Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

A star-shaped ruthenium complex with five ferrocenyl-terminated arms bridged by *trans*-platinum fragments

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Experimental Part

All commercially available chemicals were of reagent grade and were used without further purification. Ethynylferrocene and *trans*-dichlorobis(triethylphosphine)platinum(II) were purchased from Aldrich. Ruthenium carbonyl and 1,2,3,4,5-pentaphenylcyclopentadiene were purchased from Strem. 1-bromo-1,2,3,4,5-penta(*p*-bromophenyl)cyclopentadiene (**3**) was prepared according to a literature procedure (A. Carella, J. Jaud, G. Rapenne, J. P. Launay, *Chem. Commun.* 2003, 2434). Toluene was dried over CaH_2, THF over sodium with benzophenone and diethylamine over KOH. All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Flash column chromatography was carried out on silica gel 230-400 mesh from SDS. NMR Spectra were recorded on Bruker AM 250 or Avance 500 spectrometers and full assignments were made using COSY, ROESY, HMBC and HMQC methods. Chemical shifts are defined with respect to TMS = 0 ppm for ^{1}H and ^{13}C NMR spectra and to H_3PO_4 for ^{31}P NMR spectra and were measured relative to residual solvent peaks. The following abbreviations have been used to describe the signals: s for singlet; d for doublet; t for triplet; q for quadruplet; m : for multiplet.

UV-Visible-Near Infra-Red spectra were recorded on a Shimadzu UV-3100 spectrometer. FAB and DCI mass spectrometry was performed using a Nermag R10-10. Cyclic voltammetry was performed with an AUTOLAB PGSTAT 100 potentiostat using a Pt disc (1mm diameter) as working electrode and a Pt counter electrode. The reference electrode used was the saturated calomel electrode (SCE).

1,2,3,4,5-penta(4-(triisopropylsilylacetylene)phenyl)cyclopentadiene (4)

In a Schlenk tube, 1-bromo-1,2,3,4,5-penta(4-bromophenyl)cyclopentadiene (**3**) (300 mg, 0.32 mmol, 1 eq), TIPSA (1.4 mL, 6.4 mmol, 20 eq), diisopropylamine (2 mL) and freshly distilled THF (4 mL) were degassed under argon during 20 min. CuI (12 mg, 0.06 mmol, 20 mol %) and $Pd(PPh_3)_4$ (40 mg, 0.03 mmol, 10 mol %) were added and the mixture was heated

at 80°C overnight. The same amounts of additional CuI, TIPSA and Pd^0 were added and the mixture was heated at 80°C for another 24 hours. Solvents were removed under reduced pressure and the crude material was column chromatographed (SiO_2, cyclohexane/CH_2Cl_2 (0-10%)) to give a fluorescent yellow glassy solid (350 mg, 81 %). MS: (DCI/NH_3) 1349 $[MH]^+$, 1381 $[M+2NH_3]^+$; High Resolution LSI Calculated $[M]^+$: 1346.8706 ($C_{90}H_{126}Si_5$) Found: 1346.8687 (100% $[M]^+$). ^{1}H NMR: (250 MHz, CD_2Cl_2) δ 7.34 (d, 6H, J = 8 Hz, H_{b-f}), 7.21 (d, 4H, J = 8 Hz, H_d), 7.17 (d, 2H, J = 8 Hz, H_a), 7.02 (d, 4H, J = 8 Hz, H_e), 6.96 (d, 4H, J = 8 Hz, H_c), 5.16 (s, 1H, H_g), 1.14 (m, 105 H, TIPS); ^{13}C NMR: (100 MHz, CD_2Cl_2) δ 146.80; 144.11; 137.92; 135.71; 135.23; 132.37; 131.74; 131.49; 129.95; 128.76; 128.30; 122.24; 122.02; 121.74; 106.83; 106.78; 106.72; 91.34; 91.23; 90.57; 62.11; 18.43; 18.39; 11.30; 11.26.

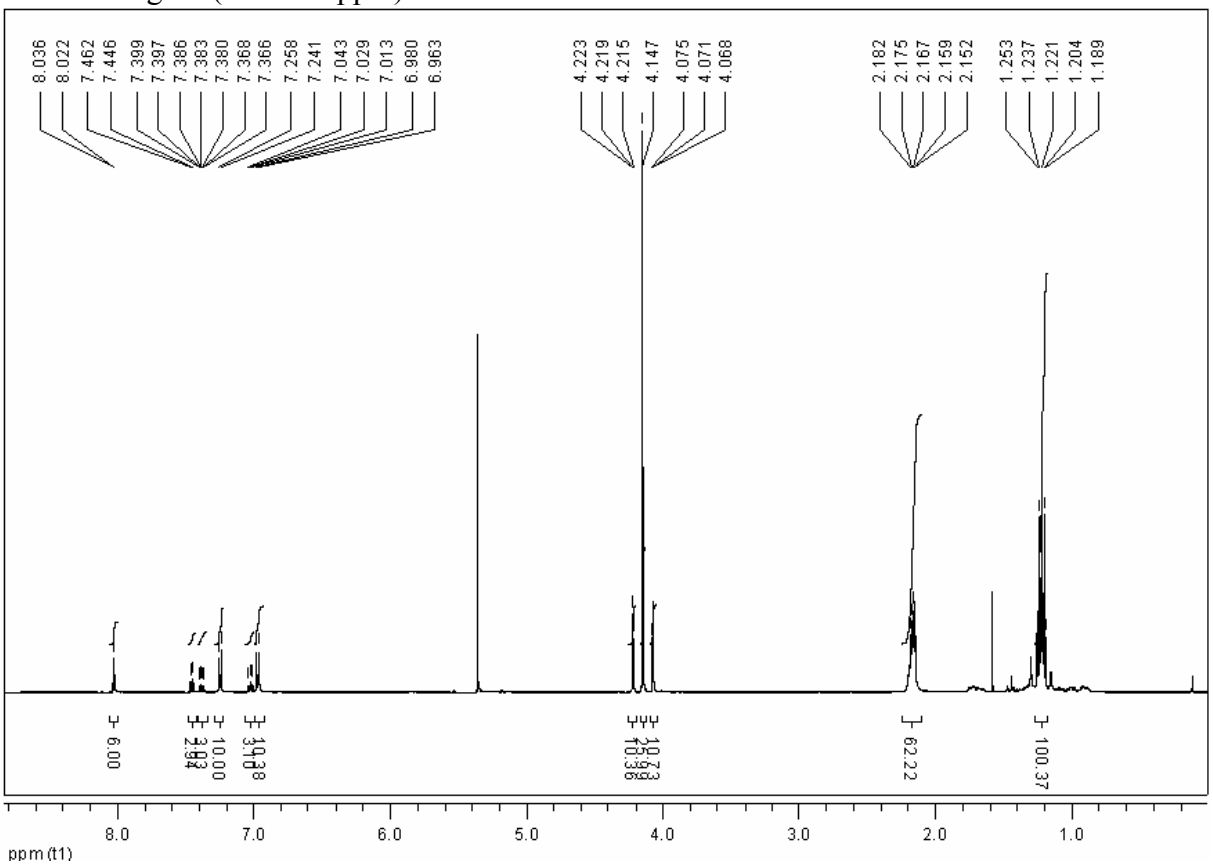
η^5-1,2,3,4,5-penta[4-{*trans*-ethynyl-(ethynylferrocenyl)-bis(triethylphosphine)platinum(II)} phenyl] cyclopentadienyl hydrotris(indazol-1-yl)borate ruthenium(II) (1)

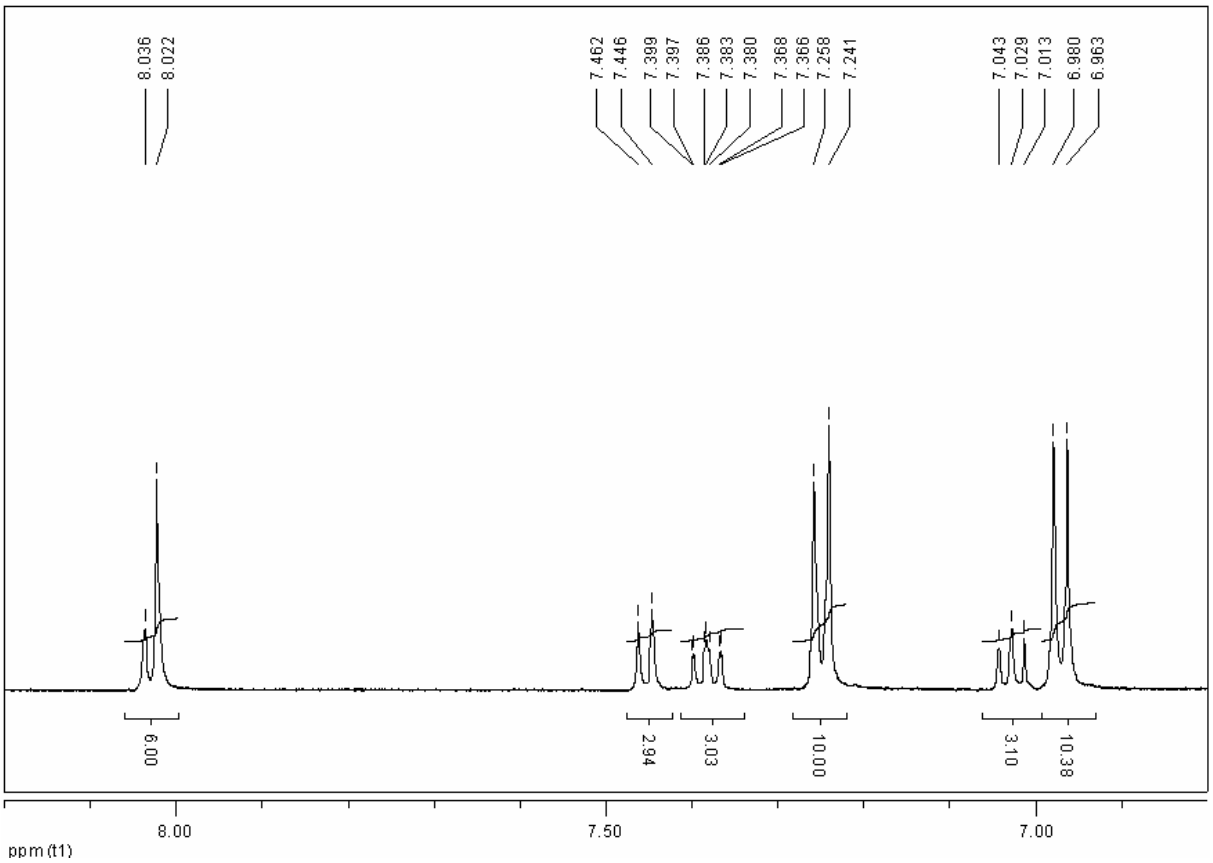
In a Schlenk tube, η^5-1,2,3,4,5-penta(4-(ethynyl)phenyl)cyclopentadienyl hydrotris(indazol-1-yl)borate ruthenium(II) freshly prepared (**8**) (12 mg, 0.011 mmol, 1 eq), THF (2 mL) and diethylamine (1 mL) were degassed under argon during 20 min. *Trans*-chloro-(ferrocenylethynyl)-bis(triethylphosphine)platinum(II) (**2**) (50 mg, 0.073 mmol, 6.3 eq) and CuI (2 mg, 0.010 mmol, 0.9 eq) were added and the mixture was stirred at room temperature for 8 hours. The same amounts of additional CuI and platinum complex were added and the solution was stirred at room temperature overnight. Solvents were removed under reduced pressure and the crude material was column chromatographed (SiO_2, cyclohexane/Et_2O (0-20 %)) to give an orange solid (20 mg, 41%). MS: (ES/MS) 2113 $[M]^{2+}$, 1409 $[M]^{3+}$; (MALDI-TOF) 4226.2 $[M]^+$ (calc 4226.98); ^{1}H NMR: (500 MHz, CD_2Cl_2) δ 8.04 (d, 3H, J = 6.8 Hz, H_e), 8.02 (s, 3H, H_a), 7.45 (d, 3H, J = 8.7 Hz, H_b), 7.38 (m, 3H, H_c), 7.25 (d, 10H, J = 8.5 Hz, H_1), 7.03 (t, 3H, J = 7.6 Hz, H_d), 6.97 (d, 10H, J = 8.5 Hz, H_2), 4.22 (t, 10H, J = 1.8 Hz, subst. Cp), 4.15 (s, 25H, Cp), 4.07 (t, 10H, J = 1.8 Hz, subst. Cp), 2.17 (m, 60H, CH_2) 1.22 (m, 90H, CH_3); ^{13}C NMR: (125 MHz, CD_2Cl_2) δ 143.37; 140.31; 133.24; 130.92; 129.61; 127.69; 126.01; 123.06; 120.03; 119.98; 111.36; 109.21; 108.78; 104.86; 102.62; 87.52; 72.95; 70.09; 69.31; 66.97; 16.23; 8.15; ^{31}P NMR: (200 MHz, CD_2Cl_2) δ 11.30 (s, $J_{^{195}Pt\text{-}P}$ = 2374 Hz); ^{195}Pt NMR: (500 MHz, CD_2Cl_2) δ - 4742; UV/Vis (CH_2Cl_2; λ_{max} (ε)=264 (225000),

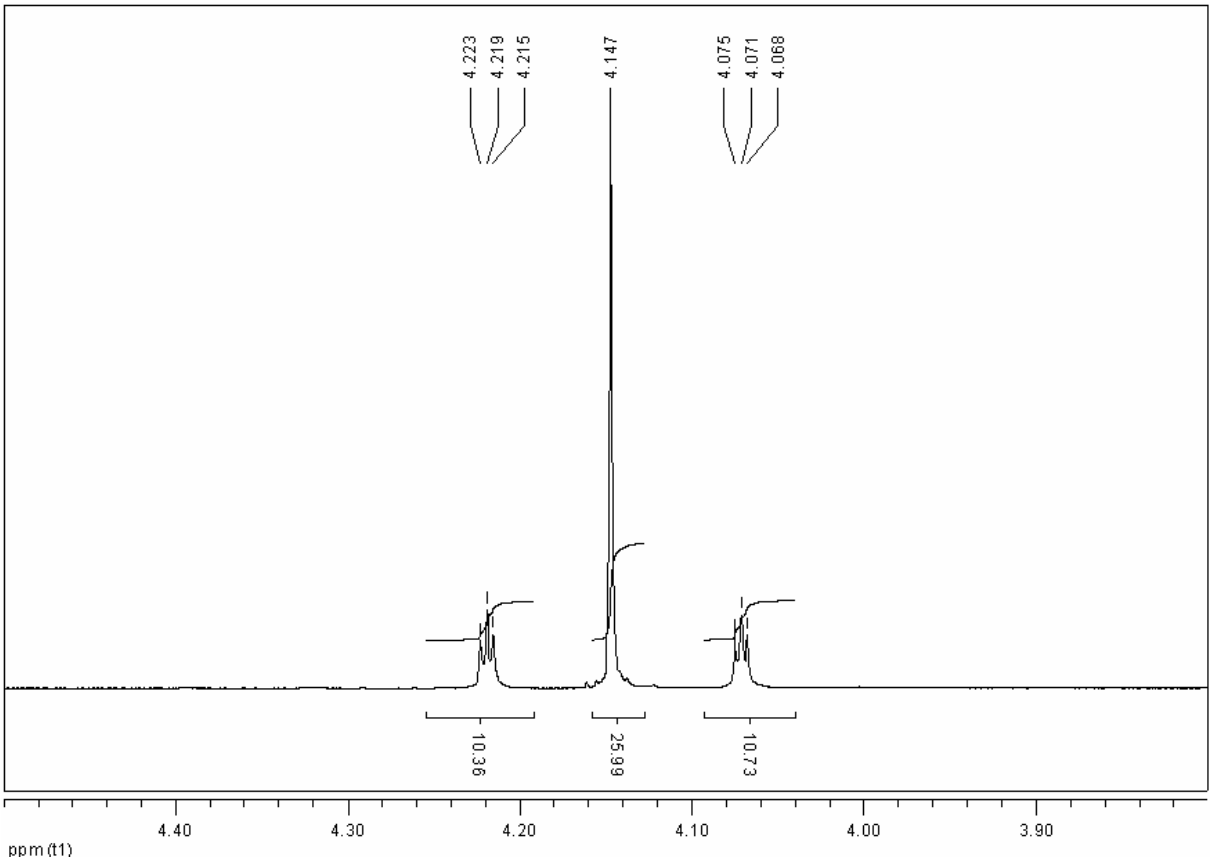
306 (169200), 359 (58000), 436 (10400). CV(CH_2Cl_2, $^nBu_4NPF_6$,), $E_{Fe(II)-Fe(III)}$ (V/SCE): +0.31 rev, (5 e) ; $E_{Ru(II):Ru(III)}$ (V/SCE): 0.60 rev (1 e) (Sweep rate: 100 $mV.s^{-1}$). UV/Vis λ_{max}/nm (ε in $mol^{-1}.L.cm^{-1}$): (CH_2Cl_2) 231 (133000), 265 (85300), 292 (95500), 348 (135000).

Spectral characterization data of 1

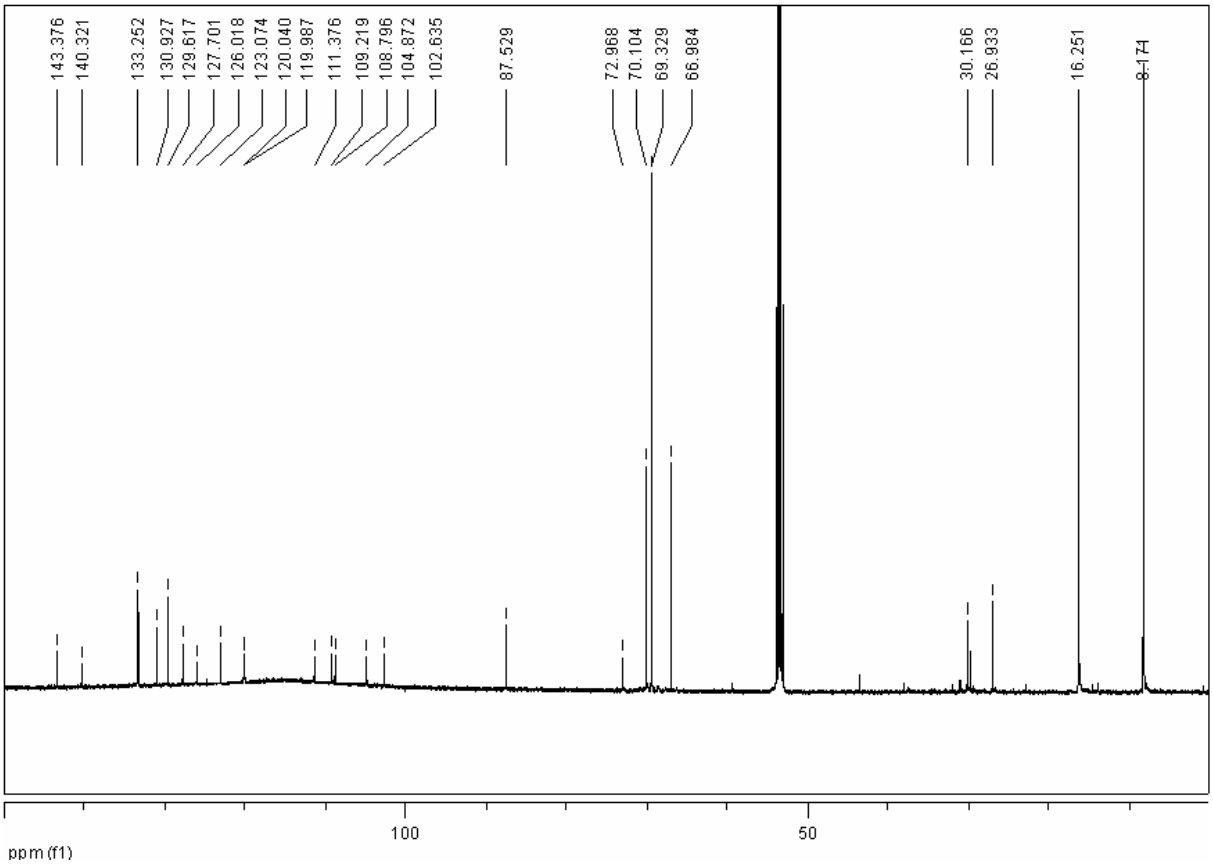
^{1}H-NMR : Full spectrum and zoom on the ferrocene region (4.1 - 4.6 ppm) and on the aromatic region (6.9 - 8.1 ppm)



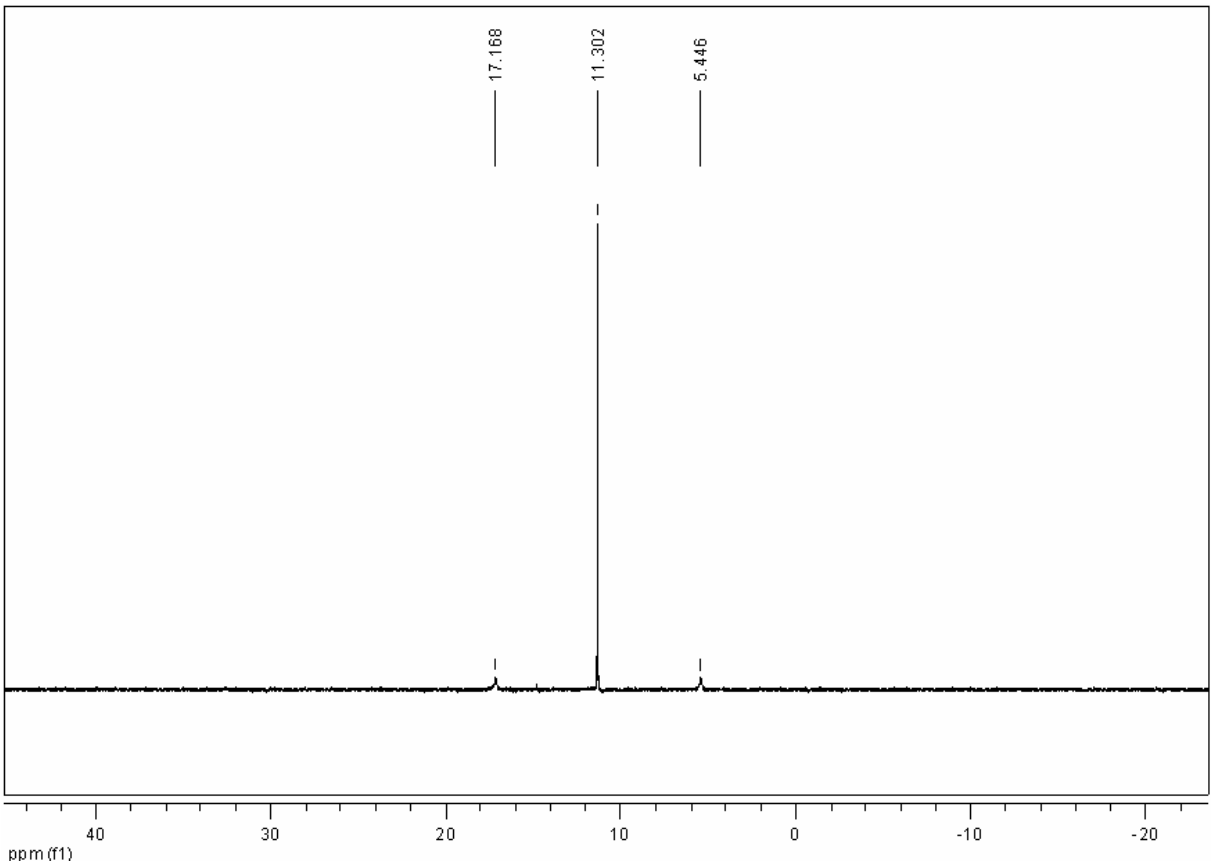




^{13}C-NMR



^{31}P-NMR



^{195}Pt-NMR