1084.0 (s), 908.63 (m), 803.52 (w)  $\text{cm}^{-1}$ . HRMS for  $\text{C}_{10}\text{H}_{16}\text{O}$ : calcd 152.12012 g/mol, found 152.12007 g/mol.

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