Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Terminal Alkyne Coupling Reactions through a Ring: Mechanistic Insights and Regiochemical Switching

*Caroline M. Storey, Matthew R. Gyton, Rhiann E. Andrew, and Adrian B. Chaplin**

anie_201807028_sm_miscellaneous_information.pdf

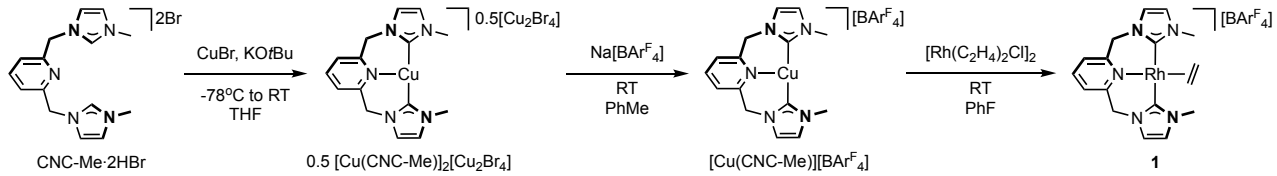
Table of contents

1 General experimental methods

All manipulations were performed under an atmosphere of argon using Schlenk and glove box techniques. Glassware was oven-dried at 150 °C overnight and flamed under vacuum prior to use. THF was dried over Na/benzophenone, vacuum distilled and stored under argon. Fluorobenzene and 1,2-difluorobenzene were stirred over alumina, dried over CaH_2, vacuum distilled and then stored under argon over thoroughly vacuum-dried 3 Å molecular sieves. Hexane was stored over a potassium mirror under an argon atmosphere. Hexamethyldisiloxane was dried over Na/K alloy, vacuum distilled and stored over thoroughly vacuum-dried 3 Å molecular sieves under argon. DMSO was freeze–pump–thaw degassed, placed under argon, and dried five times over thoroughly vacuum-dried 3 Å molecular sieves. Anhydrous CH_2Cl_2, CH_3CN, diethyl ether, pentane and toluene (<0.005% H_2O) were purchased from ACROS or Sigma-Aldrich and freeze–pump–thaw degassed three times before being placed under argon over thoroughly vacuum-dried 3 Å molecular sieves. CD_2Cl_2 and 1,2-$C_2D_4Cl_2$ were freeze–pump–thaw degassed three times before being placed under argon over thoroughly vacuum-dried 3 Å molecular sieves. CuBr was purified by successive washes with acetic acid and H_2O under nitrogen before being dried *in vacuo*. CNC-Me·2HBr,[1] [Cu(CNC-12)][BAr^F_4],[2] [$Rh(C_2H_4)_2Cl]_2$,[3] 3,5-di-*tert*-butylphenyl acetylene,[4] and Na[BAr^F_4][5] were synthesised using literature protocols. All other solvents and reagents are commercial products and were used as received. NMR spectra were recorded on Bruker spectrometers at 298 K unless otherwise stated. Variable temperature data was collected on Bruker Avance 500 MHz and Avance III 600 MHz spectrometers. Chemical shirts are quoted in ppm and coupling constants in Hz. Low-resolution electrospray ionisation mass spectra (LR ESI-MS) were recorded on an Agilent 6130B single Quad spectrometer. High-resolution electrospray ionisation mass spectra (HR ESI-MS) were recorded on a Bruker MaXis II spectrometer. IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer at 298 K. Microanalyses were performed by Stephen Boyer at London Metropolitan University.

2 Preparation of [Rh(CNC-Me)(C_2H_4)][BAr^F_4] 1

Scheme S1: Preparation of **1** from CNC-Me·2HBr



2.1 $[Cu(CNC\text{-}Me)]_2[Cu_2Br_4]$†

A solution of KO*t*Bu (650 mg, 5.79 mmol) in THF (20 mL) was slowly added to a vigorously stirred suspension of CNC-Me·2HBr (950 mg, 2.21 mmol) and CuBr (950 mg, 6.62 mmol) in THF (80 mL) maintained at −78 °C. The orange suspension was stirred for 1 h, warmed to RT, and then stirred for a further 16 h. The resulting yellow suspension was reduced to dryness and the residue extracted with excess CH_3CN (*ca*. 450 mL) to afford the product as a pale yellow powder on removal of the volatiles *in vacuo*. Yield: 670 mg (55%).

† Through comparison to [Cu(CNC-12)]$_2$[Cu_2Br_4] this complex is formulated as a dimer in the solid-state, but monomer in solution.[2] The latter assignment is consistent with the high symmetry observed by NMR spectroscopy and similarity of this data to that of [Cu(CNC-Me)][BAr^F_4].

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.75 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.30 (d, $^3J_{HH}$ = 7.7, 2H, py), 7.18 (d, $^3J_{HH}$ = 1.8, 2H, NCH), 6.95 (d, $^3J_{HH}$ = 1.8, 2H, NCH), 5.39 (s, 4H, py$\underline{C}H_2$), 3.84 (s, 6H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 178.9 (s, NCN), 156.1 (s, py), 139.2 (s, py), 122.8 (s, py), 122.4 (s, NCH), 122.2 (s, NCH), 56.5 (s, py$\underline{C}H_2$), 38.9 (s, CH_3).

HR ESI-MS (positive ion, 4 kV): 330.0769 ([*M*]$^+$, calcd 330.0774) *m/z*.

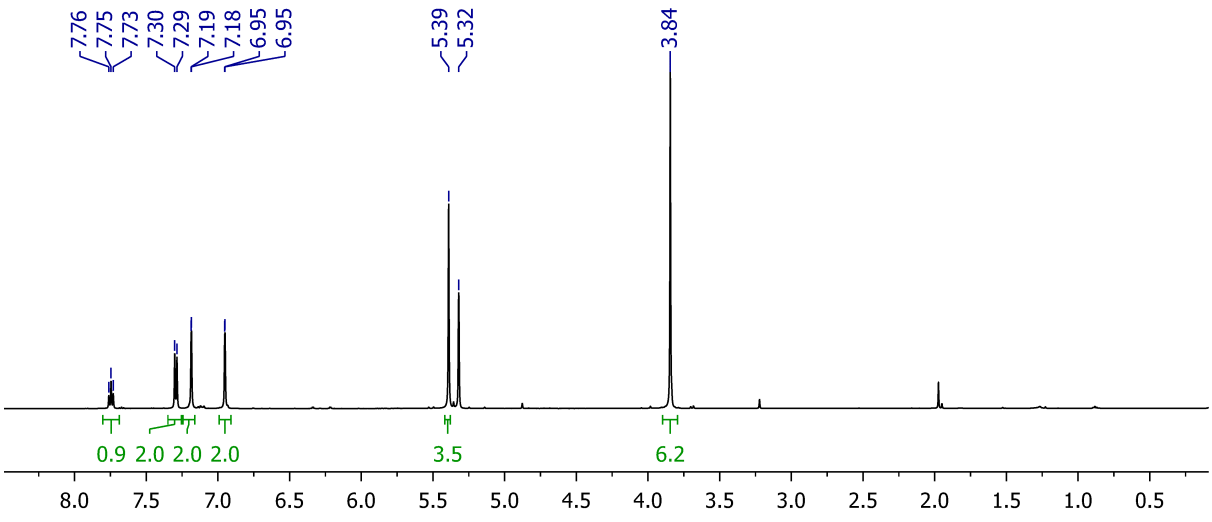


Figure S1: ^{1}H NMR spectrum of $[Cu(CNC\text{-}Me)]_2[Cu_2Br_4]$ (CD_2Cl_2, 500 MHz)

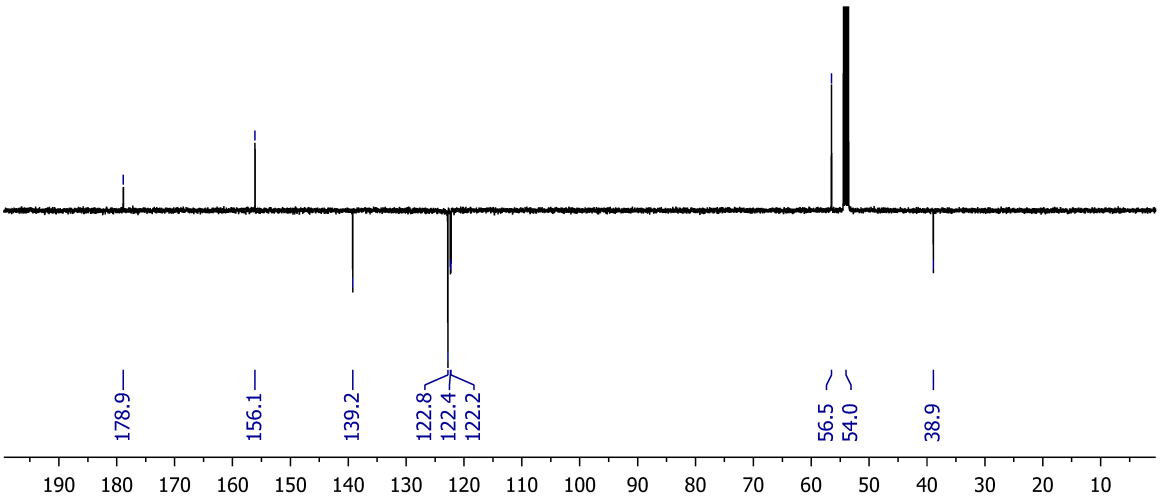


Figure S2: $^{13}C\{^{1}H\}$ APT NMR spectrum of $[Cu(CNC\text{-}Me)]_2[Cu_2Br_4]$ (CD_2Cl_2, 126 MHz)

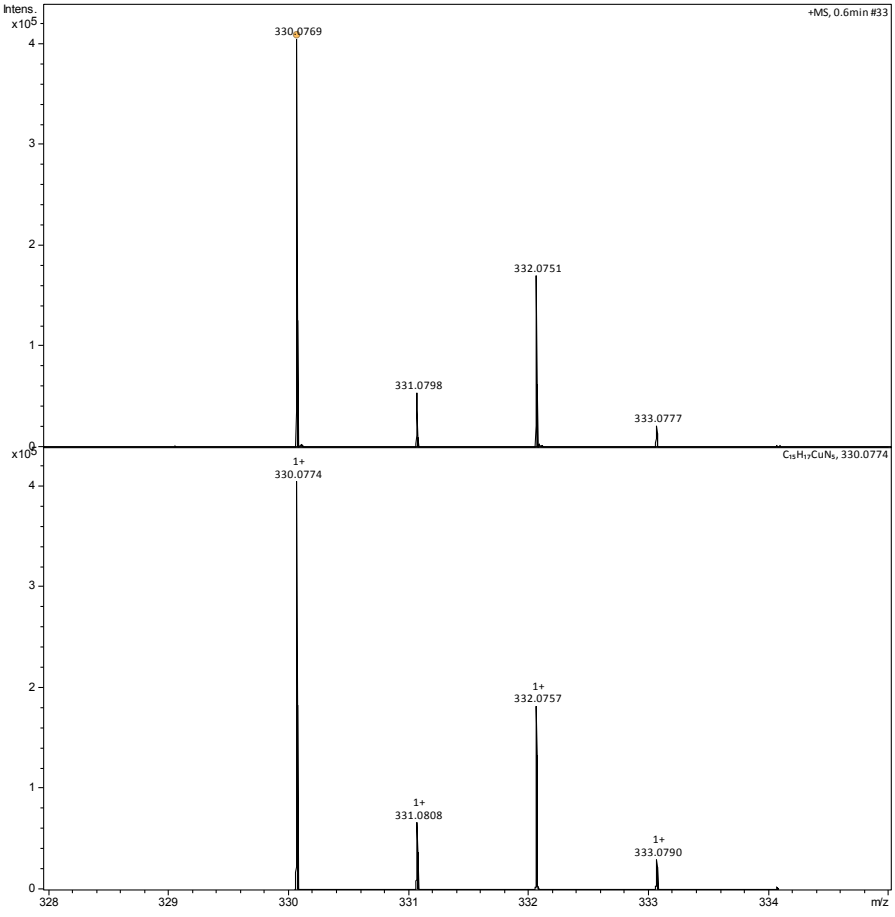


Figure S3: HR ESI-MS spectrum of $[Cu(CNC\text{-}Me)]_2[Cu_2Br_4]$

2.2 [Cu(CNC-Me)][BAr$^{F}_{4}$]

A suspension of [Cu(CNC-Me)]$_2$[Cu$_2$Br$_4$] (50.0 mg, 45.1 µmol) and Na[BAr$^{F}_{4}$] (99.9 mg, 113 µmol) in toluene (10 mL) was vigorously stirred for 48 h at RT. The suspension was filtered and the residue extracted with CH_2Cl_2 (*ca*. 50 mL). The combined filtrates were reduced to dryness to afford the product as a yellow powder. Yield: 69.3 mg (64%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.86 (t, $^{3}J_{HH}$ = 7.6, 1H, py), 7.66 – 7.78 (m, 8H, Ar^{F}), 7.55 (br, 4H, Ar^{F}), 7.46 (d, $^{3}J_{HH}$ = 7.8, 2H, py), 7.11 (s, 2H, NCH), 7.02 (s, 2H, NCH), 5.21 (s, 4H, py$\underline{C}H_2$), 3.88 (s, 6H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 180.0 (s, NCN),* 162.2 (q, $^{1}J_{CB}$ = 50 Hz, Ar^{F}) 154.5 (s, py), 140.4 (s, py), 135.3 (s, Ar^{F}), 129.4 (qq, $^{2}J_{FC}$ = 32, $^{3}J_{CB}$ = 3, Ar^{F}), 125.2 (q, $^{1}J_{FC}$ = 271, Ar^{F}), 124.6 (s, py), 123.0 (s, NCH), 121.5 (s, NCH), 118.0 (sept., $^{3}J_{FC}$ = 4, Ar^{F}), 55.3 (s, py$\underline{C}H_2$), 39.4 (s, CH_3). * As a consequence of limited solubility in this solvent, location of this signal required an HMBC experiment.

HR ESI-MS (positive ion, 4 kV): 330.0781 ([*M*]$^{+}$, calcd 330.0774) *m/z*.

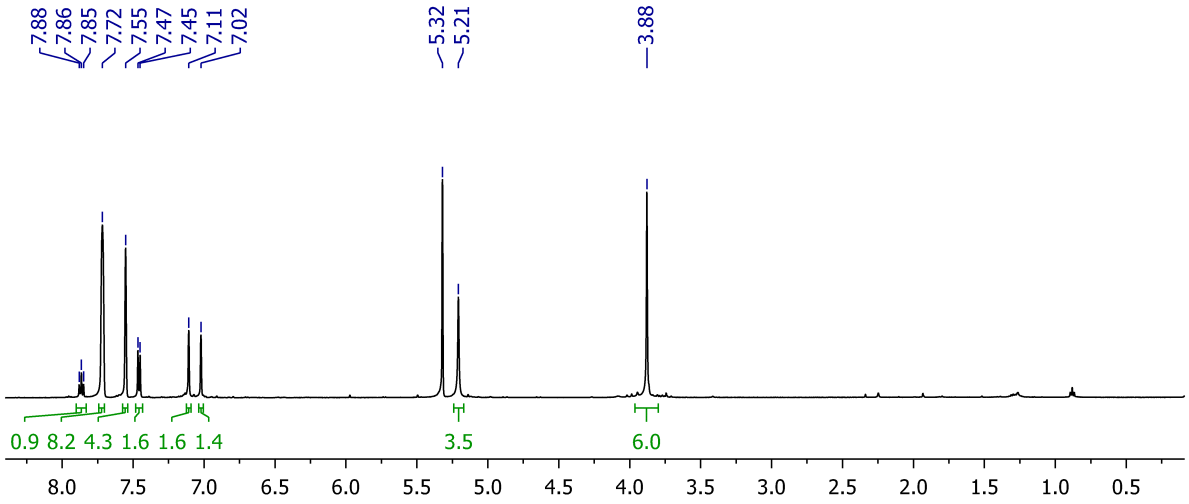


Figure S4: ^{1}H NMR spectrum of [Cu(CNC-Me)][BAr$^{F}_{4}$] (CD_2Cl_2, 500 MHz)

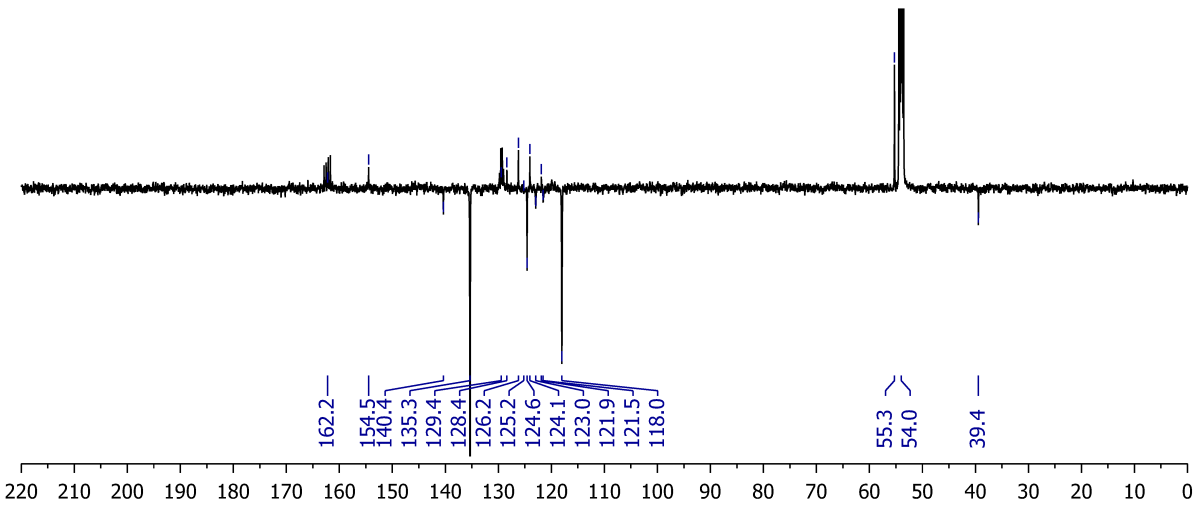


Figure S5: ^{13}C{^{1}H} APT NMR spectrum of [Cu(CNC-Me)][BAr$^{F}_{4}$] (CD_2Cl_2, 126 MHz)

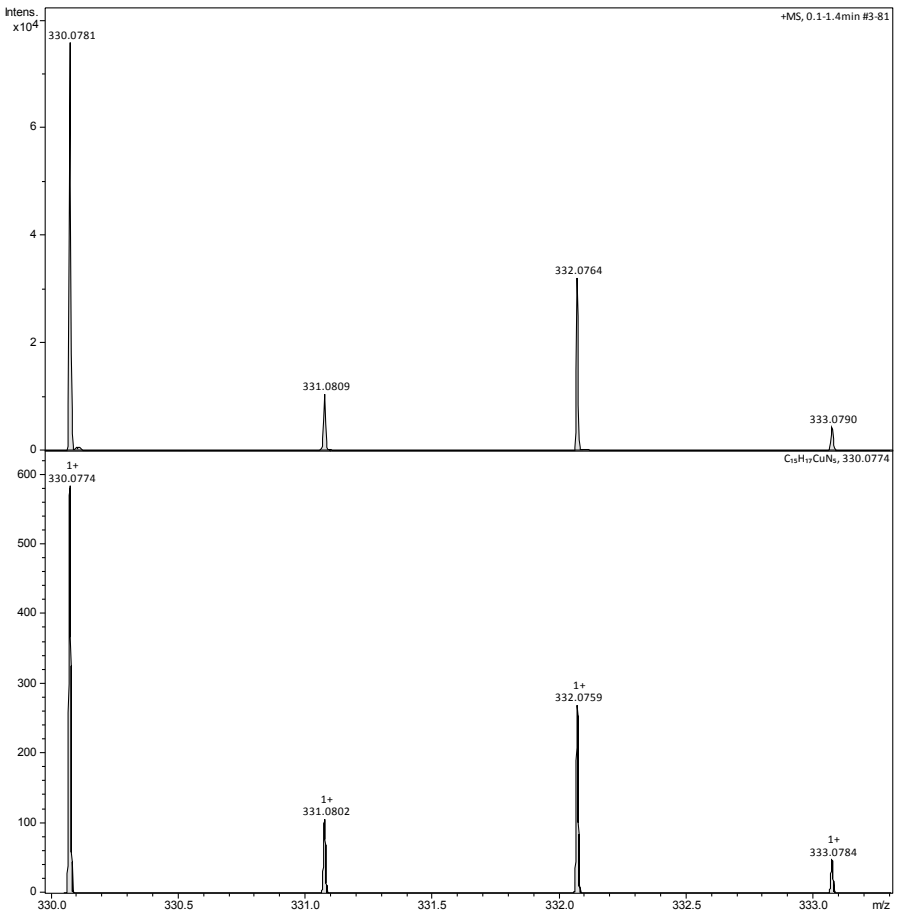


Figure S6: HR ESI-MS spectrum of [Cu(CNC-Me)][BAr$^{F}_{4}$]

2.3 [Rh(CNC-Me)(C_2H_4)][BAr^F_4] 1

A solution of $[Rh(C_2H_4)_2Cl]_2$ (14.0 mg, 36.0 µmol) in fluorobenzene (2 mL) was added to a solution of [Cu(CNC-Me)][BAr^F_4] (73.3 mg, 61.4 µmol) in fluorobenzene (1 mL). The resulting red suspension was stirred for 1 h at RT, filtered, and the resulting solution layered with excess hexane (*ca*. 20 mL). The product was obtained as red crystals on diffusion at −30 °C. Yield: 74.8 mg (97%). Crystals suitable for X-ray diffraction were grown from Et_2O/pentane at RT.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.79 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.70 – 7.74 (m, 8H, Ar^F), 7.55 (br, 4H, Ar^F), 7.44 (d, $^3J_{HH}$ = 7.7, 2H, py), 7.04 (d, $^3J_{HH}$ = 1.8, 2H, NCH), 6.73 (d, $^3J_{HH}$ = 1.8, 2H, NCH), 5.74 (br, 2H, py$\underline{CH_2}$), 5.04 (br, 2H, py$\underline{CH_2}$), 3.49 (br, 4H, C_2H_4), 3.46 (s, 6H, NCH_3).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 184.8 (d, $^1J_{RhC}$ = 40, NCN), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 155.9 (s, py), 139.4 (s, py), 135.3 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 125.2 (q, $^1J_{FC}$ = 271, Ar^F), 124.0 (s, py), 122.9 (s, NCH), 120.8 (s, NCH), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F), 56.2 (d, $^3J_{RhC}$ = 2, py$\underline{CH_2}$), 36.5 (s, NCH_3). The C_2H_4 resonance could not be unambiguously located, presumably as it is too broad to be observed at this temperature.

HR ESI-MS (positive ion, 4 kV): 402.0424 ([*M*−C_2H_4+O_2]$^+$, calcd 402.0796) *m/z*.

Anal. Calcd for $C_{49}H_{33}BF_{24}N_5Rh$ (1261.52 g·mol^{-1}): C, 46.65; H, 2.64; N, 5.55. Found: C, 46.72; H, 2.69; N, 5.61).

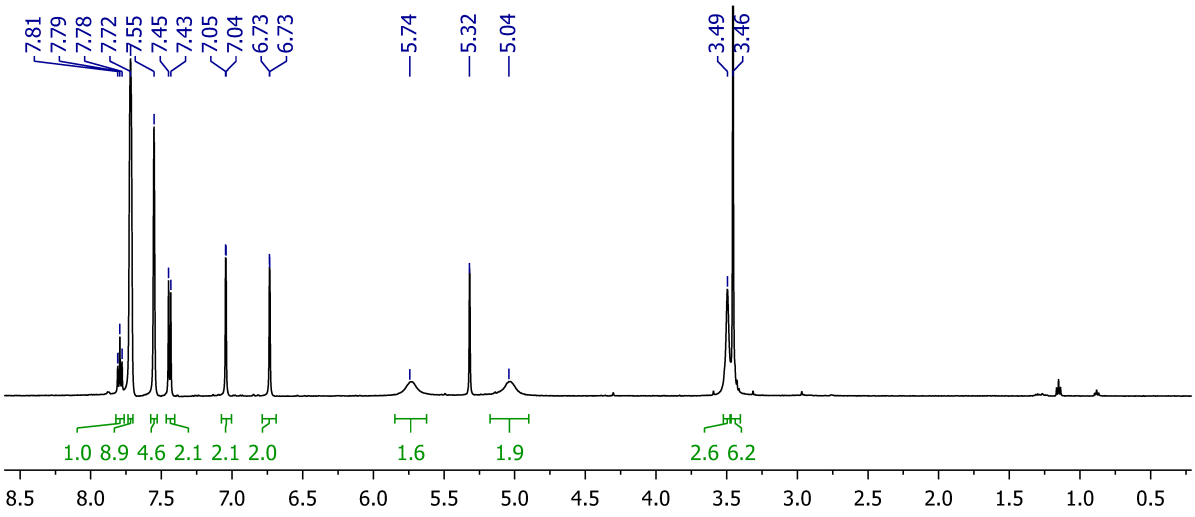


Figure S7: ^{1}H NMR spectrum of [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** (CD_2Cl_2, 500 MHz)

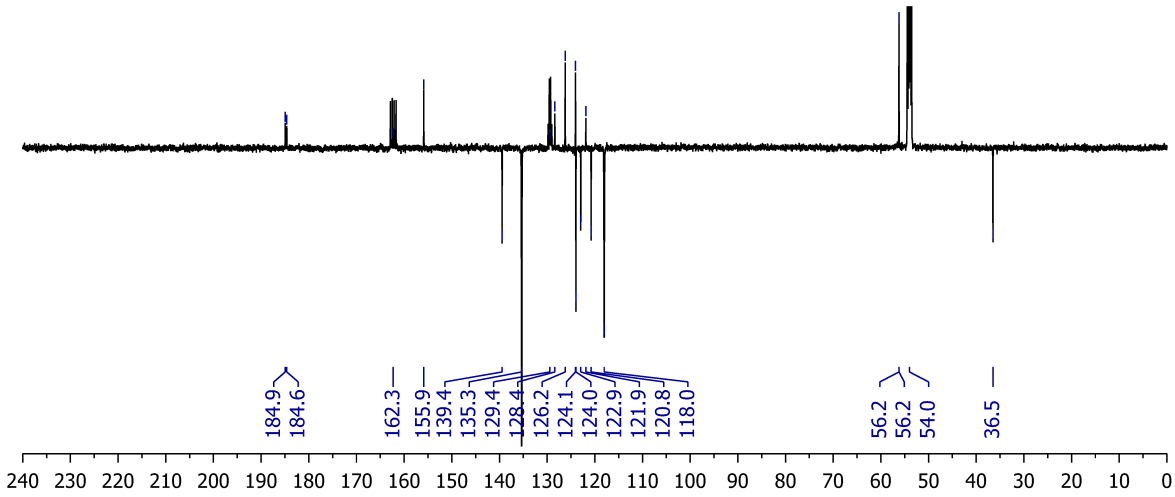


Figure S8: $^{13}C\{^{1}H\}$ NMR APT spectrum of [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** (CD_2Cl_2, 126 MHz)

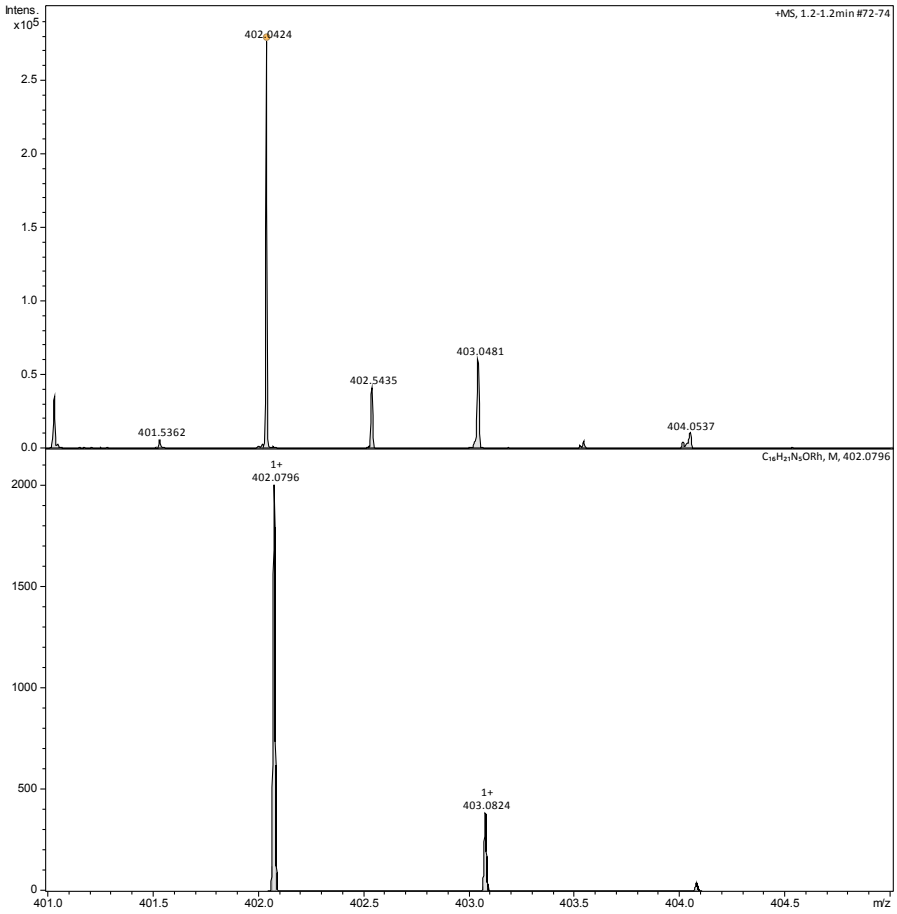
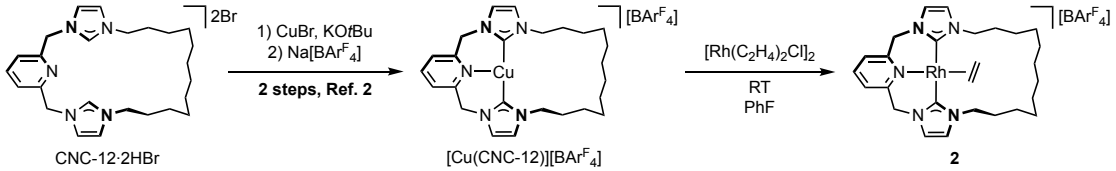


Figure S9: HR ESI-MS spectrum of [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1**

3 Preparation of [Rh(CNC-12)(C_2H_4)][BAr^F_4] 2

Scheme S2: Preparation of **2** from CNC-12·2HBr



3.1 [Cu(CNC-12)][BAr^F_4]

Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/hexane at –25 °C. This is a polymorph of the previously reported structure,[2] notable for the presence of only one unique cation/anion pair in the asymmetric unit.

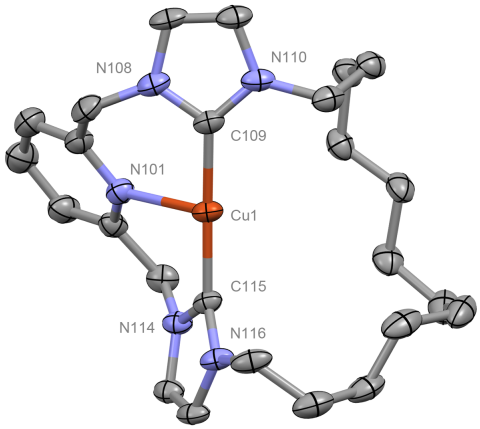


Figure S10: Solid-state structure of [Cu(CNC-12)][BAr^F_4]. Thermal ellipsoids drawn at 30% probability level; anion, CH_2Cl_2 solvent, and hydrogen atoms omitted for clarity. Selected data: Cu1–N101, 2.245(3) Å; Cu1–C109, 1.907(4) Å; Cu1–C115, 1.898(3) Å; C109–Cu1–C115, 176.3(2)°.

3.2 [Rh(CNC-12)(C_2H_4)][BAr^F_4] 2

A solution of $[Rh(C_2H_4)_2Cl]_2$ (46.1 mg, 119 µmol) in fluorobenzene (7 mL) was added to a solution of [Cu(CNC-12)][BAr^F_4] (263 mg, 197 µmol) in fluorobenzene (5 mL). The resulting red suspension was stirred for 1 h at RT, filtered, and the solution layered with excess hexane (*ca*. 50 mL). The product was obtained as red crystals on diffusion at −30 °C. Yield: 239 mg (87%). Crystals grown in this way were suitable for analysis by X-ray diffraction.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.83 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.67 – 7.77 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 7.48 (d, $^3J_{HH}$ = 7.7, 2H, py), 7.05 (d, $^3J_{HH}$ = 2.0, 2H, NCH), 6.78 (d, $^3J_{HH}$ = 2.0, 2H, NCH), 5.32 (vbr, fwhm = 125 Hz, 4H, pyCH_2), 3.76 (dd, $^3J_{HH}$ = 8.8, 7.6, 4H, NCH_2), 3.41 (s, 4H, C_2H_4), 1.79 (br, 4H, CH_2), 1.19 – 1.56 (m, 16H, CH_2).
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 181.9 (d, $^1J_{RhC}$ = 41, NCN), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 155.8 (s, py), 139.8 (s, py), 135.4 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 125.2 (q, $^1J_{FC}$ = 271, Ar^F), 124.1 (s, py), 121.7 (s, NCH),

121.4 (s, NCH), 118.0 (sept., $^{3}J_{FC}$ = 4, Ar^{F}), 56.3 (s, py$\underline{C}H_2$), 49.9 (s, CH_2), 47.0 (s, C_2H_4), 31.5 (s, CH_2), 28.9 (s, CH_2), 27.6 (s, CH_2), 27.6 (s, CH_2), 24.4 (s, CH_2).

HR ESI-MS (positive ion, 4 kV): 508.1935 (100%, $[M-C_2H_4]^+$, calcd 508.1942), 540.1835 (30%, $[M-C_2H_4+O_2]^+$, calcd 540.1840) *m/z*.

Despite multiple attempts, satisfactory microanalysis data could not be obtained for this compound. Data is consistent with partial loss/substitution of ethylene during the analysis.

Anal. Calcd for $C_{59}H_{51}BF_{24}N_5Rh$ (1399.77 g·mol^{-1}): C, 50.63; H, 3.67; N, 5.00. Calcd for $C_{59}H_{51}BF_{24}N_5Rh - C_2H_4$ (1371.72 g·mol^{-1}): C, 49.91; H, 3.45; N, 5.11. Calcd for $C_{59}H_{51}BF_{24}N_5Rh - C_2H_4 + O_2$ (1403.71 g·mol^{-1}): C, 48.77; H, 3.38; N, 4.99. Found: C, 50.15; H, 3.62; N, 4.88.

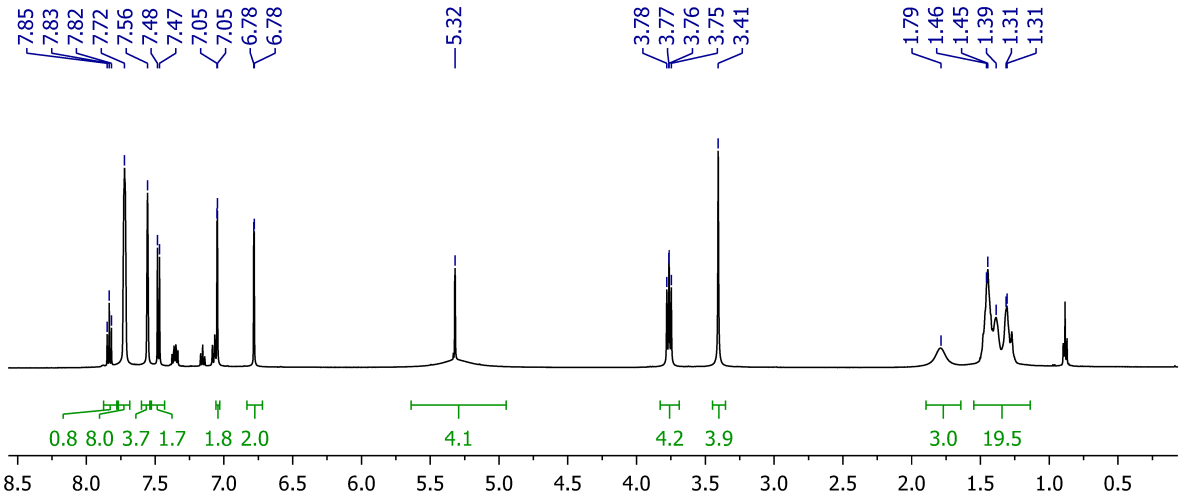


Figure S11: ^{1}H NMR spectrum of [Rh(CNC-12)(C_2H_4)][BAr^{F}_4] **2** (CD_2Cl_2, 500 MHz)

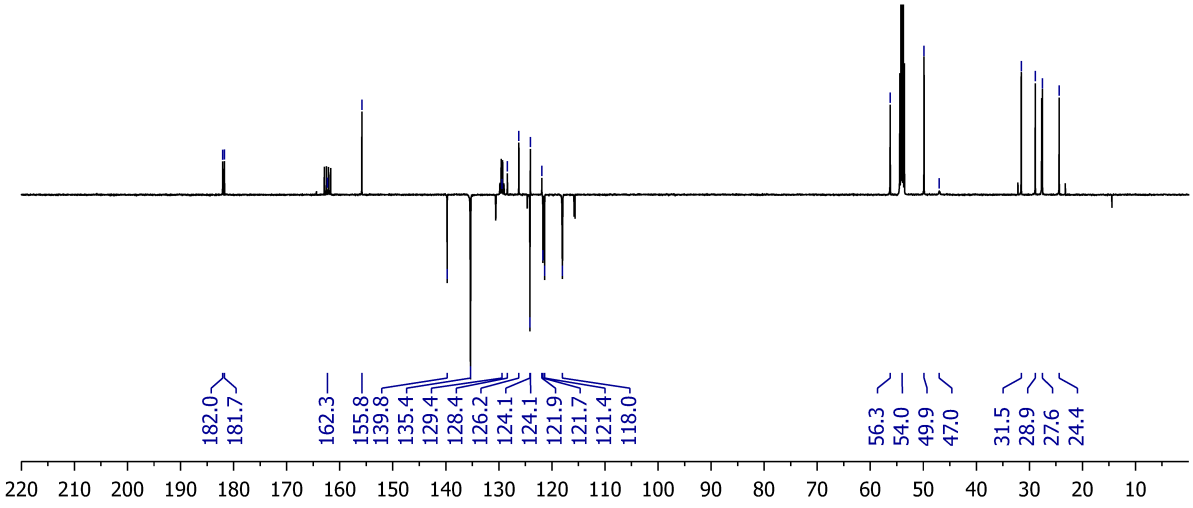


Figure S12: $^{13}C\{^{1}H\}$ APT NMR spectrum of [Rh(CNC-12)(C_2H_4)][BAr^{F}_4] **2** (CD_2Cl_2, 126 MHz)

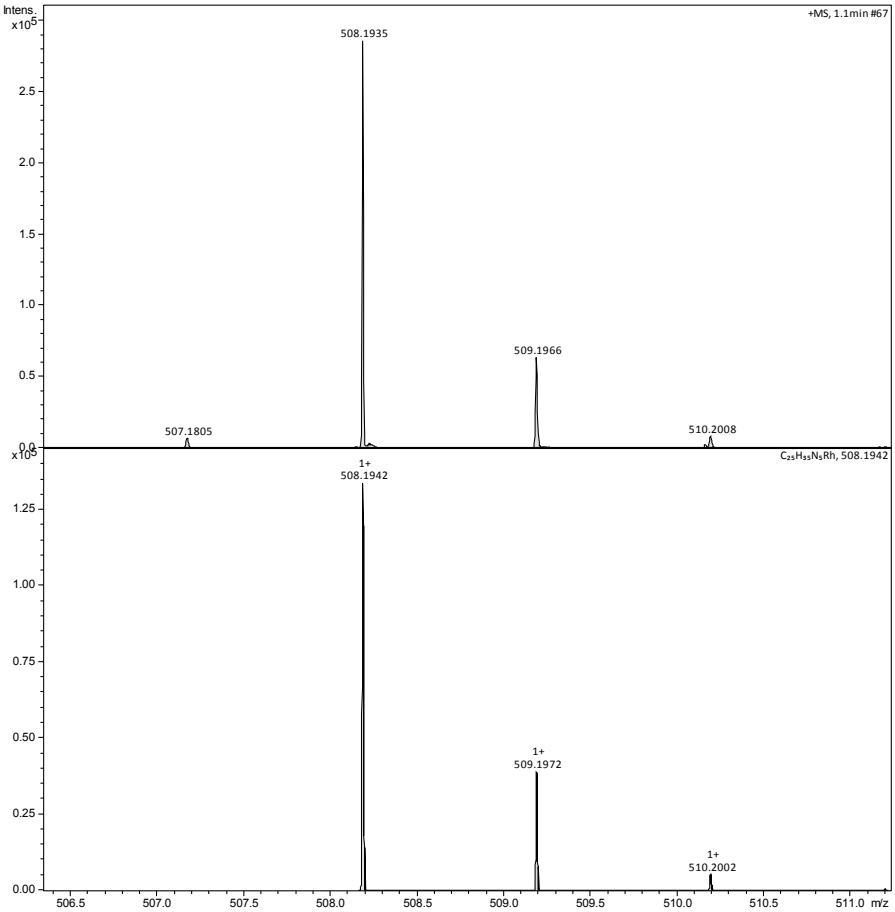


Figure S13: HR ESI-MS spectrum of [Rh(CNC-12)(C_2H_4)][BAr^F_4] **2**

4 Preparation of [Rh(CNC-Me)(CO)][BAr^F_4] 3

A solution of [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** (13.1 mg, 10.4 µmol) in CD_2Cl_2 (0.5 mL) was freeze-pump-thaw degassed and placed under an atmosphere of CO (1 atm). The resulting yellow solution was concentrated to dryness *in vacuo* to afford the product as a bright yellow powder. Yield: 13.0 mg (99%). Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/pentane at RT.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.87 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.67 – 7.77 (m, 8H, Ar^F), 7.55 (s, 4H, Ar^F), 7.50 (d, $^3J_{HH}$ = 7.7, 2H, py), 7.13 (d, $^3J_{HH}$ = 1.9, 2H, NCH), 6.97 (d, $^3J_{HH}$ = 1.8, 2H, NCH), 5.46 (br, 2H, py$C\underline{H}_2$), 5.06 (br, 2H, py$C\underline{H}_2$), 3.83 (s, 6H, NCH_3).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 193.6 (d, $^1J_{RhC}$ = 80, CO), 182.9 (d, $^1J_{RhC}$ = 42, NCN), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 156.0 (s, py), 141.5 (s, py), 135.4 (s, Ar^F), 129.6 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 125.2 (q, $^1J_{FC}$ = 271, Ar^F), 124.9 (s, py), 122.7 (s, NCH), 121.7 (s, NCH), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F), 55.8 (d, $^3J_{RhC}$ = 2, py$\underline{C}H_2$), 38.4 (s, NCH_3).

HR ESI-MS (positive ion, 4 kV): 398.0495 ([*M*]$^+$, calcd 398.0483) *m/z*.

Anal. Calcd for $C_{48}H_{29}BF_{24}N_5ORh$ (1261.47 g·mol^{-1}): C, 45.70; H, 2.32; N, 5.55. Found: C, 45.59; H, 2.37; N, 5.67).

IR (CH_2Cl_2): ν(CO) 1980 cm^{-1}.

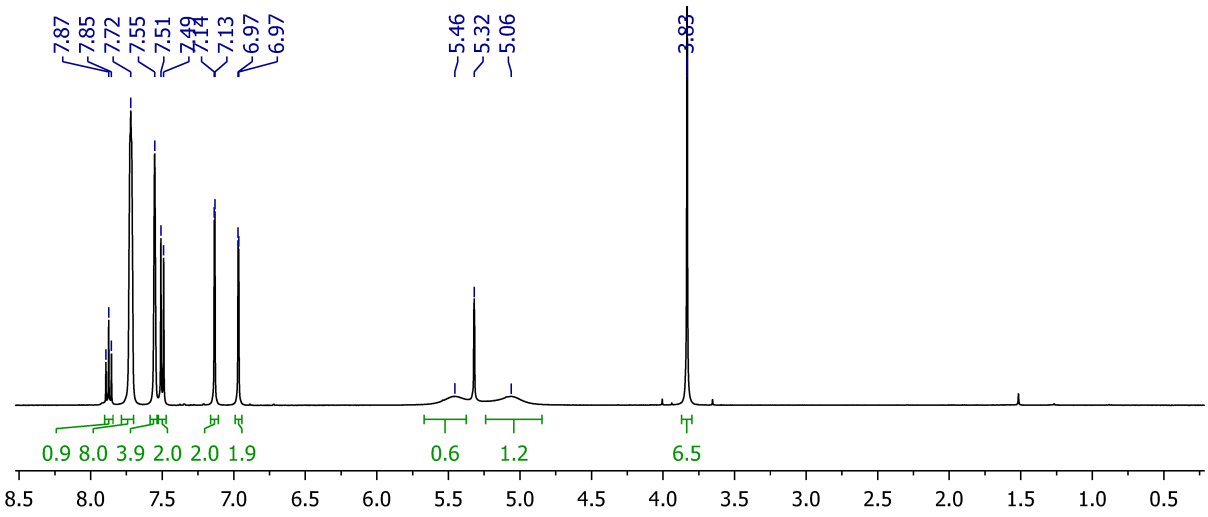


Figure S14: ^{1}H NMR spectrum of [Rh(CNC-Me)(CO)][BAr$^{F}_{4}$] **3** (CD_2Cl_2, 400 MHz)

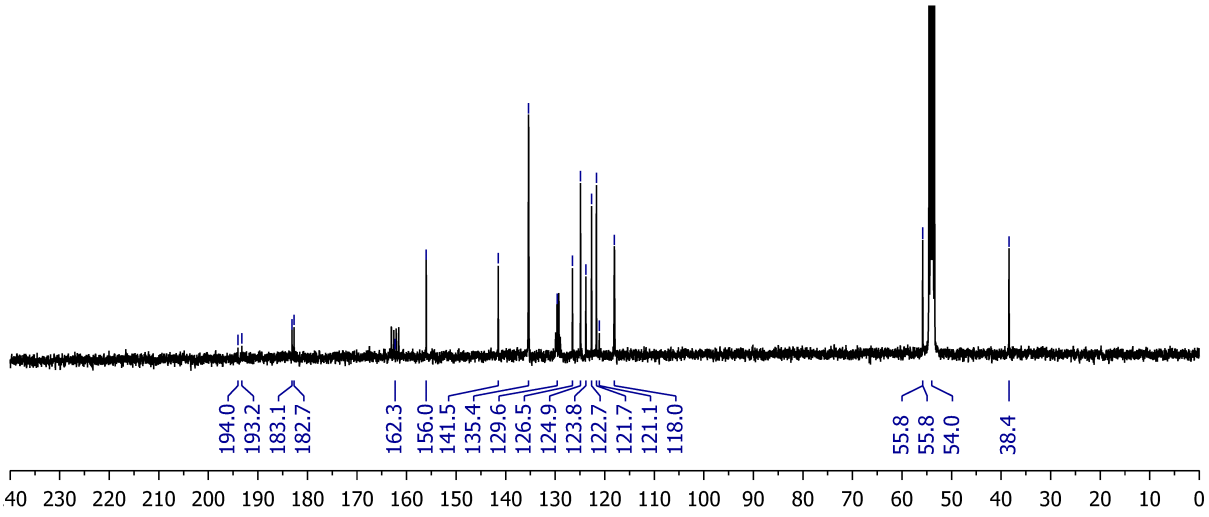


Figure S15: ^{13}C{^{1}H} NMR spectrum of [Rh(CNC-Me)(CO)][BAr$^{F}_{4}$] **3** (CD_2Cl_2, 101 MHz)

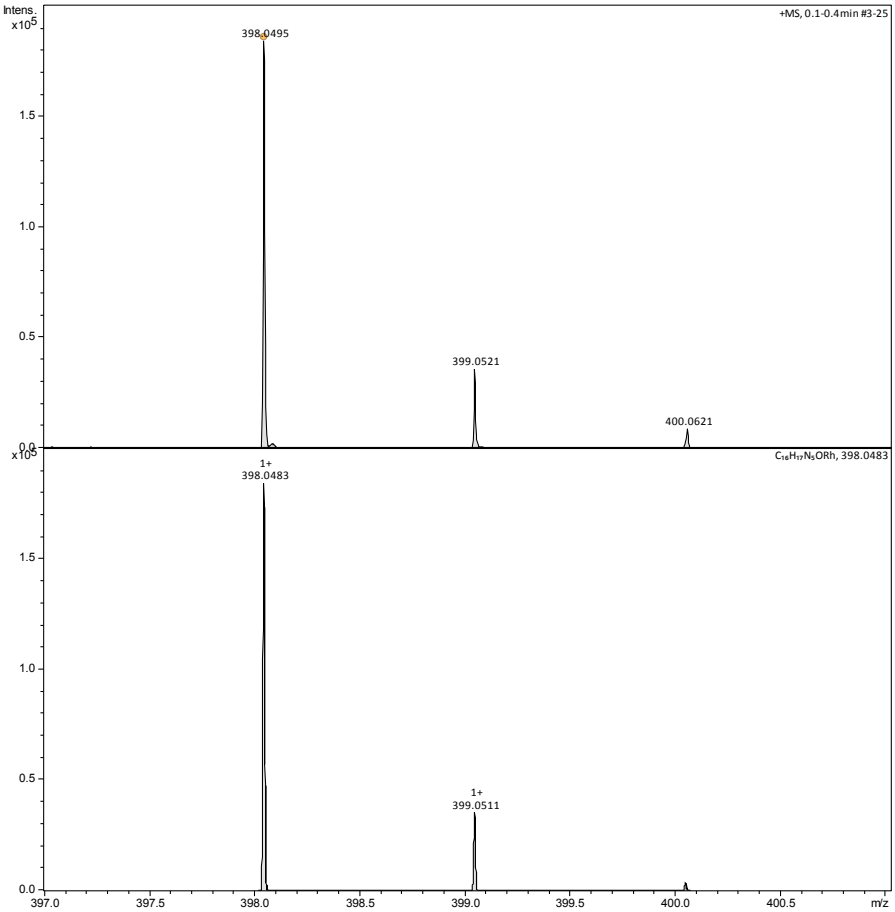


Figure S16: HR ESI-MS spectrum of [Rh(CNC-Me)(CO)][BAr^F_4] **3**

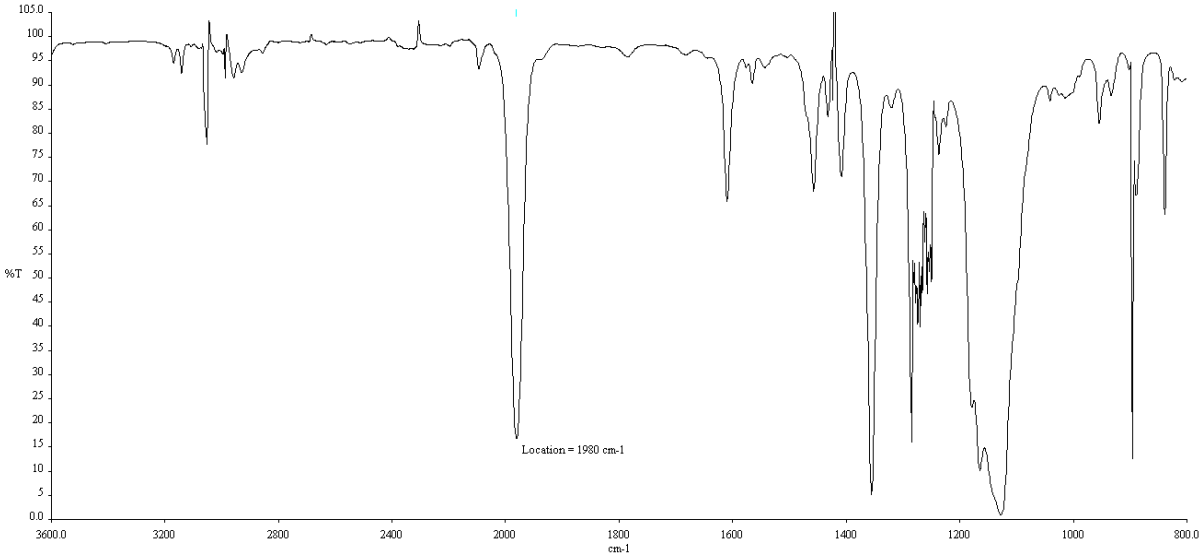


Figure S17: FT-IR spectrum of [Rh(CNC-Me)(CO)][BAr^F_4] **3** (CH_2Cl_2, 293 K).

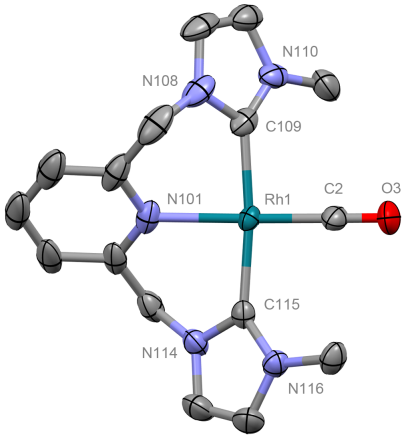


Figure S18: Solid-state structure of [Rh(CNC-Me)(CO)][BAr^F_4] **3**. Thermal ellipsoids drawn at 50% probability level; anion and hydrogen atoms omitted for clarity. Selected data: Rh1–C2, 1.809(3) Å; C2–O3, 1.145(4) Å; Rh1–N101, 2.140(2) Å; Rh1–C109, 2.039(3) Å; Rh1–C115, 2.031(3) Å; N101–Rh1–C2, 179.0(1)°; C109–Rh1–C115, 172.9(1)°.

5 Preparation of [Rh(CNC-12)(CO)][BAr^F_4] 4

A solution of [Rh(CNC-12)(C_2H_4)][BAr^F_4] **2** (14.1 mg, 10.1 µmol) in CD_2Cl_2 (0.5 mL) was freeze-pump-thaw degassed and placed under an atmosphere of CO (1 atm). The resulting yellow solution was concentrated to dryness *in vacuo* to afford the product as a bright yellow powder. Yield: 13.2 mg (94%).

Characterisation data are in excellent agreement with that previously reported for this compound, prepared alternatively using a Ag_2O-based transmetallation strategy employing CNC-12·2HBr, Na[BAr^F_4] and [$Rh(CO)_2Cl]_2$.[6]

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.89 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.67 – 7.78 (m, 8H, Ar^F), 7.55 (s, 4H, Ar^F), 7.51 (d, $^3J_{HH}$ = 7.7, 2H, py), 7.14 (d, $^3J_{HH}$ = 1.9, 2H, NCH), 7.01 (d, $^3J_{HH}$ = 1.9, 2H, NCH), 5.45 (d, $^2J_{HH}$ = 14.9, 2H, py$C\underline{H}_2$), 5.03 (d, $^2J_{HH}$ = 14.9, 2H, py$C\underline{H}_2$), 4.30 (br, 2H, NCH_2), 3.99 (br, 2H, NCH_2), 1.93 (br, 2H, CH_2), 1.84 (br, 2H, CH_2), 1.10 – 1.54 (m, 16H, CH_2).

LR ESI-MS (positive ion, 4 kV): 536.3 ([*M*]$^+$, calcd 536.2) *m/z*.

IR (CH_2Cl_2): ν(CO) 1978 cm^{-1}.

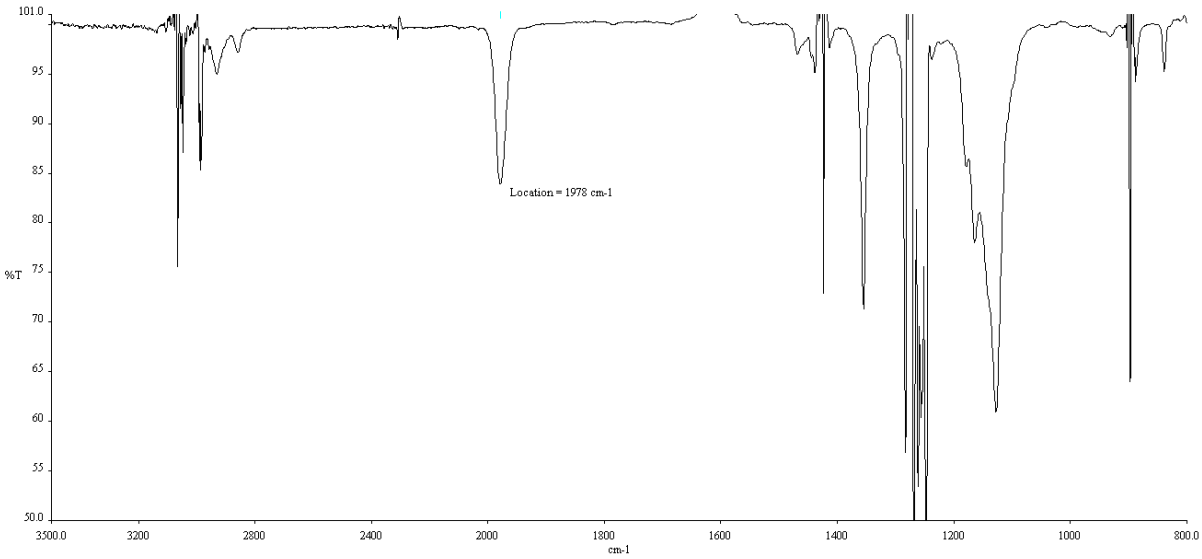


Figure S19: FT-IR spectrum of [Rh(CNC-12)(CO)][BAr^F_4] **4** (CH_2Cl_2, 293 K).

6 Preparation of [Rh(CNC-Me)($SOMe_2$)][BAr^F_4] 5

DMSO (1.24 µL, 17.5 µmol) was added to a stirred solution of [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** (19.8 mg, 15.7 µmol) in CH_2Cl_2 (*ca.* 2 mL) at RT. After 30 min, the orange solution was concentrated to dryness and the residue washed with hexane (*ca.* 5 mL). Subsequent recrystallisation of this crude material from CH_2Cl_2/hexane afforded the product as a red crystalline solid. Yield: 15.9 mg (77%). Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/pentane at RT.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.67 – 7.77 (m, 8H, Ar^F), 7.69 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.55 (s, 4H, Ar^F), 7.33 (d, $^3J_{HH}$ = 7.7, 2H, py), 7.08 (d, $^3J_{HH}$ = 1.9, 2H, NCH), 6.81 (d, $^3J_{HH}$ = 1.8, 2H, NCH), 5.87 (br, 2H, py$C\underline{H}_2$), 4.95 (br, 2H, py$C\underline{H}_2$), 3.83 (s, 6H, NCH_3), 3.15 (br d, $^3J_{RhH}$ = 25, 6H, SCH_3).
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 186.7 (d, $^1J_{RhC}$ = 45, NCN), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 157.7 (s, py), 139.4 (s, py), 135.3 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 125.1 (q, $^1J_{FC}$ = 271, Ar^F), 123.3 (s, py), 123.1 (s, NCH), 121.9 (s, NCH), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F), 56.4 (d, $^3J_{RhC}$ = 2, py$\underline{C}H_2$), 52.8 (br d, $^2J_{RhC}$ = 30, SCH_3) 39.0 (s, NCH_3).
Anal. Calcd for $C_{49}H_{35}BF_{24}N_5ORhS$ (1311.13 g·mol^{-1}): C, 44.87; H, 2.69; N, 5.34. Found: C, 44.81; H, 2.82; N, 5.22).

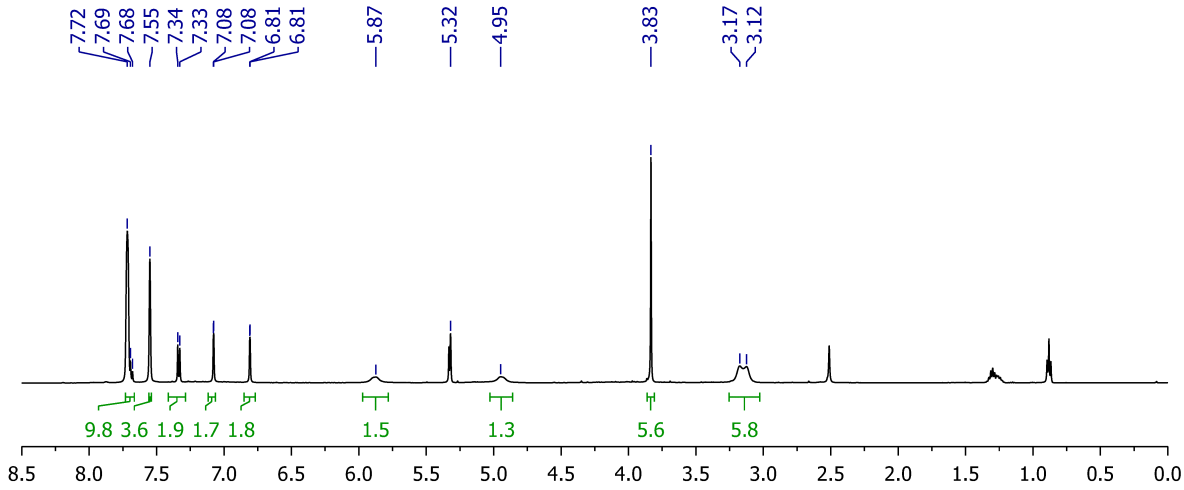


Figure S20: ^{1}H NMR spectrum of [Rh(CNC-Me)(SOMe$_2$)][BAr$^F_4$] **5** (CD_2Cl_2, 500 MHz)

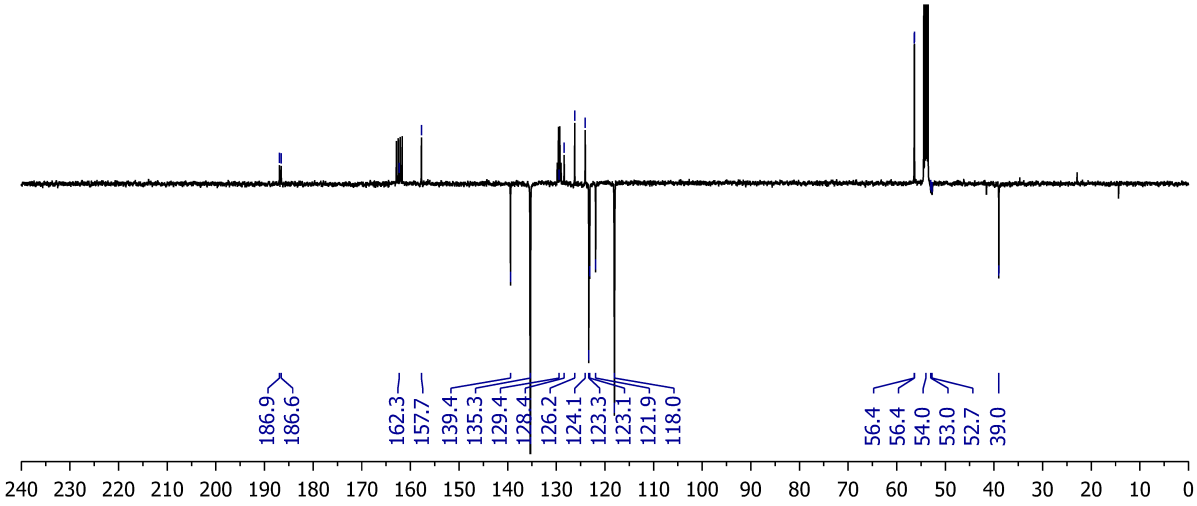


Figure S21: $^{13}C\{^{1}H\}$ APT NMR spectrum of [Rh(CNC-Me)(SOMe$_2$)][BAr$^F_4$] **5** (CD_2Cl_2, 126 MHz)

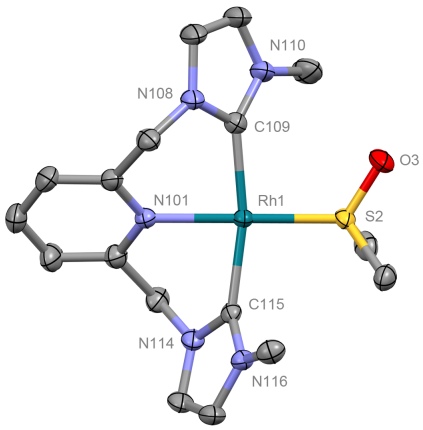


Figure S22: Solid-state structure of [Rh(CNC-Me)(SOMe$_2$)][BAr$^F_4$] **5**. Thermal ellipsoids drawn at 50% probability level; anion and hydrogen atoms omitted for clarity. Selected data: Rh1–S2, 2.1773(5) Å; Rh1–N101, 2.088(2) Å; Rh1–C109, 2.035(2) Å; Rh1–C115, 2.037(2) Å; N101–Rh1–S2, 173.99(5)°; C109–Rh1–C115, 167.42(8)°.

7 NMR scale reactions of [Rh(CNC-Me)L][BAr^F_4] (L = C_2H_4, 1; $SOMe_2$, 5) with HC≡CAr'

7.1 Kinetic studies using [Rh(CNC-Me)(C_2H_4)][BAr^F_4] 1

Variable concentration data:

Solutions of [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** (5 or 10 mmolL^{-1}) and HC≡CAr' (50 or 100 mmolL^{-1}) in CD_2Cl_2 (*ca.* 0.5 mL) were prepared in J. Young's valve NMR tubes at RT and then held at –78 °C until being placed into a NMR spectrometer pre-equilibrated to 298 K and then monitored by ^{1}H NMR spectroscopy (400 MHz, Figure S23).

Analysis of the resulting time-course data through integration of the HC≡CAr' resonance indicated the reaction was zero order in alkyne and first order in catalyst (Table S1). Slight deviation from linear [HC≡CAr'] dependence was noted over extended reaction times, which we attribute to non-negligible catalyst decomposition. This effect was deconvoluted by modelling the data over a reduced time period, as indicated in Figure S23.

Rate law: $-\frac{1}{2}\,d[HC{\equiv}CAr']/dt = d[Ar'CCC(CH_2)Ar']/dt = k[\text{catalyst}]$

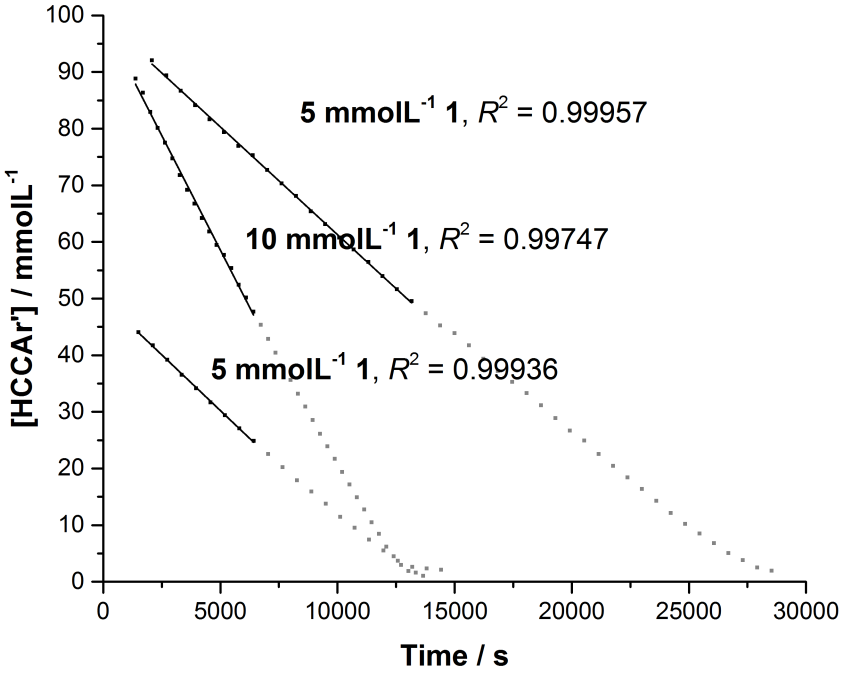


Figure S23: Kinetic data for the homocoupling of HC≡CAr' (50/100 mmolL^{-1}) catalysed by [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** (5/10 mmolL^{-1}) in CD_2Cl_2 at 298 K. Grey points are not included in the fit.

Table S1: Kinetic parameters for the homocoupling of HC≡CAr'.

Catalyst	[catalyst] / mmolL^{-1}	[HC≡CAr'] / mmolL^{-1}	T / K	R^2 (fit)	k / 10^{-5} s^{-1}	$t_{1/2}$ / h
1	5[a]	100	298	0.99954	38	4
1	5[a]	50	298	0.99927	39	4
1	10[a]	100	298	0.99747	40	2
1	5[b]	100	288	0.99023	8.7 ± 0.2	16.1
1	5[b]	100	293	0.99933	17.20 ± 0.09	8.1
1	5[b]	100	298	0.99894	32.9 ± 0.2	4.2
1	5[b]	100	303	0.99881	65.7 ± 0.5	2.1
1	5[b]	100	308	0.99922	129.7 ± 0.8	1.1
5	5[a]	100	298	0.98729	4	36

[a] Samples prepared with low precision. [b] Samples prepared with high precision

Variable temperature data:

To a chilled flask charged with [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** (18.9 mg, 15.0 µmol) and HC≡CAr' (64.2 mg, 298 µmol) was added chilled CD_2Cl_2 (3.0 mL) in an inert atmosphere glove box. The resulting solution was partitioned into chilled J. Young's valve NMR tubes (0.5 mL / tube), which were sealed and immediately frozen in liquid nitrogen. The samples were then individually thawed and placed into a NMR spectrometer pre-equilibrated to the required temperature and monitored by ^{1}H NMR spectroscopy (600 MHz, 288 – 308 K, Figures S24 – 26).

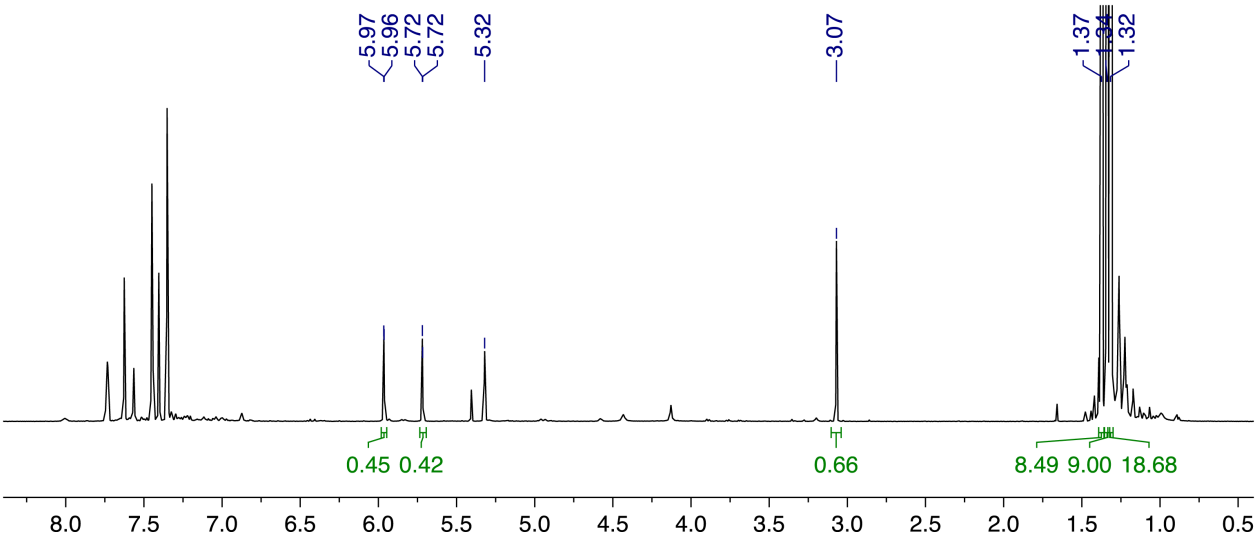


Figure S24: ^{1}H NMR spectrum collected during the homocoupling of HC≡CAr' (100 mmolL^{-1}) catalysed by [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** (5 mmolL^{-1}) in CD_2Cl_2 at 298 K (t = 4.4 h, *ca.* 50% conversion, 600 MHz).

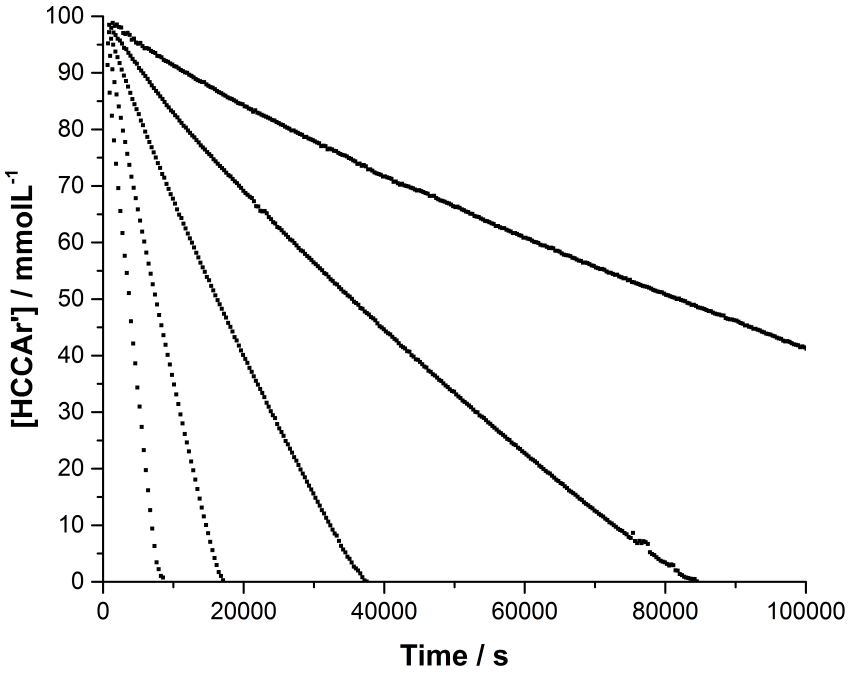


Figure S25: Kinetic data collected for the homocoupling of HC≡CAr' (100 mmolL^{-1}) catalysed by [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** (5 mmolL^{-1}) in CD_2Cl_2 at 288 – 308 K.

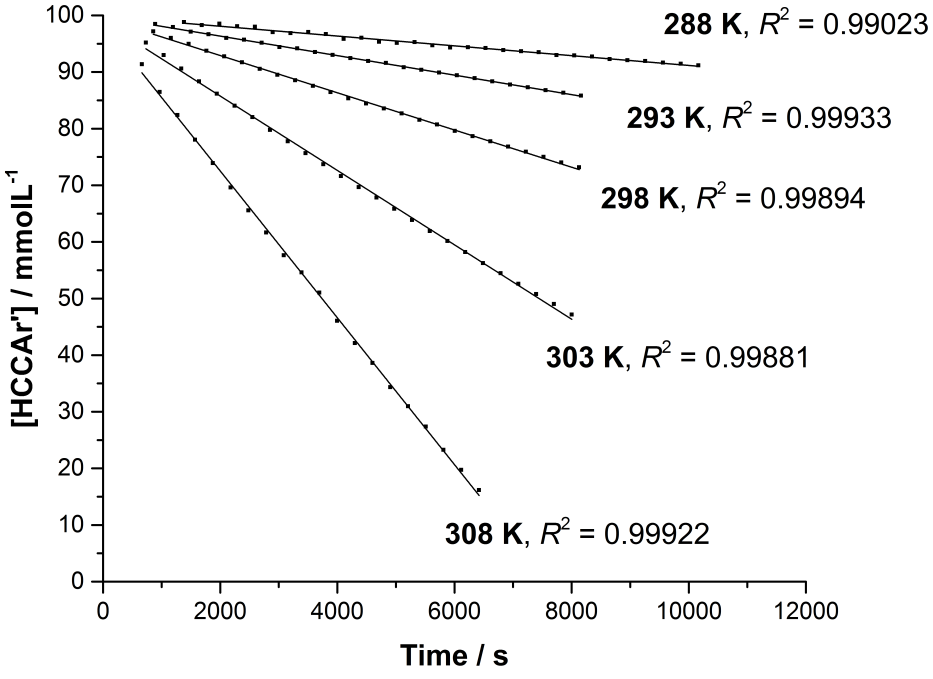


Figure S26: Fitted kinetic data for the homocoupling of HC≡CAr' (100 mmolL^{-1}) catalysed by [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** (5 mmolL^{-1}) in CD_2Cl_2 at 288 – 308 K.

The resulting time-course data was analysed through integration of the HC≡CAr' resonance to obtain the rate constants over the temperature range (Table S1). Slight deviation from linear [HC≡CAr'] dependence was noted over extended reaction times, which we attribute to non-negligible catalyst decomposition. This effect was deconvoluted by modelling the data over a reduced time period, as indicated in Figure S26. The corresponding activation parameters for the reaction were obtained using the Eyring equation (Figure S27).

Activation parameters: $\Delta G^{\ddagger}$ (298 K) = 93 ± 3 kJmol^{-1}

$\Delta H^{\ddagger}$ = 97 ± 1 kJmol^{-1}

$\Delta S^{\ddagger}$ = 15 ± 5 JK^{-1}mol^{-1}

R^2 (fit) = 0.99914

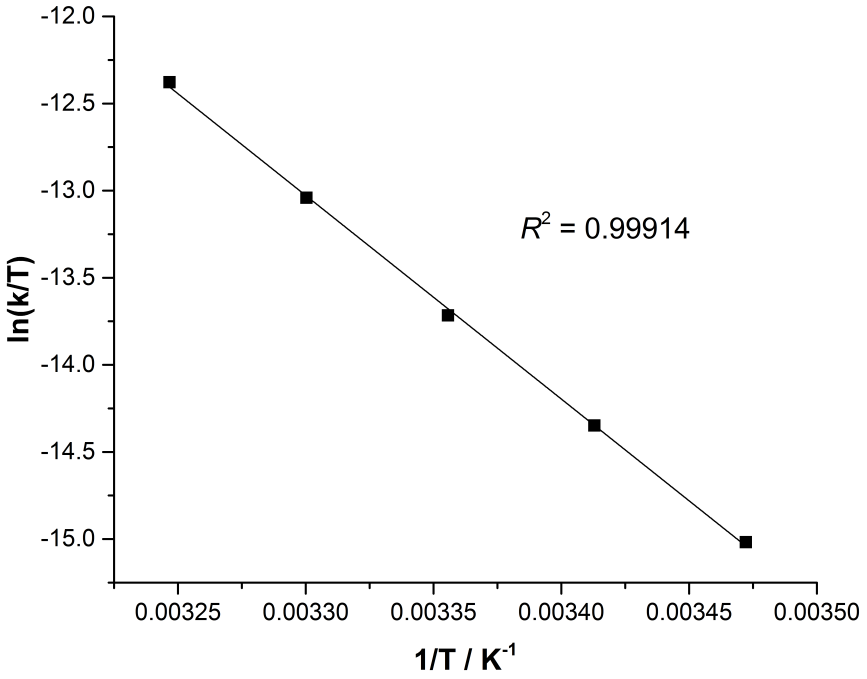


Figure S27: Eyring plot for the homocoupling of HC≡CAr' catalysed by [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** in CD_2Cl_2.

7.2 Isolation of Ar'CCC(CH_2)Ar'

A solution of [Rh(CNC-Me)(C_2H_4)][BAr^F_4] **1** (30.0 mg, 23.8 µmol) and HC≡CAr' (102 mg, 475 µmol) in CH_2Cl_2 (4.8 mL) was stirred at 25 °C for 6 h. The solution was freeze-pump-thaw degassed and placed under an atmosphere of CO (1 atm) to afford a yellow solution, which was concentrated to dryness and the residue extracted with hexane through a short plug of alumina. The hexane solution was stirred over KHMDS (30.0 mg, 150 µmol) for 3 h at RT. The resulting suspension was filtered and the filtrate washed with HCl (2 molL^{-1}, 3 × 15 mL) and water (3 × 15 mL) before being dried over $MgSO_4$. Concentration under reduced pressure gave the desired product as a pale yellow solid. Yield: 74.6 mg (73%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.62 (d, $^{4}J_{HH}$ = 1.6, 2H, *t*Bu$_2$C$_6$H$_3$), 7.42 – 7.46 (m, 2H, 2 × *t*Bu$_2$C$_6$H$_3$), 7.39 (d, $^{4}J_{HH}$ = 1.6, 2H, *t*Bu$_2$C$_6$H$_3$), 5.96 (s, 1H, CH_2), 5.71 (s, 1H, CH_2), 1.37 (s, 18H, *t*Bu), 1.33 (s, 18H, *t*Bu).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 151.6 (s, *t*Bu$_2$C$_6$H$_3$), 151.5 (s, *t*Bu$_2$C$_6$H$_3$), 137.2 (s, *t*Bu$_2$C$_6$H$_3$), 132.1 (s, C(CH_2)), 126.4 (s, *t*Bu$_2$C$_6$H$_3$), 123.6 (s, *t*Bu$_2$C$_6$H$_3$), 123.2 (s, *t*Bu$_2$C$_6$H$_3$), 122.7 (s, *t*Bu$_2$C$_6$H$_3$), 121.0 (s, *t*Bu$_2$C$_6$H$_3$), 119.8 (s, CH_2), 92.5(s, CCAr'), 88.4 (s, CCAr'), 35.4 (s, *t*Bu{C}), 35.3 (s, *t*Bu{C}), 31.8 (s, *t*Bu{CH_3}), 31.6 (s, *t*Bu{CH_3}).

HR ESI-MS (positive ion, 4 kV): 451.3341 ([*M*+Na]$^{+}$, calcd 451.3335) *m/z*.

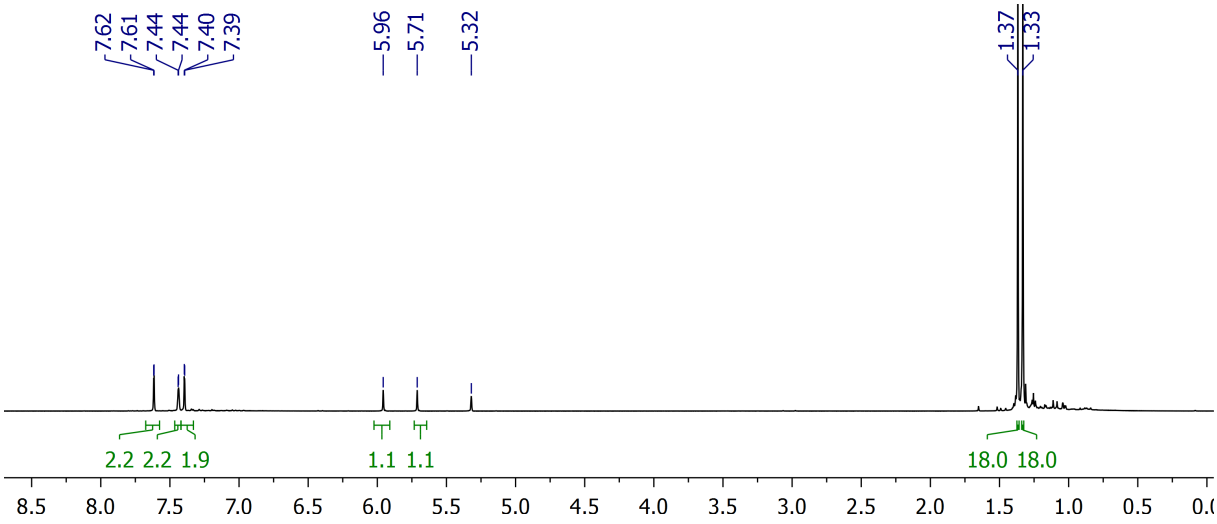


Figure S28: ^{1}H NMR spectrum of Ar'CCC(CH_2)Ar' (CD_2Cl_2, 500 MHz)

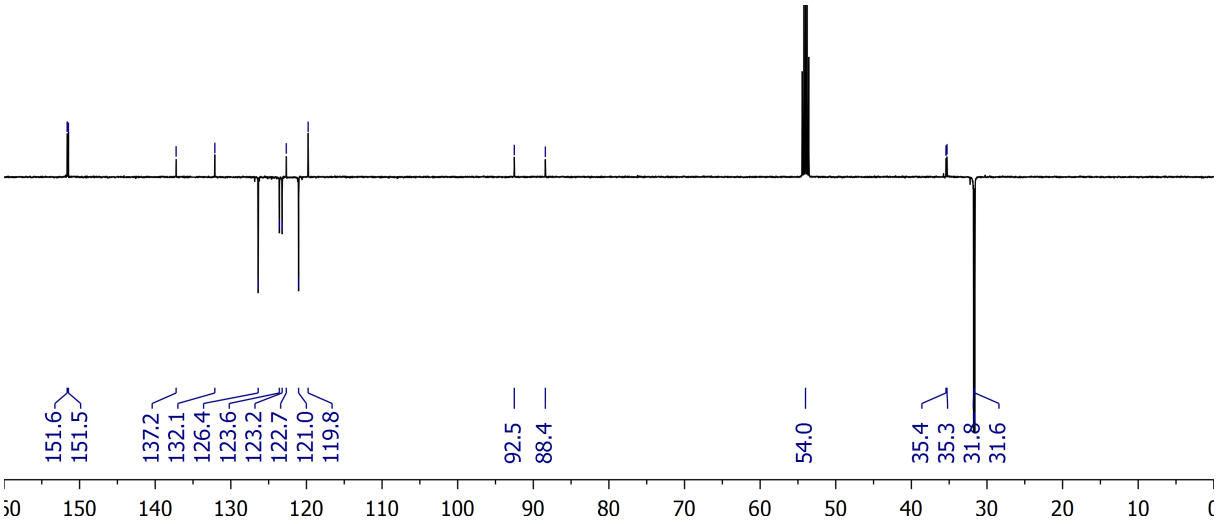


Figure S29: ^{13}C{^{1}H} APT NMR spectrum of Ar'CCC(CH_2)Ar' (CD_2Cl_2, 126 MHz)

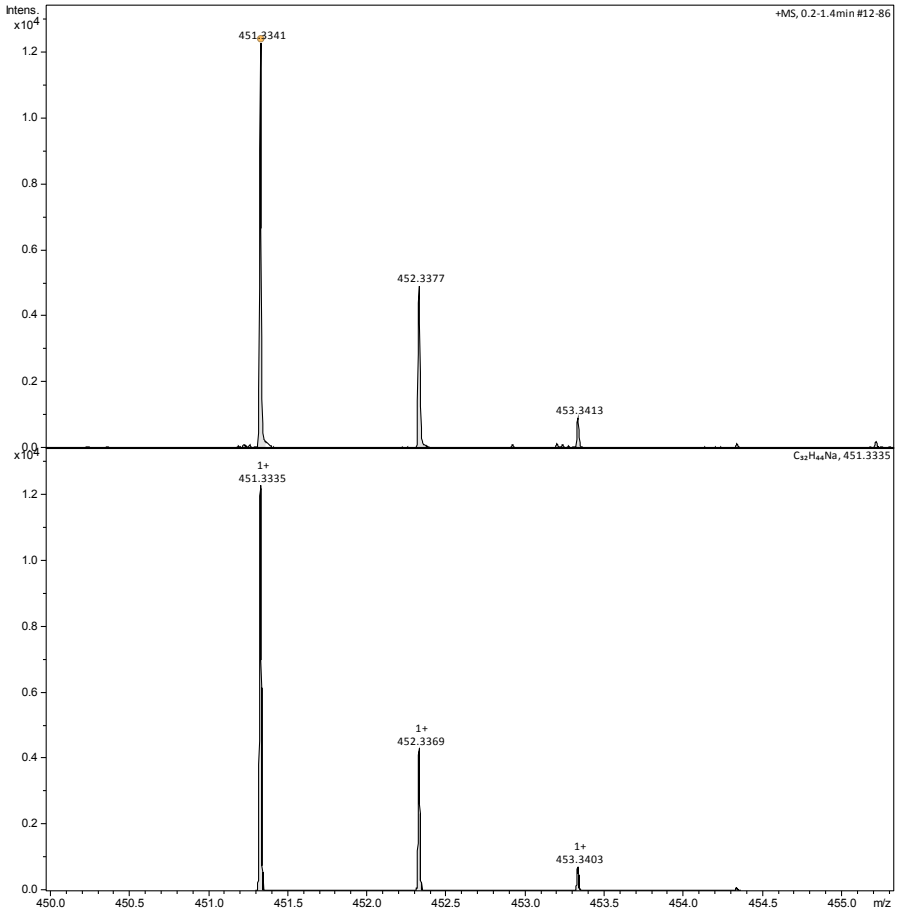


Figure S30: HR ESI-MS spectrum of Ar'CCC(CH_2)Ar'

7.3 Kinetic studies using [Rh(CNC-Me)($SOMe_2$)][BAr^F_4] 5

A solution of [Rh(CNC-Me)($SOMe_2$)][BAr^F_4] **5** (3.3 mg, 2.5 µmol) and HC≡CAr' (10.8 mg, 50.3 µmol) in CD_2Cl_2 (0.5 mL) was prepared in J. Young's valve NMR tubes at RT and then held at –78 °C until being placed into a NMR spectrometer pre-equilibrated to 298 K and then monitored by ^{1}H NMR spectroscopy (400 MHz, Figures S30 and 31).

The resulting time-course data was analysed through integration of the HC≡CAr' resonance to obtain the rate constant at 298 K (Table S1). During the period of the reaction monitored (*ca*. 15.5 h) a persistent organometallic intermediate corresponding to *ca.* 50 – 60% relative to [**5**]$_0$ was observed.

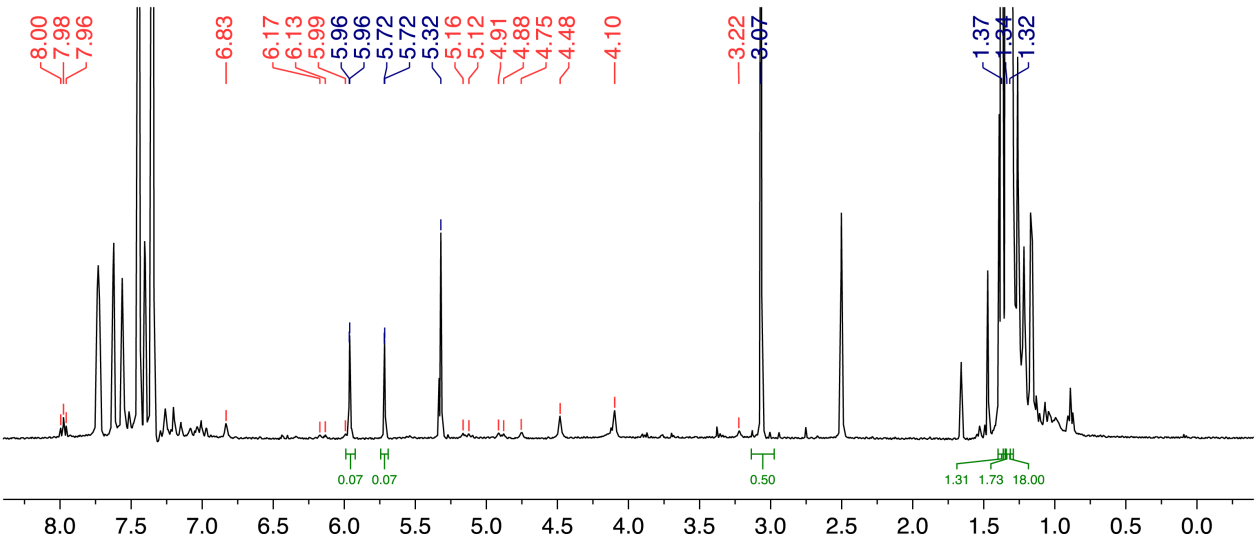


Figure S31: ^{1}H NMR spectrum collected during the homocoupling of HC≡CAr' (100 mmolL^{-1}) catalysed by [Rh(CNC-Me)(SOMe$_2$)][BAr$^F_4$] **5** (5 mmolL^{-1}) in CD_2Cl_2 at 298 K (*t* = 10.0 h, *ca.* 16% conversion, 400 MHz). Selected signals attributed to an organometallic intermediated are highlighted in red.

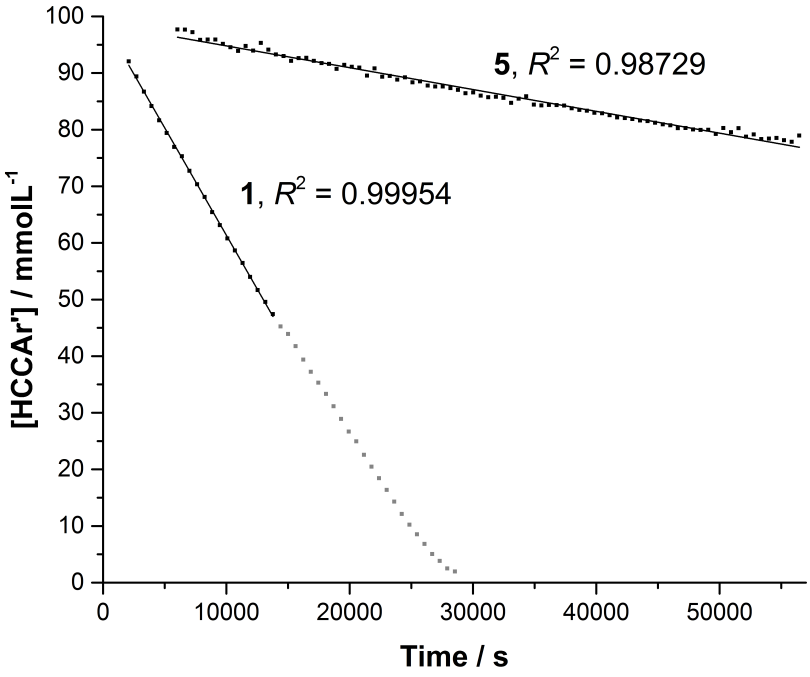


Figure S32: Kinetic data for the homocoupling of HC≡CAr' (100 mmolL^{-1}) catalysed by [Rh(CNC-Me)L][BAr$^F_4$] (L = C_2H_4, **1**; $SOMe_2$, **5**) (5 mmolL^{-1}) in CD_2Cl_2 at 298 K.

7.4 *in situ* characterisation of [Rh(CNC-Me)(CCAr'){C(CH$_2$)Ar'}(DMSO)][BAr$^F_4$] 6

To a chilled J. Young's valve NMR tube charged with [Rh(CNC-Me)(SOMe$_2$)][BAr$^F_4$] **5** (13.2 mg, 10.0 µmol) and HC≡CAr' (6.4 mg, 29.9 µmol) was added chilled CD_2Cl_2 (0.5 mL) in an inert atmosphere glove box. The tube was sealed and immediately frozen in liquid nitrogen. The sample was then thawed and placed into a

NMR spectrometer pre-equilibrated to 278 K and analyzed by ^{1}H NMR spectroscopy (600 MHz, Figures S32 and 33).

Under these conditions [Rh(CNC-Me)(CCAr')$\{C(CH_2)Ar'\}$(DMSO)][BAr^F_4] **6** could be comprehensively characterised *in situ* and there was negligible catalytic turnover observed. Attempts to collect NMR spectroscopic data at 298 K were frustrated by the onset of catalysis.

^{1}H NMR (600 MHz, CD_2Cl_2, 278 K): δ 7.94 (t, $^{3}J_{HH}$ = 7.8, 1H, py), 7.70 – 7.77 (m, 8H, Ar^F), 7.57 (d, $^{3}J_{HH}$ = 7.7, 1H, py), 7.55 (br, 4H, Ar^F), 7.52 (d, $^{3}J_{HH}$ = 7.7, 1H, py), 7.24 (s, 1H, NCH), 7.22 (s, 2H, tBu$_2$C$_6$H$_3$), 7.16 – 7.18 (m, 2H, tBu$_2$C$_6$H$_3$), 7.06 (s, 1H, NCH), 7.04 (s, 1H, NCH), 7.02 (s, 1H, NCH), 6.79 (s, 2H, tBu$_2$C$_6$H$_3$), 6.22 (d, $^{2}J_{HH}$ = 14.9, 1H, pyCH_2), 5.95 (d, $^{2}J_{HH}$ = 15.4, 1H, pyCH_2), 5.10 (d, $^{2}J_{HH}$ = 15.0, 1H, pyCH_2), 4.88 (d, $^{2}J_{HH}$ = 15.5, 1H, pyCH_2), 4.79 (d, $^{3}J_{RhH}$ = 2.9, 1H, C(CH_2)Ar'), 4.48 (s, 3H, NCH_3), 4.04 (s, 3H, NCH_3), 3.21 (d, $^{3}J_{RhH}$ = 2.2, 1H, C(CH_2)Ar'), 1.23 (s, 18H, tBu), 1.20 (s, 18H, tBu).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 278 K): δ 177.0 (d, $^{1}J_{RhC}$ = 39, NCN), 176.6 (d, $^{1}J_{RhC}$ = 40, NCN), 162.1 (q, $^{1}J_{CB}$ = 50, Ar^F), 157.2 (s, py), 155.6 (s, py), 153.8 (d, $^{1}J_{RhC}$ = 38, C(CH$_2$)Ar'), 151.9 (d, $^{3}J_{RhC}$ = 12, tBu$_2$C$_6$H$_3$), 150.8 (s, tBu$_2$C$_6$H$_3$), 149.7(s, tBu$_2$C$_6$H$_3$), 149.5 (s, tBu$_2$C$_6$H$_3$), 140.3 (s, py), 135.2 (br, Ar^F), 129.2 (qq, $^{2}J_{FC}$ = 32, $^{3}J_{CB}$ = 3, Ar^F), 126.4 (s, py), 125.6 (s, py), 125.0 (q, $^{1}J_{FC}$ = 272, Ar^F), 124.6 (s, tBu$_2$C$_6$H$_3$), 124.1 (obscured, NCH), 123.7 (s, NCH), 123.6 (s, tBu$_2$C$_6$H$_3$), 121.7 (s, NCH), 121.5 (s, NCH), 120.2 (s, 2 × tBu$_2$C$_6$H$_3$), 119.9 (s, C(CH$_2$)Ar'), 118.0 (sept., $^{3}J_{FC}$ = 4, Ar^F), 111.8 (d, $^{2}J_{RhC}$ = 11, CCAr'), 101.9 (d, $^{1}J_{RhC}$ = 55, CCAr'), 55.7 (s, pyCH$_2$), 55.3 (s, pyCH$_2$), 39.4 (s, NCH_3), 38.8 (s, NCH_3), 35.0 (s, tBu{C}), 34.9 (s, tBu{C}), 31.8 (s, tBu{CH_3}), 31.5 (s, tBu{CH_3}).

HR ESI-MS (positive ion, 4 kV): 798.3985 ([M-DMSO]$^{+}$, calcd 798.3977) m/z.

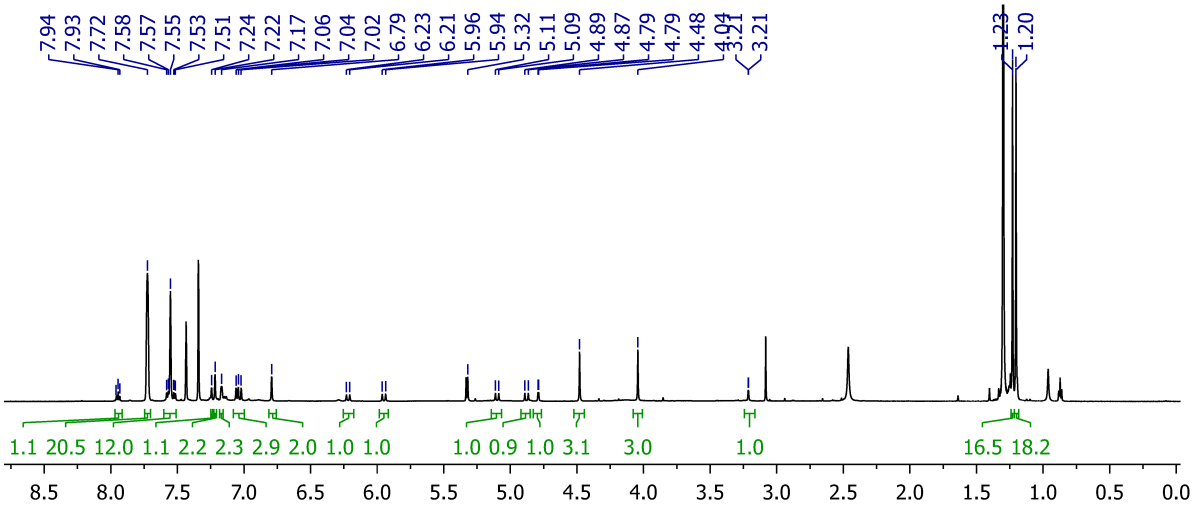


Figure S33: ^{1}H NMR spectrum collected during the homocoupling of HC≡CAr' (60 mmolL^{-1}) catalysed by [Rh(CNC-Me)($SOMe_2$)][BAr^F_4] **5** (20 mmolL^{-1}) in CD_2Cl_2 (278 K, 600 MHz). Only signals attributed to the organometallic intermediated are labeled.

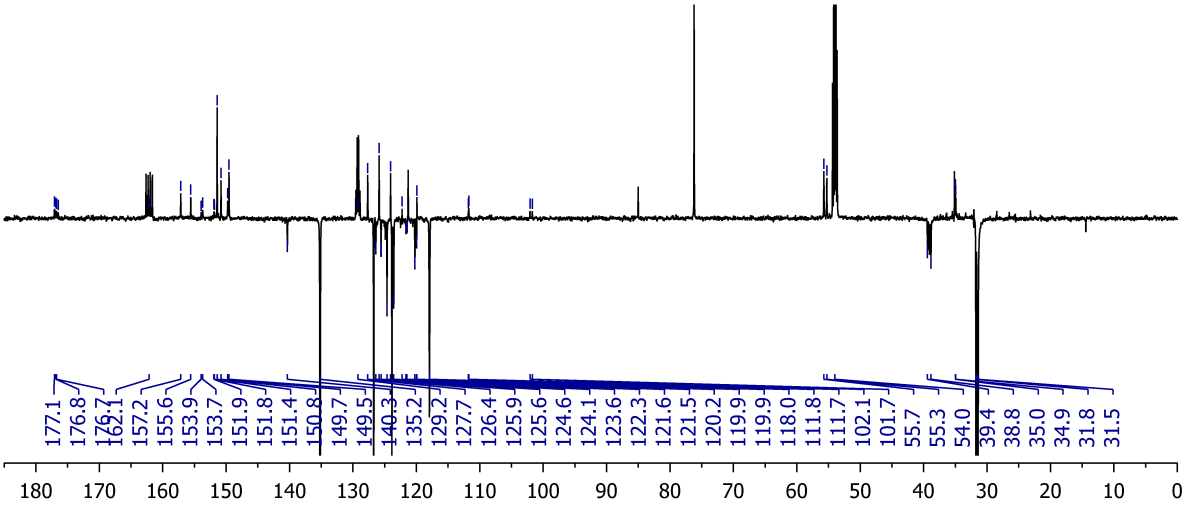


Figure S34: $^{13}C\{^{1}H\}$ APT NMR spectrum collected during the homocoupling of HC≡CAr' (60 mmolL^{-1}) catalysed by [Rh(CNC-Me)(SOMe$_2$)][BAr$^F{}_4$] **5** (20 mmolL^{-1}) in CD_2Cl_2 (278 K, 151 MHz). Only signals attributed to the organometallic intermediated are labeled.

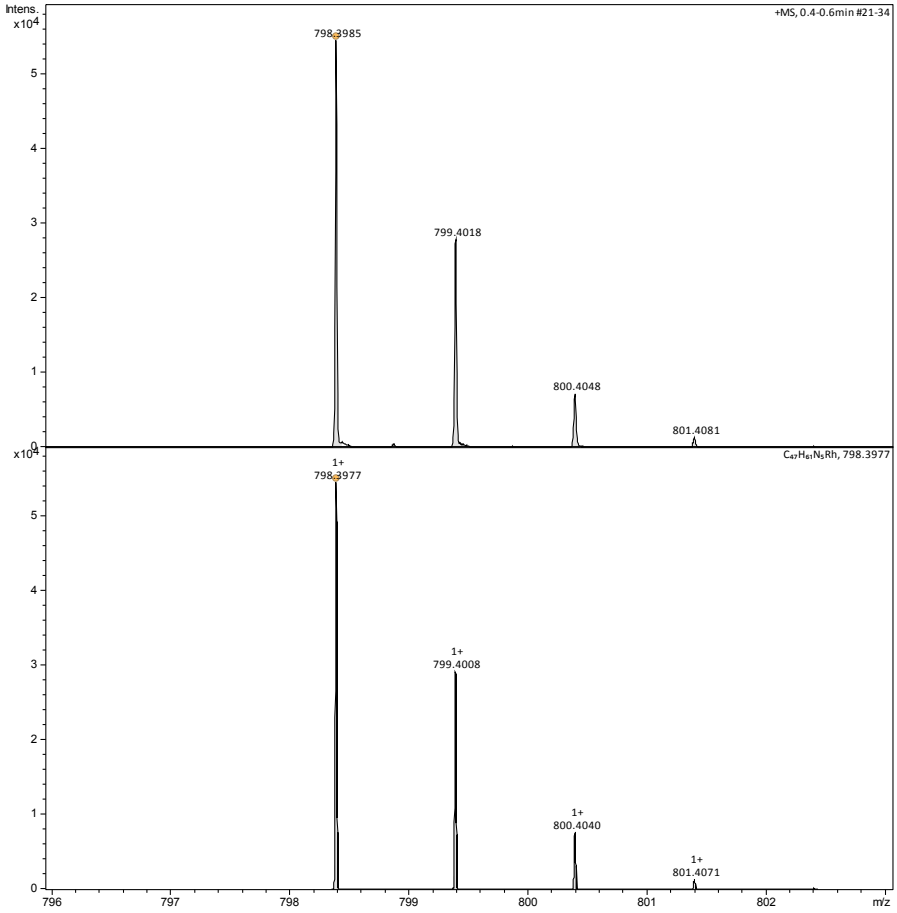


Figure S35: HR ESI-MS spectrum of an aliquot collected during the homocoupling of HC≡CAr' (60 mmolL^{-1}) catalysed by [Rh(CNC-Me)(SOMe$_2$)][BAr$^F{}_4$] **5** (20 mmolL^{-1}) in CD_2Cl_2 (278 K).

8 NMR scale reaction of [Rh(CNC-12)(C_2H_4)][BAr^F_4] 2 with HC≡CAr'

A solution of [Rh(CNC-12)(C_2H_4)][BAr^F_4] **2** (14.7 mg, 10.0 µmol) and HC≡CAr' (4.5 mg, 21.0 µmol) in CD_2Cl_2 (0.5 mL) was prepared in a J. Young's valve NMR tube. Analysis after 5 min at RT by ^{1}H NMR spectroscopy indicated quantitative conversion of **2** into **7** (Figure S36).

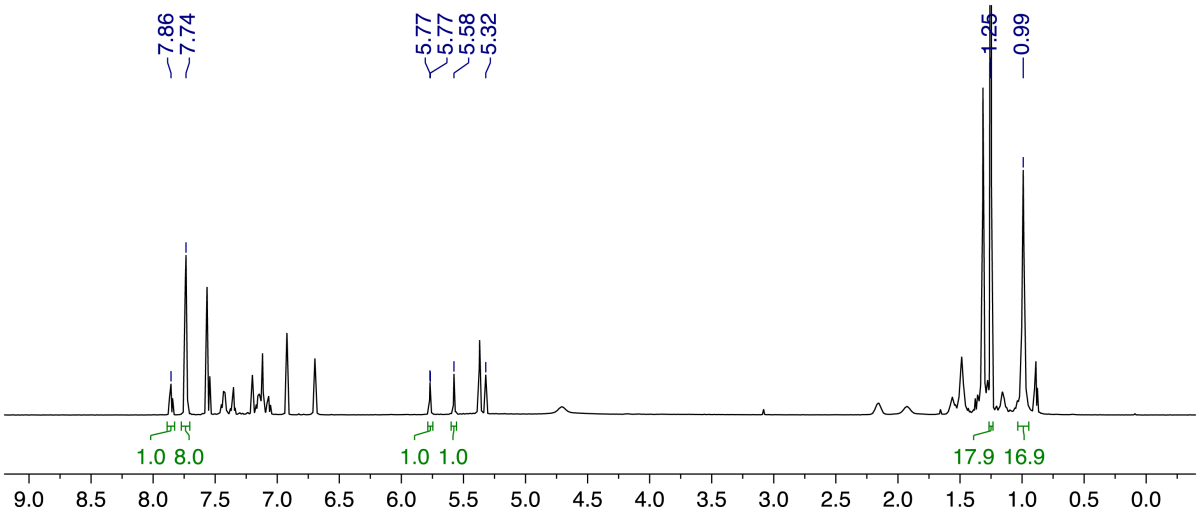


Figure S36: ^{1}H NMR spectrum collected after 5 min for the reaction between **2** and HC≡CAr' (CD_2Cl_2, 600 MHz). Key signals and integrals associated with the product **7** provided.

9 Preparation of [Rh(CNC-12)(CCAr'){C(CH_2)Ar'}][BAr^F_4] 7

A solution of [Rh(CNC-12)(C_2H_4)][BAr^F_4] **2** (45.1 mg, 30.6 µmol) and HCCAr' (13.1 mg, 61.1 µmol) in CH_2Cl_2 (1.5 mL) was stirred at RT for 30 min. The volatiles were removed *in vacuo* and the product was obtained as yellow-orange rods following recrystallisation of the residue from CH_2Cl_2–hexane (1:10, 20 mL) at –30 °C. Yield: 37.8 mg (47%). Crystals grown in this way were suitable for analysis by X-ray diffraction.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.86 (t, $^3J_{HH}$ = 7.6, 1H, py), 7.70 – 7.77 (m, 8H, Ar^F), 7.56 (s, 4H, Ar^F), 7.54 (t, $^4J_{HH}$ = 1, 1H, *t*$Bu_2C_6\underline{H}_3$), 7.43 (d, $^3J_{HH}$ = 7.6, 2H, py), 7.20 (t, $^4J_{HH}$ = 1.6, 1H, *t*$Bu_2C_6\underline{H}_3$), 7.14 (vbr, fwhm = 12 Hz, 2H, NCH), 7.12 (br, 2H, NCH), 6.92 (d, $^4J_{HH}$ = 1.6, 2H, *t*$Bu_2C_6\underline{H}_3$), 6.69 (br, 2H, *t*$Bu_2C_6\underline{H}_3$), 5.76 (d, $^3J_{RhH}$ = 2.1, 1H, C($C\underline{H}_2$)Ar'), 5.57 (s, 1H, C($C\underline{H}_2$)Ar'), 5.25 (vbr, fwhm ≈ 300 Hz, 2H, py$C\underline{H}_2$), 4.70 (vbr, fwhm = 43 Hz, 2H, NCH_2), 4.62 (vbr, fwhm ≈ 150 Hz, 2H, py$C\underline{H}_2$), 3.88 (vbr, fwhm ≈ 400 Hz, 2H, NCH_2), 2.16 (br, 2H, CH_2), 1.92 (br, 2H, CH_2), 1.43 – 1.62 (m, 8 H, CH_2), 1.27 – 1.35 (m, 6H, CH_2), 1.25 (s, 18H, *t*Bu), 1.10 – 1.21 (m, 2H, CH_2), 0.99 (vbr, fwhm = 7 Hz, 18H, *t*Bu).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 172.9 (d, $^1J_{RhC}$ = 38, NCN), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 157.7 (d, $^1J_{RhC}$ = 27, $\underline{C}(CH_2)$Ar'), 156.1 (s, py), 155.5 (br, *t*$Bu_2\underline{C}_6H_3$), 151.0 (s, *t*$Bu_2\underline{C}_6H_3$), 141.1 (s, py), 135.4 (br, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 127.0 (s, *t*$Bu_2\underline{C}_6H_3$), 125.9 (s, *t*$Bu_2\underline{C}_6H_3$), 125.4 (s, *t*$Bu_2\underline{C}_6H_3$), 125.17 (q, $^1J_{FC}$ = 271, Ar^F), 125.15 (s, py), 122.9 (s, NCH), 122.6 (s, NCH), 122.2 (s, *t*$Bu_2\underline{C}_6H_3$), 120.8 (s, *t*$Bu_2\underline{C}_6H_3$), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F), 114.6 (s, C($\underline{C}H_2$)Ar'), 104.7 (d, $^2J_{RhC}$ = 15, C$\underline{C}$Ar'), 85.0 (d, $^1J_{RhC}$ = 72, $\underline{C}$CAr'), 54.9 (br, py$C\underline{H}_2$), 50.9 (br,

NCH_2), 35.4 (s, *t*Bu{C}), 35.1 (s, *t*Bu{C}), 31.7 (s, *t*Bu{CH_3}), 31.4 (s, *t*Bu{CH_3}), 28.9 (s, CH_2), 28.5 (s, CH_2), 28.4 (s, CH_2), 25.3 (br, CH_2). One of the quaternary $tBu_2\underline{C}_6H_3$ resonances was not unambiguously located.

HR ESI-MS (positive ion, 4 kV): 936.5399 ($[M]^+$, calcd 936.5385) *m*/*z*.

Anal. Calcd for $C_{89}H_{91}BF_{24}N_5Rh$ (1799.60 g·mol^{-1}): C, 59.37; H, 5.09; N, 3.89. Found: C, 59.37; H, 4.94; N, 3.93.

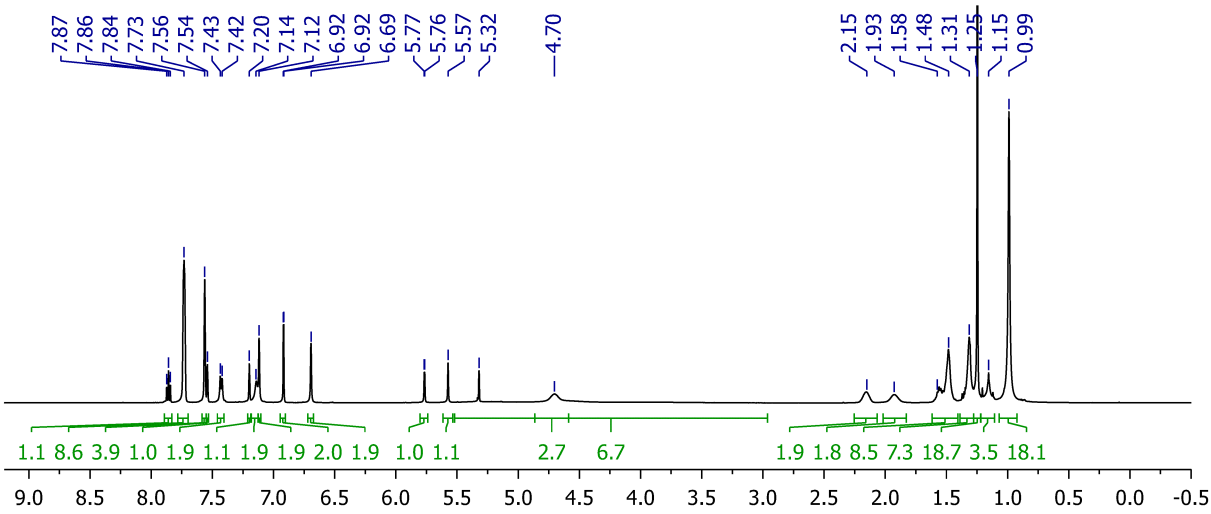


Figure S37: ^{1}H NMR spectrum of [Rh(CNC-12)(CCAr')$\{C(CH_2)Ar'\}$][BAr^F_4] **7** (298 K, CD_2Cl_2, 500 MHz)

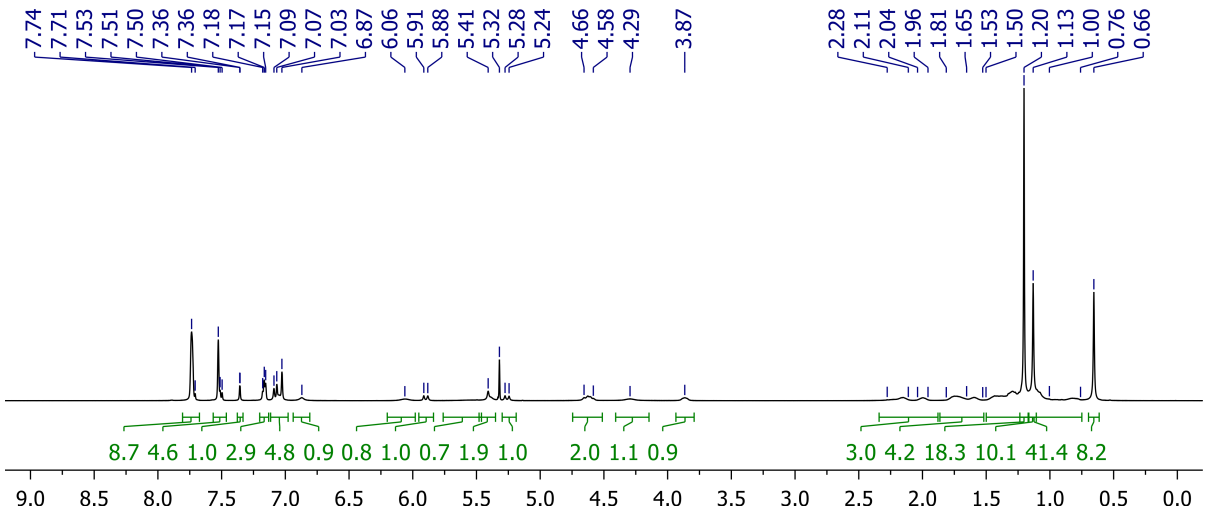


Figure S38: ^{1}H NMR spectrum of [Rh(CNC-12)(CCAr')$\{C(CH_2)Ar'\}$][BAr^F_4] **7** (200 K, CD_2Cl_2, 500 MHz)

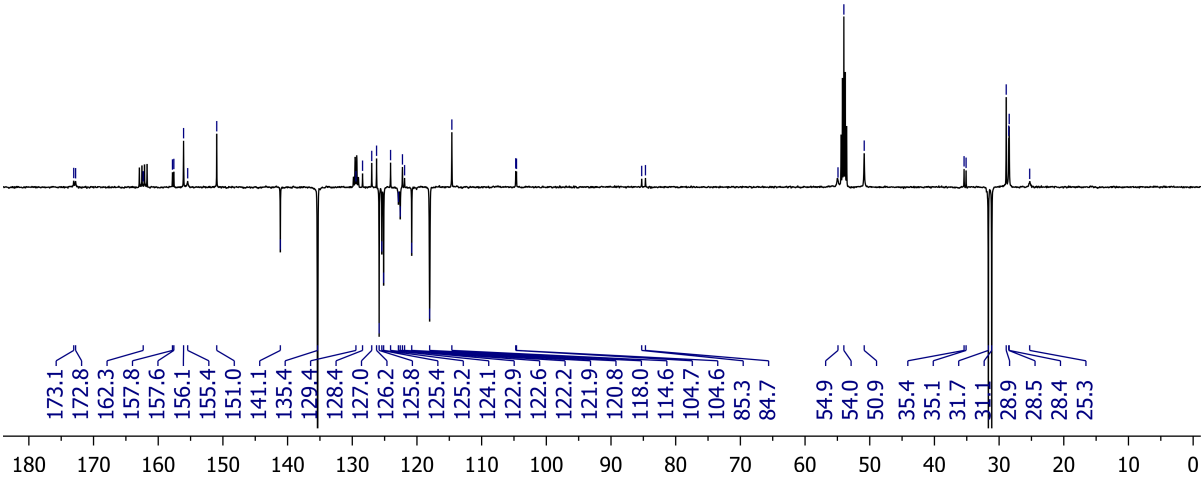


Figure S39: $^{13}C\{^{1}H\}$ APT NMR spectrum of [Rh(CNC-12)(CCAr')$\{C(CH_2)Ar'\}$][BAr^F_4] **7** (CD_2Cl_2, 126 MHz)

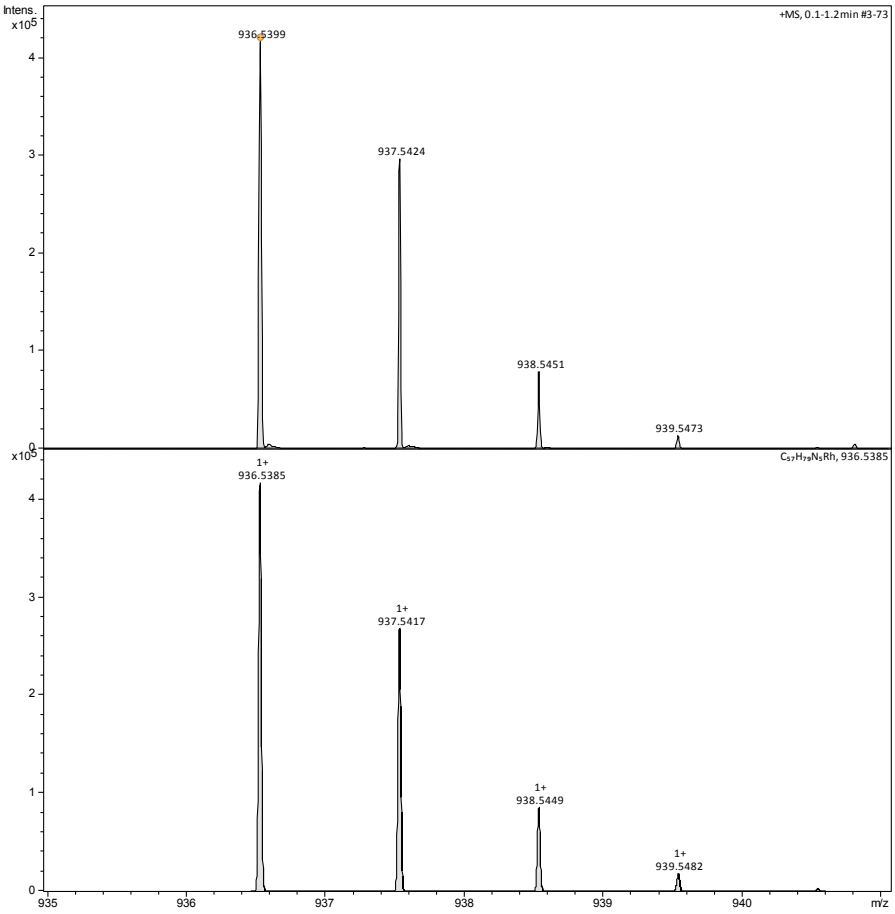


Figure S40: HR ESI-MS Spectrum of [Rh(CNC-12)(CCAr')$\{C(CH_2)Ar'\}$][BAr^F_4] **7**

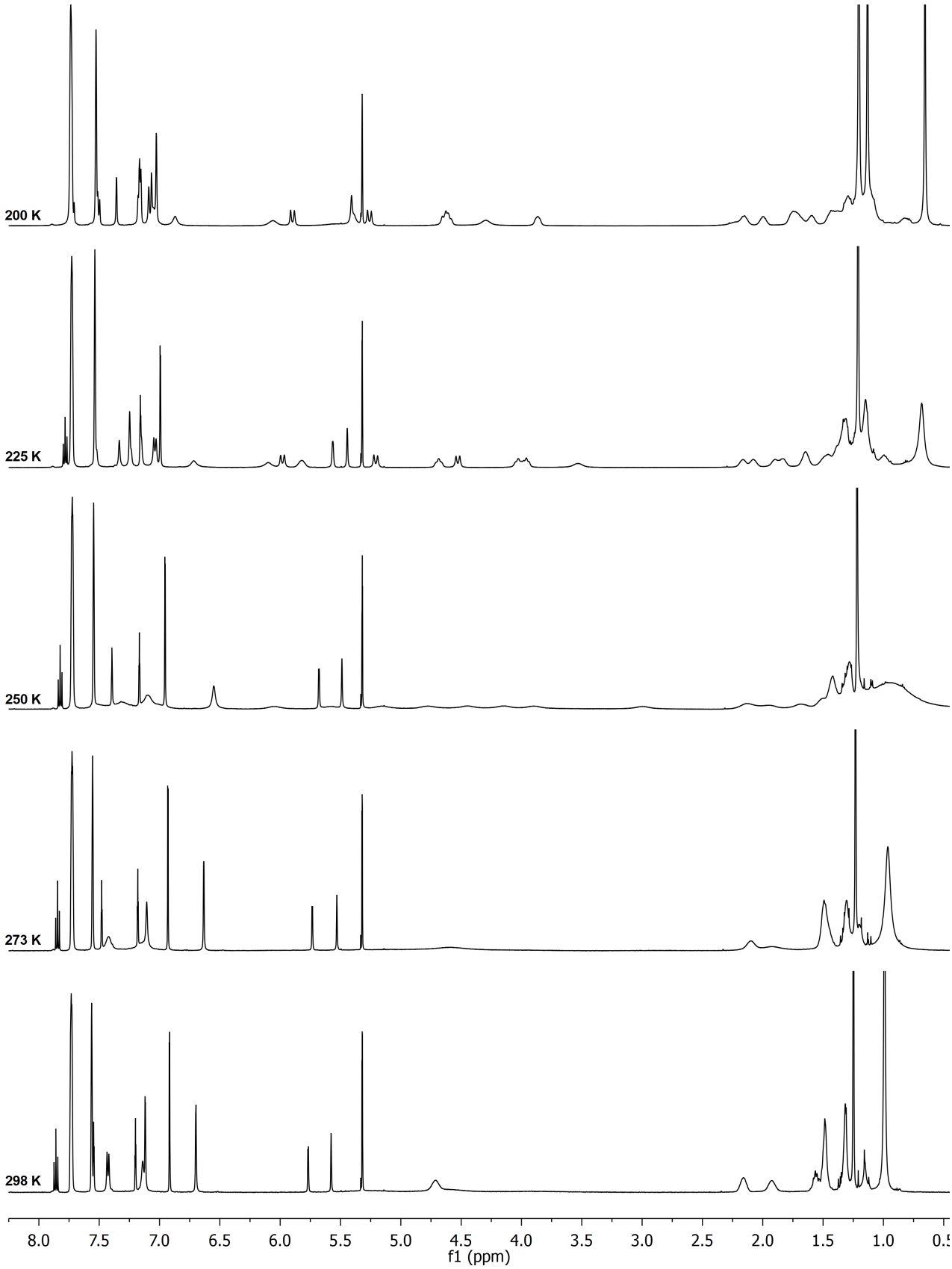


Figure S41: Variable temperature ^{1}H NMR spectra of [Rh(CNC-12)(CCAr')$\{C(CH_2)Ar'\}$][BAr^F_4] **7** (CD_2Cl_2, 500 MHz)

10 NMR scale reactions of [Rh(CNC-12)(CCAr')\{C(CH_2)Ar'\}][BAr^F_4] 7

10.1 Kinetic studies

Solutions of [Rh(CNC-12)(CCAr')\{C(CH_2)Ar'\}][BAr^F_4] **7** (0.02 molL^{-1}) in 1,2-dichloroethane-d_4 (0.4 mL) in sealed J. Young's valve NMR tubes were placed into a NMR spectrometer pre-equilibrated to the required temperature and monitored by ^{1}H NMR spectroscopy (500 MHz, 328 – 348 K, Figures S41 and 42).

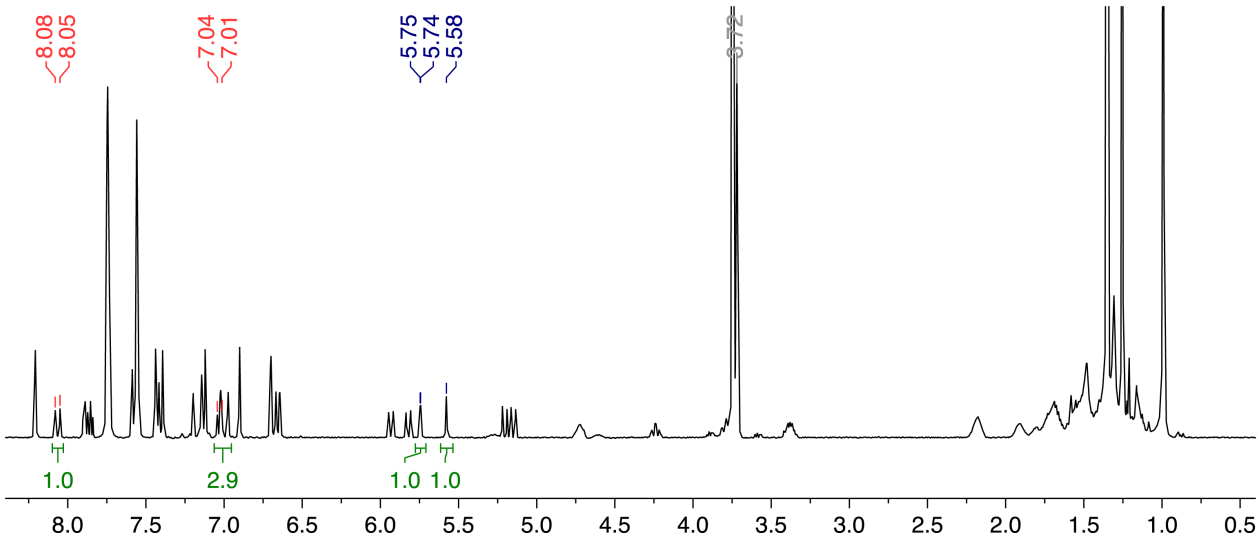


Figure S42: ^{1}H NMR spectrum collected during the formation of **8** from **7** (20 mmolL^{-1}) in 1,2-$C_2D_4Cl_2$ at 328 K (*ca.* 50% conversion, 500 MHz). Alkenyl signals for **7** in blue, and for **8** in red.

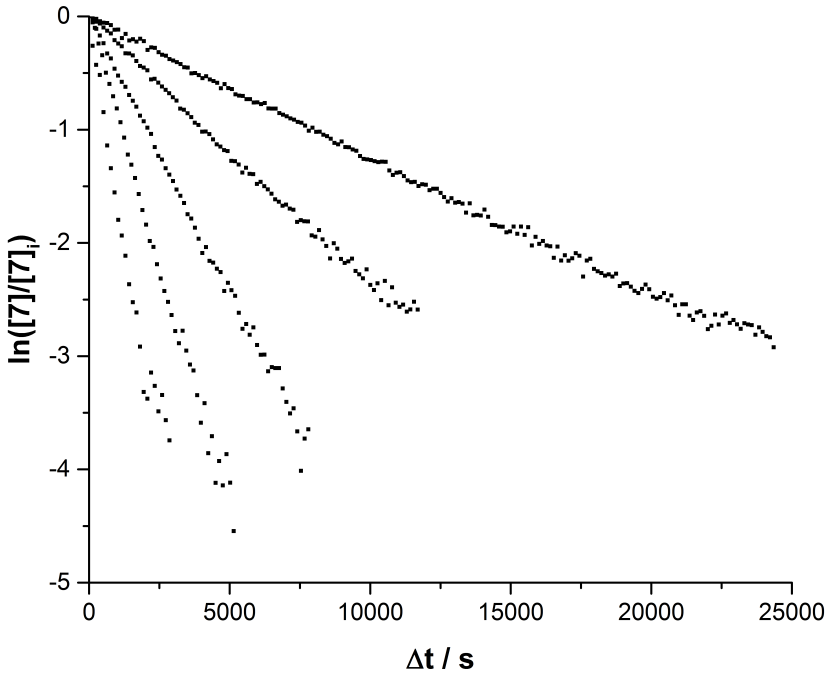


Figure S43: Kinetic data collected for the formation of **8** from **7** in 1,2-$C_2D_4Cl_2$ at 328 – 348 K, where [**7**]/[**7**]$_i$ is the concentration relative to the first spectrum recorded.

The resulting time-course data was analysed through integration of the lowest frequency alkenyl resonance of **7** (δ 5.58 at 328 K) to obtain the rate constants over the temperature range (Table S2). The corresponding activation parameters for the reaction were obtained using the Eyring equation (Figure S27).

Rate law: $-d[\mathbf{7}]/dt = d[\mathbf{8}]/dt = k[\mathbf{7}]$

Table S2: Kinetic parameters for the formation of **8** from **7**.

T / K	R^2 (fit)	k / 10^{-4} s^{-1}	$t_{1/2}$ / h
328	0.99872	1.250 ± 0.004	1.5
333	0.99933	2.44 ± 0.01	0.8
338	0.99894	4.91 ± 0.02	0.4
343	0.99881	8.9 ± 0.1	0.2
348	0.99922	16.3 ± 0.4	0.1

Activation parameters:

$\Delta G^{\ddagger}$ (298 K) = 106 ± 3 kJmol^{-1}

$\Delta H^{\ddagger}$ = 119 ± 1 kJmol^{-1}

$\Delta S^{\ddagger}$ = 44 ± 4 JK^{-1}mol^{-1}

R^2 (fit) = 0.99942

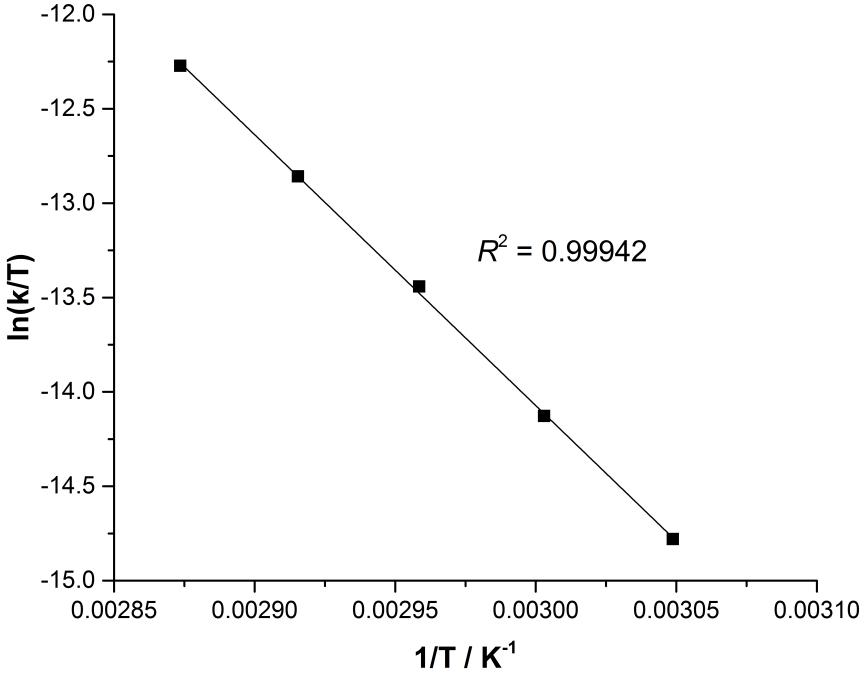


Figure S44: Eyring plot for the formation of **8** from **7** in 1,2-$C_2D_4Cl_2$.

10.2 Synthesis of DC≡CAr'

To a solution of HCCAr' (250 mg, 1.17 mmol) in tetrahydrofuran (5.0 mL) at -78 °C was added a solution of ^{n}BuLi (1.78 molL^{-1}, 0.92 mL, 1.6 mmol) in hexanes. The resulting orange solution was stirred for 5 min at -78 °C before D_2O (0.1 mL, 5.0 mmol) was added dropwise and the suspension warmed to RT. Water (25 mL) was added and the product extracted into diethyl ether (3 × 25 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford the product as a colourless powder. Yield: 0.24 g (95%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (t, $^{4}J_{HH}$ = 1.9, 1H, *t*Bu$_2$C$_6$H$_3$), 7.36 (d, $^{4}J_{HH}$ = 1.9, 2H, *t*Bu$_2$C$_6$H$_3$), 1.33 (s, 18H, *t*Bu).

^{2}H NMR (77 MHz, $CHCl_3$): δ 3.04 (s, 1D).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 151.0 (s, *t*Bu$_2$C$_6$H$_3$), 126.5 (s, *t*Bu$_2$C$_6$H$_3$), 123.4 (s, *t*Bu$_2$C$_6$H$_3$), 121.2 (s, *t*Bu$_2$C$_6$H$_3$), 84.6 (t, $^{2}J_{CD}$ = 7, DCC), 75.7 (d, $^{1}J_{CD}$ = 38, DCC), 34.9 (s, *t*Bu{C}), 31.5 (s, *t*Bu{CH$_3$}).

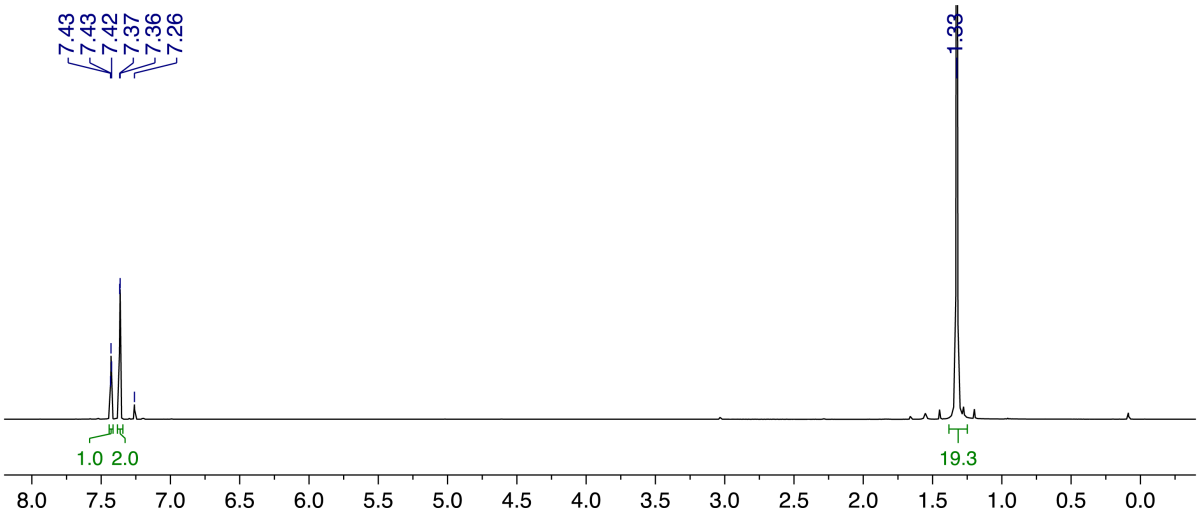


Figure S45: ^{1}H NMR spectrum of DC≡CAr' ($CDCl_3$, 500 MHz)

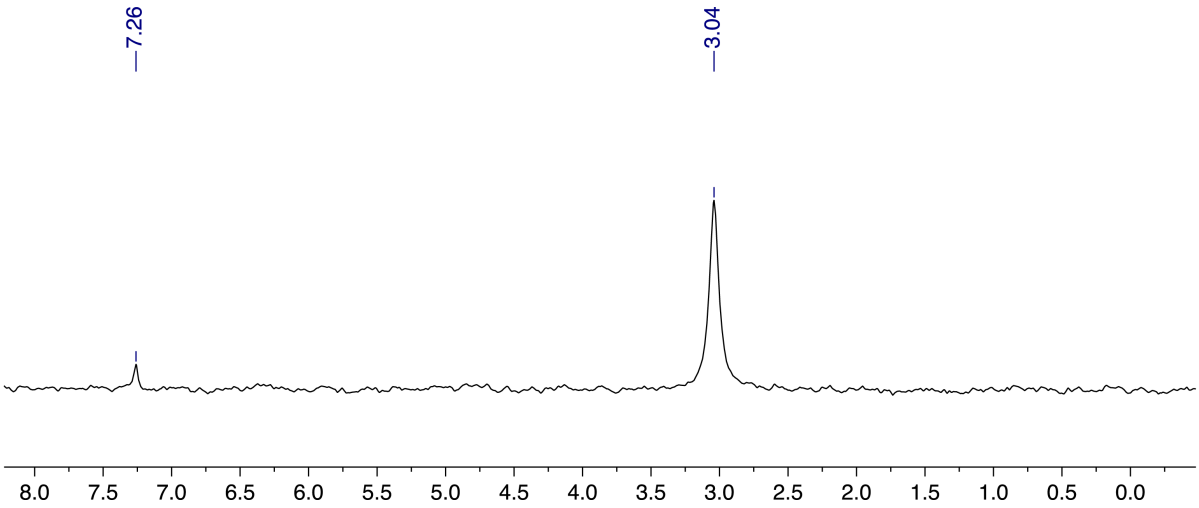


Figure S46: ^{2}H NMR spectrum of DC≡CAr' ($CHCl_3$, 77 MHz).

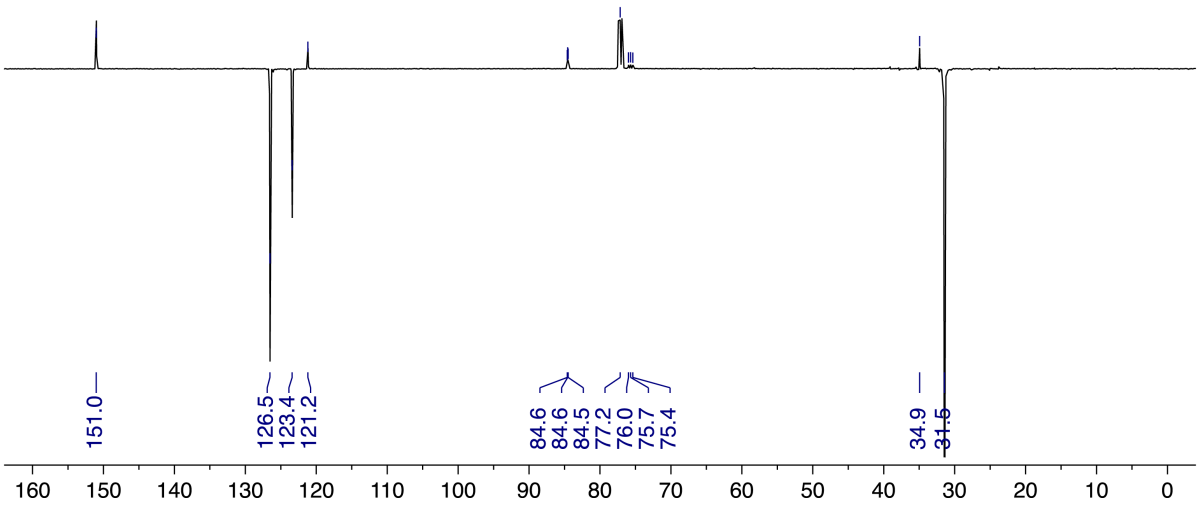


Figure S47: $^{13}C\{^{1}H\}$ APT NMR spectrum of DC≡CAr' ($CDCl_3$, 126 MHz).

10.3 Labelling experiment

A solution of [Rh(CNC-12)(CCAr'){C(CH_2)Ar'}][BAr^F_4] **7** (32.4 mg, 18.0 µmol) and DC≡CAr' (38.8 mg, 180 µmol) in 1,2-dichloroethane (1 mL) was heated at 55 °C for 18 h. The volatiles were removed *in vacuo* and the product extracted into the minimum amount of hot hexamethyldisiloxane (*ca.* 5 mL), filtered and concentrated *in vacuo* to the point of incipient crystallisation. The suspension was filtered, volatiles removed *in vacuo* and the red solid dried at 80 °C. Analysis by ^{1}H NMR indicated 58% and 60% D incorporation at the CHCHAr' and CHCHAr' positions of **8**, respectively (Figure S48). This substantial degree of D incorporation was substantiated by HR ESI-MS, which suggested a total D incorporation of 1.18 (Figure S49).

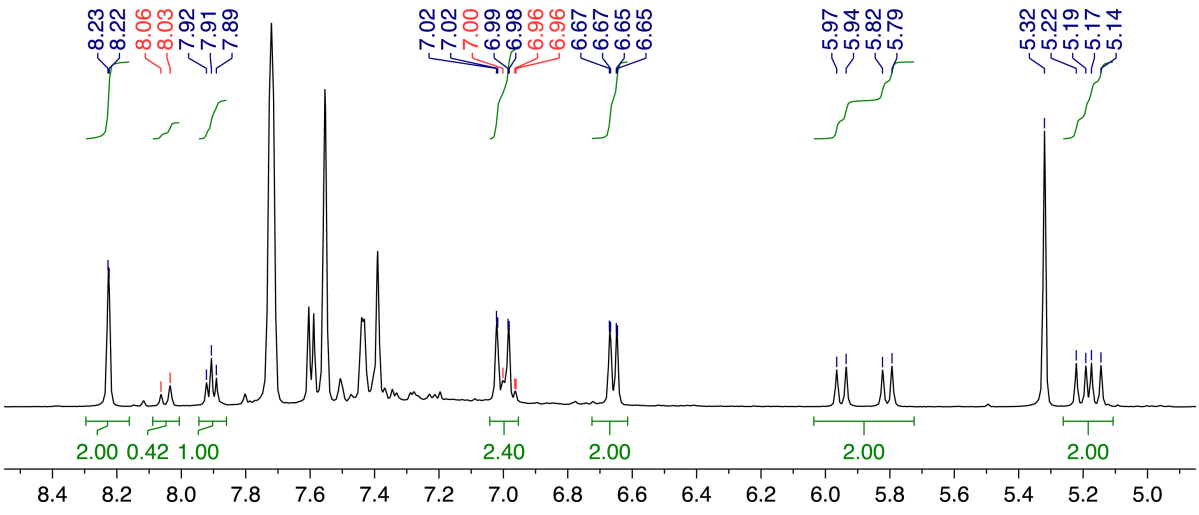


Figure S48: ^{1}H NMR spectrum of [Rh(CNC-12)(*E*-Ar'CCCHCHAr')][BAr^F_4] **8** prepared in the presence of 10 equiv DC≡CAr' (CD_2Cl_2, 600 MHz, d1 = 10 s). The CHCHAr' and CHCHAr' signals are highlighted in red.

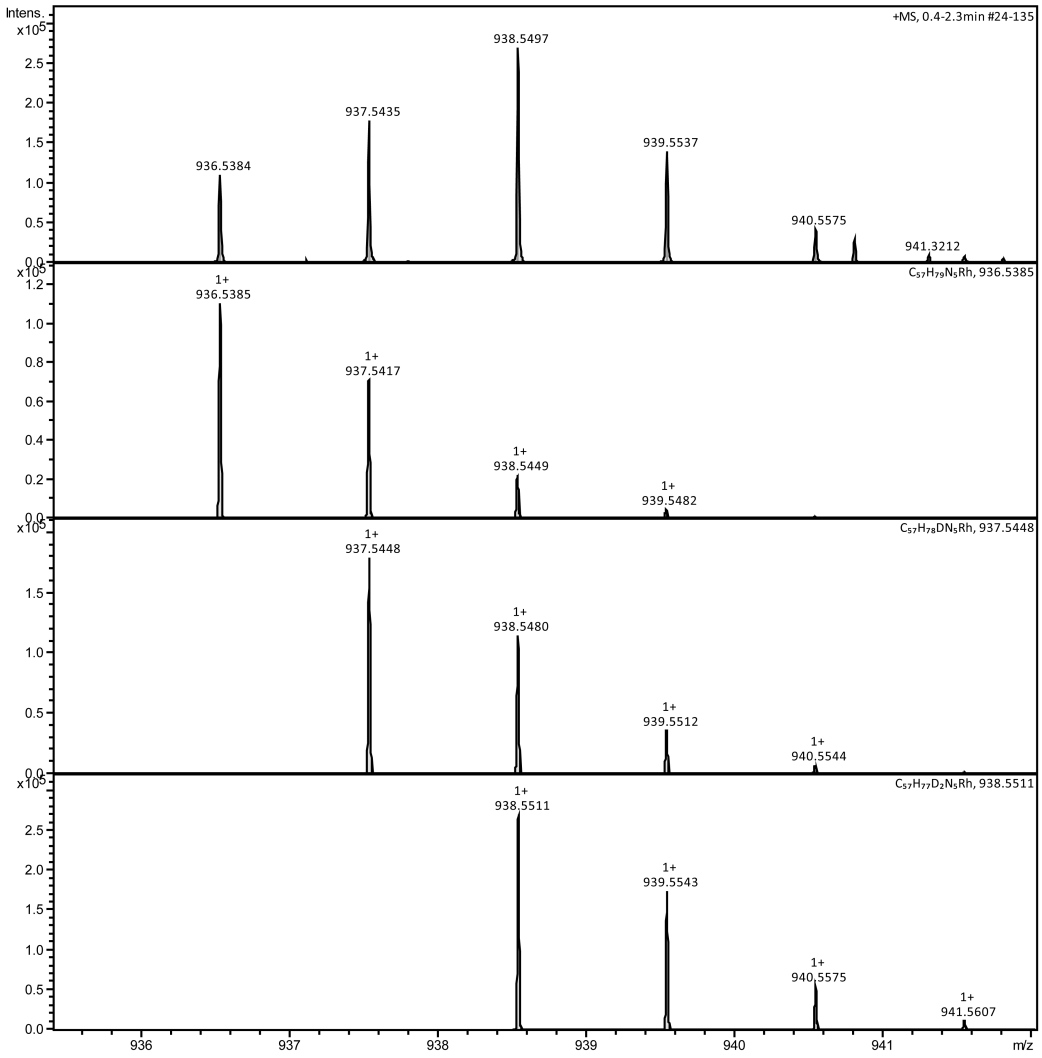


Figure S49: HR ESI-MS spectrum of [Rh(CNC-12)(*E*-Ar'CCCHCHAr')][BAr^F_4] **8** prepared in the presence of 10 equiv DC≡CAr'. Fitting gives: 27.5% $[M\text{-}d_0]^+$, 27.1% $[M\text{-}d_1]^+$, 45.4% $[M\text{-}d_2]^+$.

11 Preparation of [Rh(CNC-12)(*E*-Ar'CCCHCHAr')][BAr$^F_4$] 8

A solution of [Rh(CNC-12)(CCAr'){C(CH_2)Ar'}][BAr$^F_4$] **7** (36.2 mg, 20.1 µmol) in 1,2-$C_6H_4F_2$ (*ca*. 1 mL) was heated at 60 °C for 6 h. The volatiles were removed *in vacuo* and the product obtained by extraction with hexane (*ca*. 10 mL). Yield: 24.4 mg (68%). Crystals suitable for X-ray diffraction were grown from Et_2O/hexane at RT.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (d, $^4J_{HH}$ = 1.7, 2H, *t*$Bu_2C_6\underline{H}_3$), 8.05 (d, $^3J_{HH}$ = 15.3, 1H, CHC<u>H</u>Ar'), 7.90 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.68 – 7.77 (m, 8H, Ar^F), 7.59 (d, $^3J_{HH}$ = 7.7, 2H, py), 7.55 (br, 4H, Ar^F), 7.44 (t, $^4J_{HH}$ = 1.7, 1H, *t*$Bu_2C_6\underline{H}_3$), 7.43 (t, $^4J_{HH}$ = 1.5, 1H, *t*$Bu_2C_6\underline{H}_3$), 7.39 (d, $^4J_{HH}$ = 1.5, 2H, *t*$Bu_2C_6\underline{H}_3$), 7.02 (d, $^3J_{HH}$ = 1.8, 1H, NCH), 7.01 (d, $^3J_{HH}$ = 15.3, 1H, C<u>H</u>CHAr'), 6.98 (d, $^3J_{HH}$ = 1.8, 1H, NCH), 6.67 (d, $^3J_{HH}$ = 1.8, 1H, NCH), 6.65 (d, $^3J_{HH}$ = 1.8, 1H, NCH), 5.95 (d, $^2J_{HH}$ = 14.6, 1H, py$C\underline{H}_2$), 5.81 (d, $^2J_{HH}$ = 14.7, 1H, py$C\underline{H}_2$), 5.20 (d, $^2J_{HH}$ = 14.8, 1H, py$C\underline{H}_2$), 5.16 (d, $^2J_{HH}$ = 14.7, 1H, py$C\underline{H}_2$), 4.21 (app. dt, *J* = 13, *J* = 2, 1H, NCH_2), 3.75 (app. dt, *J* = 13, *J* = 2, 1H, NCH_2), 3.33 – 3.45 (m, 2H, NCH_2), 2.18 – 2.31 (m, 1H, CH_2), 1.05 – 1.88 (m, 19H, CH_2), 1.36 (s, 18H, *t*Bu), 1.35 (s, 18H, *t*Bu).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 182.0 (d, $^1J_{RhC}$ = 42, NCN), 181.3 (d, $^1J_{RhC}$ = 42, NCN), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 155.7 (py), 152.4 (s, *t*$Bu_2\underline{C}_6H_3$), 151.5 (s, *t*$Bu_2\underline{C}_6H_3$), 142.8 (d, $^3J_{RhC}$ = 2, CH<u>C</u>HAr'), 139.8 (s, py), 136.6 (s, *t*$Bu_2\underline{C}_6H_3$), 135.4 (br, Ar^F), 129.5 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 129 (obscured, *t*$Bu_2\underline{C}_6H_3$), 127.1 (s, *t*$Bu_2\underline{C}_6H_3$), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 124.9 (s, py), 124.8 (s, py), 123.9 (s, *t*$Bu_2\underline{C}_6H_3$), 123.2 (s, *t*$Bu_2\underline{C}_6H_3$), 121.5 – 121.7 (m, *t*$Bu_2\underline{C}_6H_3$ + 2× NCH), 121.6 (s, NCH), 121.7 (s, NCH), 120.9 (s, NCH), 120.7 (s, NCH), 118.0 (sept., $^3J_{FC}$ = 4, Ar^F), 117.2 (d, $^3J_{RhC}$ = 2, C<u>H</u>CHAr'), 88.9 (d, $^1J_{RhC}$ = 14, C<u>C</u>Ar'), 83.6 (d, $^1J_{RhC}$ = 13, <u>C</u>CAr'), 56.3 (s, 2× py<u>C</u>H_2), 49.8 (NCH_2), 49.5 (NCH_2), 35.6 (s, *t*Bu{C}), 35.4 (s, *t*Bu{C}), 33.2 (CH_2), 31.9 (s, *t*Bu{CH_3}), 31.8 (s, *t*Bu{CH_3}), 31.6 (s, CH_2), 29.8 (s, CH_2), 29.5 (s, CH_2), 28.9 (s, CH_2), 28.7 (s, CH_2), 28.5 (s, CH_2), 28.3 (s, CH_2), 25.4 (s, CH_2), 24.0 (s, CH_2).

HR ESI-MS (positive ion, 4 kV): 936.5399 ([*M*]$^+$, calcd 936.5385) *m/z*.

Anal. Calcd for $C_{89}H_{91}BF_{24}N_5Rh$ (1799.60 g·mol^{-1}): C, 59.37; H, 5.09; N, 3.89. Found: C, 59.36; H, 4.99; N, 4.01).

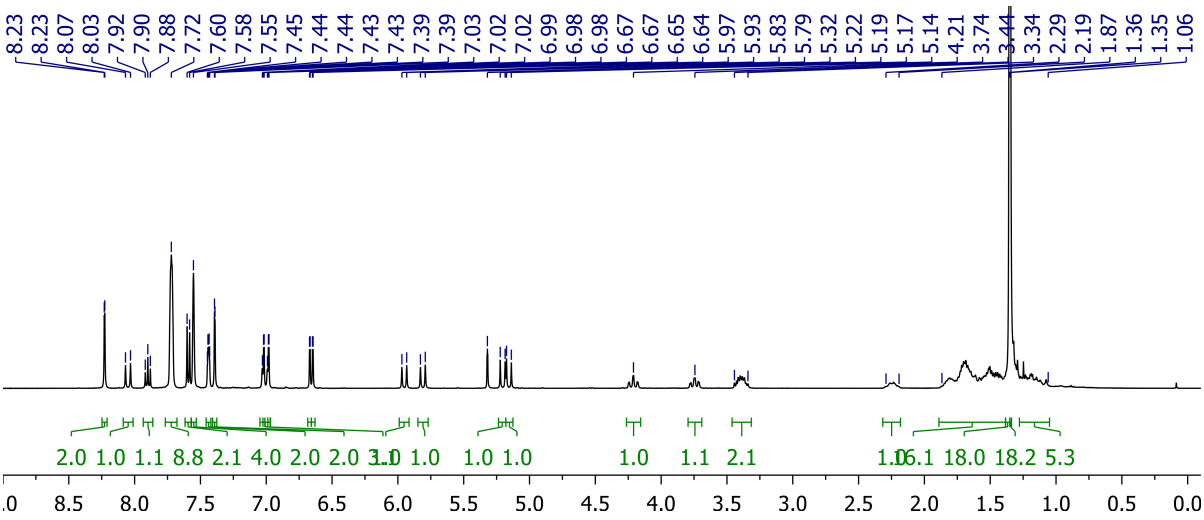


Figure S50: ^{1}H NMR spectrum of [Rh(CNC-12)(*E*-Ar'CCCHCHAr')][BAr$^{F}_{4}$] **8** (CD_2Cl_2, 400 MHz)

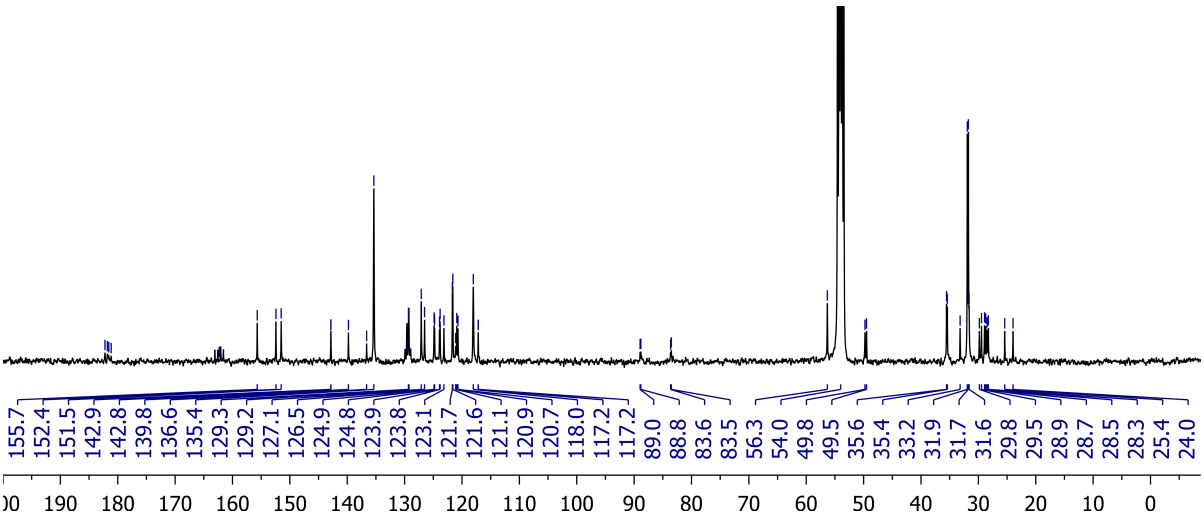


Figure S51: ^{13}C{^{1}H} NMR spectrum of [Rh(CNC-12)(*E*-Ar'CCCHCHAr')][BAr$^{F}_{4}$] **8** (CD_2Cl_2, 101 MHz)

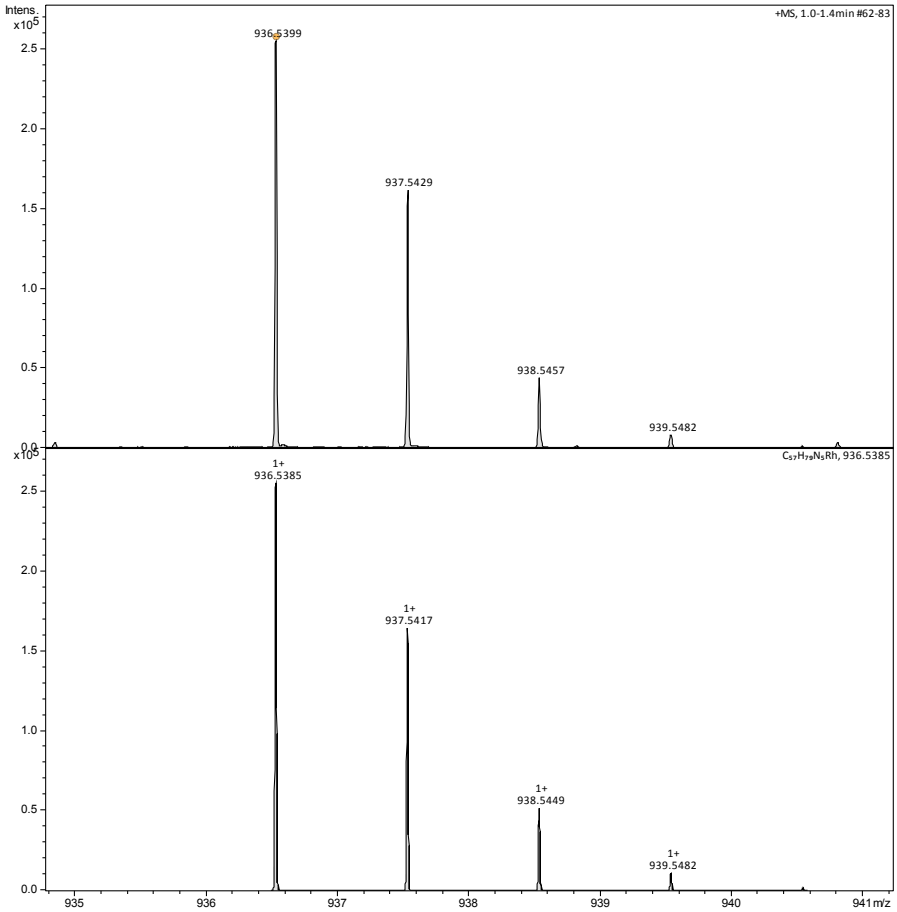


Figure S52: HR ESI-MS spectrum of [Rh(CNC-12)(*E*-Ar'CCCHCHAr')][BAr^F_4] **8**

12 NMR scale reaction of [Rh(CNC-12)(*E*-Ar'CCCHCHAr')][BAr^F_4] 8 with CO in MeCN

A solution of [Rh(CNC-12)(*E*-Ar'CCCHCHAr')][BAr^F_4] **8** (18.0 mg, 10.0 µmol) in MeCN (0.5 mL) was freeze-pump-thaw degassed, placed under an atmosphere of CO (1 atm), and then heated at 85 °C for 16 h. The solvent was removed *in vacuo* and the resulting red glass dried at 85 °C until complete removal of volatiles was established by ^{1}H NMR spectroscopy. Subsequent analysis by ^{1}H NMR spectroscopy in CD_2Cl_2 confirmed quantitative recovery of **8** (Figure S53).

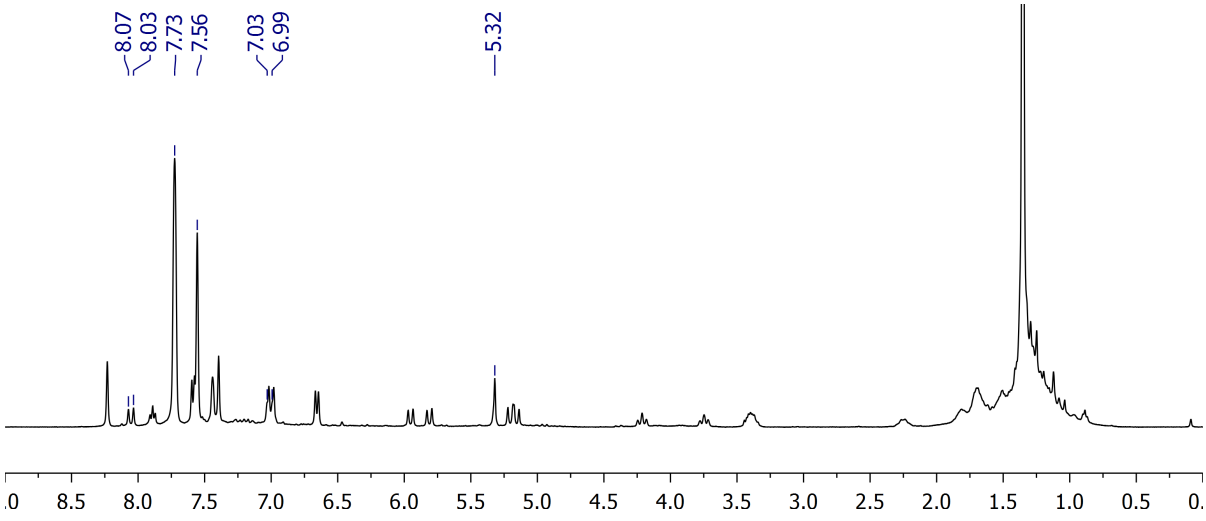


Figure S53: ^{1}H NMR spectrum of **8** after reaction with CO (1 atm) in MeCN (CD_2Cl_2, 400 MHz)

13 Preparation of PhCCC(CH_2)Ph

To a solution of [Rh(CNC-Me)(C_2H_4)][$BAr^F{}_4$] **1** (31.2 mg, 24.7 µmol) in CH_2Cl_2 (5 mL) was added HCCPh (54.3 µL, 495 µmol). The resulting orange solution stirred at 25 °C for 24 h and then freeze-pump-thaw degassed and placed under an atmosphere of CO (1 atm). The solution was concentrated *in vacuo* and the residue extracted with hexane through a short alumina plug to afford the product as a yellow oil on removal of the solvent. Yield: 32.8 mg (65 %).

Characterisation data are in excellent agreement with that previously reported for this compound.[7]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, $^3J_{HH}$ = 7.6, 2H, Ph), 7.50 – 7.58 (m, 2H, Ph), 7.29 – 7.45 (m, 6H, Ph), 5.99 (s, 1H, CH), 5.77 (s, 1H, CH).

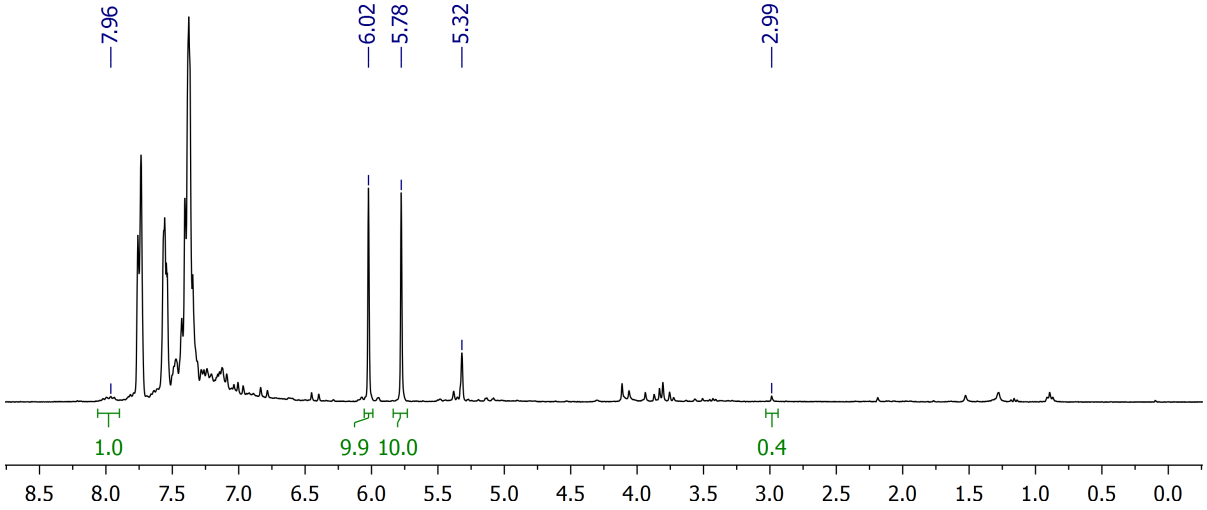


Figure S54: ^{1}H NMR spectrum of the crude reaction mixture (CD_2Cl_2, 300 MHz)

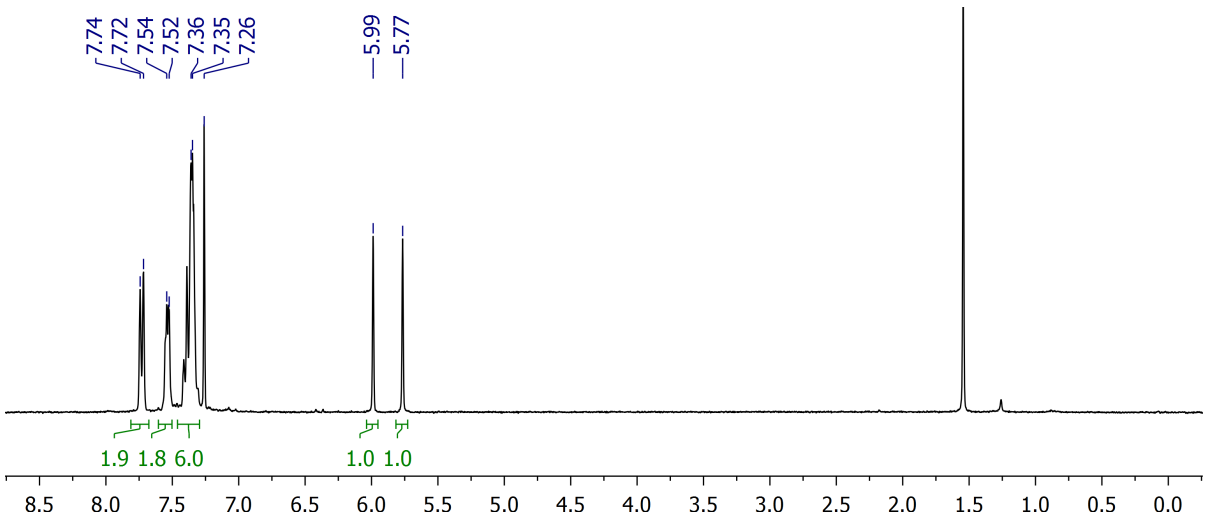


Figure S55: ^{1}H NMR spectrum of isolated PhCCC(CH_2)Ph ($CDCl_3$, 300 MHz)

14 Preparation of *E*-PhCCCHCHPh

To a solution of [Rh(CNC-12)(C_2H_4)][BAr^F_4] **2** (172 mg, 118 µmol) in CH_2Cl_2 (12 mL) was added HCCPh (27.2 µL, 248 µmol). The resulting orange solution was stirred at 50 °C for 5 h and then cooled to RT. The resulting red solution was concentrated *in vacuo* and the residue washed with cold hexane (*ca.* 10 mL). The residue was then dissolved in MeCN (*ca.* 15 mL), freeze-pump-thaw degassed and placed under an atmosphere of CO (1 atm), and stirred at 85 °C for 16 h. The solution was concentrated *in vacuo* and the residue extracted with hexane through a short alumina plug to afforded the product as a white microcrystalline powder. Yield: 20.3 mg (80% / HCCPh, 84% / **2**).

Characterisation data are in excellent agreement with that previously reported for this compound.[8]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 – 7.57 (m, 10H, Ph), 7.05 (d, $^3J_{HH}$ = 16.3, 1H, CH), 6.39 (d, $^3J_{HH}$ = 16.2, 1H, CH).

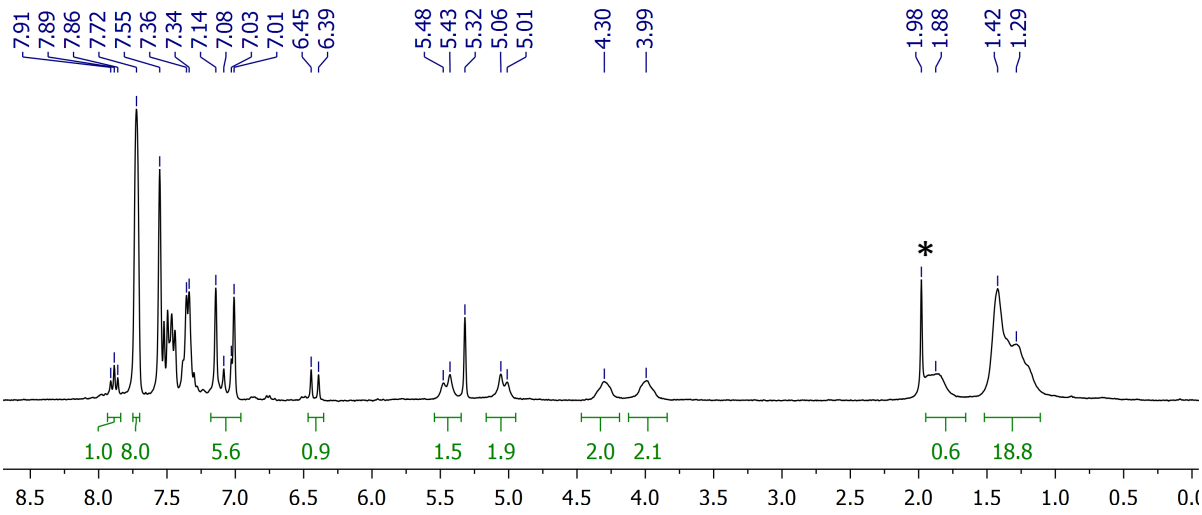


Figure S56: ^{1}H NMR spectrum of reaction mixture containing both [Rh(CNC-12)(CO)][BAr^F_4] **4** and *E*-PhCCCHCHPh (CD_2Cl_2, 300 MHz), * = MeCN

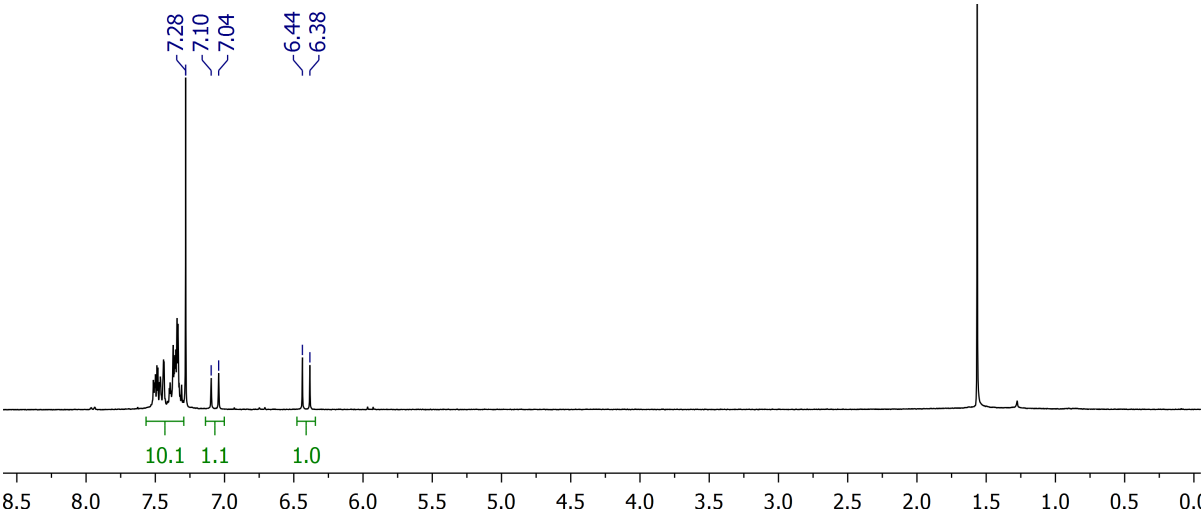


Figure S57: ^{1}H NMR spectrum of isolated *E*-PhCCCHCHPh ($CDCl_3$, 300 MHz)

15 References

[1] S. Gründemann, M. Albrecht, J. A. Loch, J. W. Faller, R. H. Crabtree, *Organometallics* **2001**, *20*, 5485–5488.

[2] R. E. Andrew, C. M. Storey, A. B. Chaplin, *Dalton Trans.* **2016**, *45*, 8937–8944.

[3] R. Cramer, J. A. McCleverty, J. Bray, *Inorg. Synth.* **1990**, *28*, 86–88.

[4] R. Zhang, X. Hao, X. Li, Z. Zhou, J. Sun, R. Cao, *Cryst. Growth Des.* **2015,** *15*, 2505–2513.

[5] W. E. Buschmann, J. S. Miller, K. Bowman-James, C. N. Miller, *Inorg. Synth.* **2002**, *33*, 83–91.

[6] R. E. Andrew, A. B. Chaplin, *Inorg. Chem.* **2015**, *54*, 312–322.

[7] R. E. Islas, J. Cárdenas, R. Gaviño, E. García-Ríos, L. Lomas-Romero, J. A. Morales-Serna, *RSC Adv.* **2017**, *7*, 9780-9789.

[8] M. J. Dabdoub, V. B. Dabdoub, J. V. Comasseto, *Tetrahedron Lett.* **1992**, *33*, 2261-2264.