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Synthesis of a Diferrocenylvinylidene Complex by Migration of a Ferrocenyl Substituent

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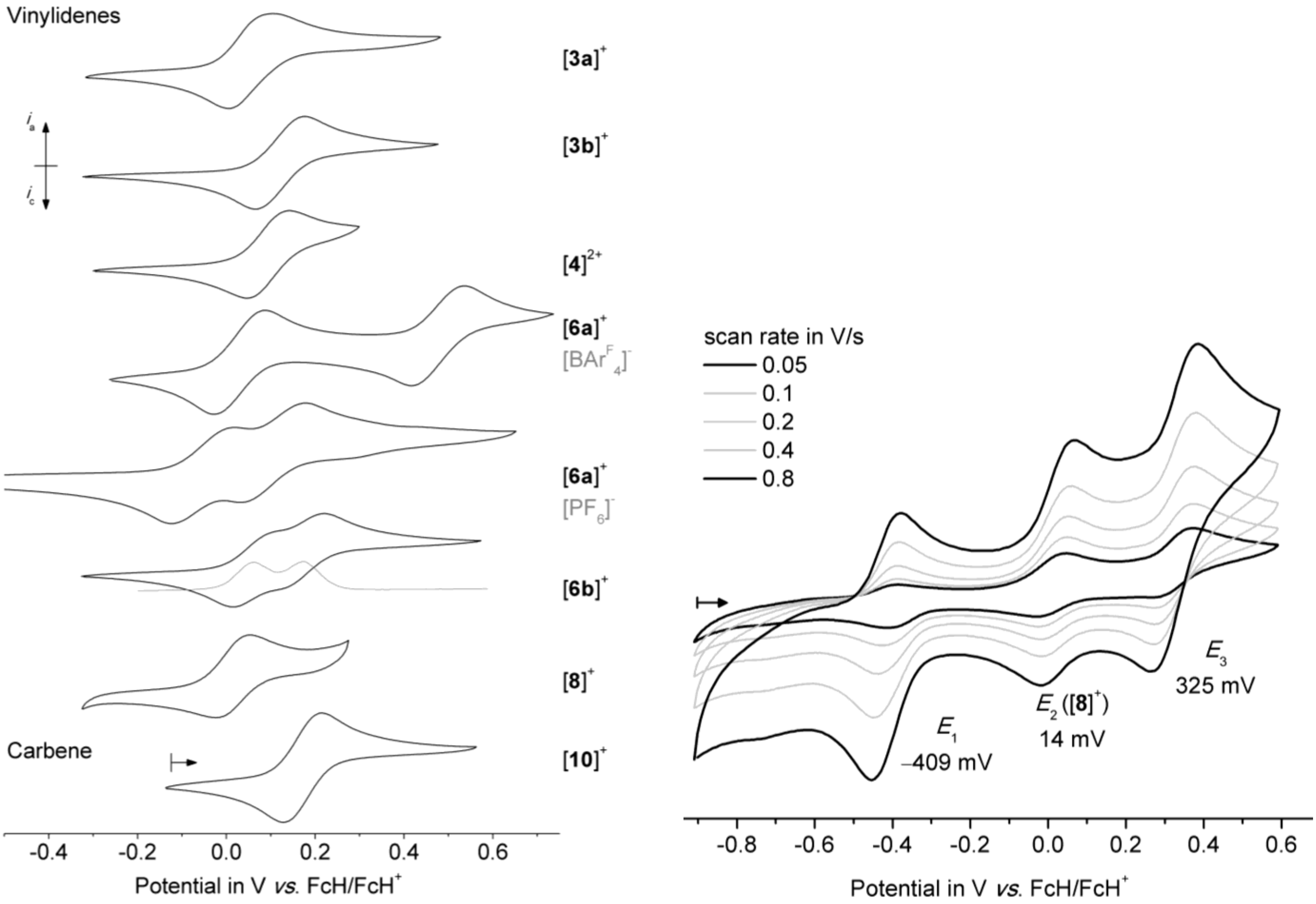

Figure S1. Left: cyclic voltammograms of the ferrocenyl-related redox processes in [**3a**,**b**]$^+$, [**4**]$^{2+}$, [**6a**,**b**]$^+$, [**8**]$^+$ and carbene [**10**]$^+$ measured in CH_2Cl_2 solutions at 25 °C with 0.1 mol·L^{-1} [NBu_4][BAr^F_4] or [NBu_4][PF_6] (if noted) electrolyte solution. (Scan rates: 100 mV·s^{-1}; GC working electrode; grey: square-wave voltammogram.) Right: cyclic voltammograms of the electrolyte solution of compound [**8**]$^+$ after several cycles (for measurement conditions, see: left). The shown CV represent the 7th cycle of each scan rate, after which no further change of the relative current could be observed.

Note: While focusing on the Fc/Fc$^+$-related event in [**8**]$^+$ did not cause a decomposition of the compound. Measurements towards the region in which the first and third process occurred, however, increased the currents for the decomposition products gradually until the shown ratio was observed. At the end of the measurements the electrode surface was partially covered with deposited/decomposed material, which might explain the appearance of the two additional redox events at –409 and 325 mV.

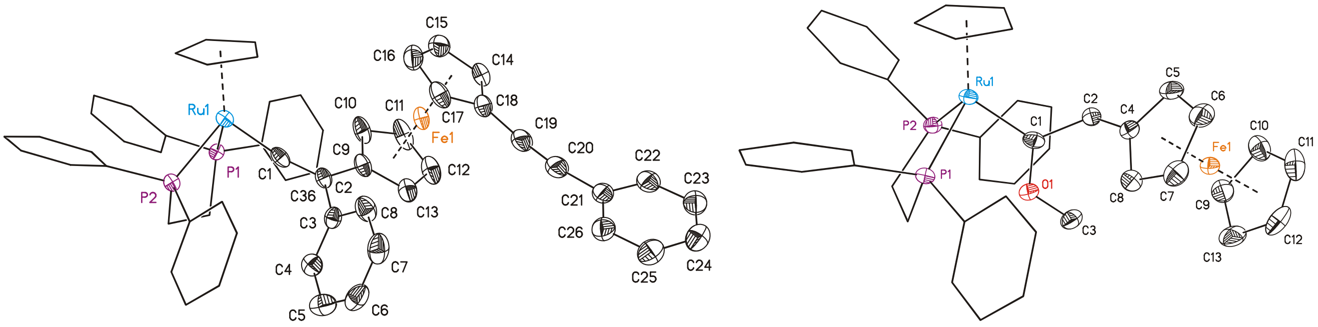

Figure S2. ORTEP (50 % probability level) of vinylidene [**3b**][BAr$^{F}_{4}$] (left) and carbene [**10**][BAr$^{F}_{4}$] (right) showing their atom labelling. H atoms and the [BAr$^{F}_{4}$]$^{-}$ counter ion are omitted for clarity.

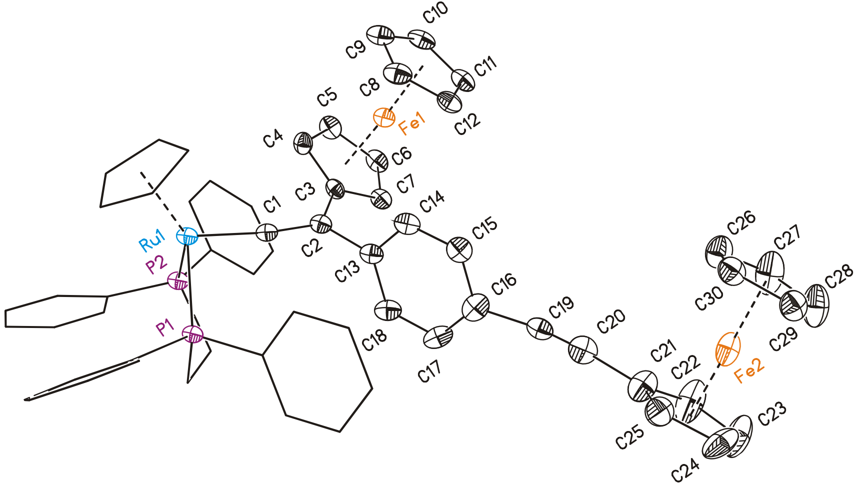

Figure S3. ORTEP (30 % probability level) of [**6b**][BAr$^{F}_{4}$] showing the labelling of the vinylidene ligand. H atoms and the [BAr$^{F}_{4}$]$^{-}$ counter ion are omitted for clarity.

Table S1. Selected bond properties (°/Å) of : [**3b**]$^{+}$, [**6a**]$^{+}$, [**6b**]$^{+}$, [**7**]$^{2+}$ and [**10**]$^{+}$.

Compound	[**3b**]$^{+}$	[**6a**]$^{+}$	[**6b**]$^{+}$	[**7**]$^{2+}$	[**10**]$^{+}$
Substitution pattern	*vinylidene*				*carbene*
R1	Ph	Fc	Fc	Fc	CH$_2$Fc
R2	Fc(CCPh)	Fc	Ph(CCFc)	C$_6$H$_4$*	OMe
distances					
Ru1=C1	1.855(3)	1.840(3)	1.857(5)	1.843(3)	1.948(2)
C1=C2	1.314(4)	1.337(11)	1.314(7)	1.311(4)	1.516(3)
C–R1	1.505(4)	1.482(11)	1.486(7)	1.475(5)	1.516(3)
C–R2	1.478(4)	1.433(12)	1.505(8)	1.498(5)	1.337(2)
Ru–Cp	1.9237(2)	1.9145(6)	1.9180(4)	1.9109(3)	1.9207(1)
Fe–Cp’	1.6627(5)	1.6539(12)	1.6520(8)	1.6445(5)	1.6465(3)
Fe–Cp	1.6629(5)	1.6394(11)	1.6657(9)	1.5935(5)	1.6479(3)
Ru–P	2.2912(7)	2.297(2)	2.3128(13)	2.2901(10)	
	2.3161(7)	2.295(2)	2.2973(13)	2.2741(9)	
angles					
R1–C–R2	118.4(3)	121.6(7)	116.7(4)	118.6(3)	115.02(18)
torsion angles and plane intersections					
C2–C1–O1–C3					11.0(3)
O1–C1–C2–C4					85.0(2)
RuCpC1···C1C2O1	76.31(19)	60.0(4)	72.8(3)	61.82(15)	8.7(4)

Experimental Details

General. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Unless stated otherwise, no particular care was taken to exclude air upon work-up of reaction products. Reaction flasks were heated at reduced pressure with a heat gun and flushed with nitrogen. This procedure was repeated thrice. If necessary, solvents were deoxygenated by standard procedures. For column chromatography silica with a particle size of 60 μm was used.

Reagents. Tetrahydrofuran, dichloromethane, hexane and toluene were dried and purified with an Innovative Technologies Solvent Purification System and stored over molecular sieve (4 Å). Alkynes and ferrocenyl derivatives were synthesized according to published procedures (see below). Further starting materials were purchased from commercial suppliers and used without further purification, except otherwise noted. Characterization of compound [**4**][BAr^F_4] has recently been described by our group.[2] An additional solid state structure is given in the Supporting Information. The synthetic procedure for **1**,[1] which is frequently synthesized in our working group, follows those reported in literature. The synthesis of Na[BAr^F_4] has been synthesized and purified according to our recently reported procedure.[2] We thank the group of Prof. H. Lang for the shipment of iodoferrocene.

Instruments. *FT-IR* spectra were recorded on an Agilent Cary 630 FTIR spectrometer sing ATR or transmission mode from solutions between CaF_2 plates. *NMR* spectra were recorded on a Bruker Avance Neo 400 MHz (^{1}H: 400.13 MHz, ^{13}C: 100.63 MHz, ^{31}P: 161.97 MHz, ^{19}F: 376.46 MHz), Bruker Avance IIIHD 500 MHz (^{1}H: 500.10 MHz, ^{13}C: 125.8 MHz, ^{31}P: 202.4 MHz, ^{19}F: 470.6 MHz, ^{11}B: 160.5 MHz) and Bruker Avance IIIHD 600 MHz (^{1}H: 600.10 MHz, ^{13}C: 150.9 MHz, ^{31}P: 242.9 MHz) spectrometers at room temperature. They are reported with chemical shifts in δ (ppm) units downfield from tetramethylsilane with the solvent as the reference signal (chloroform-d_1: ^{1}H at 7.26 ppm and ^{13}C{^{1}H} at 77.16 ppm, benzene-d_6: ^{1}H: 7.16 ppm and ^{13}C{^{1}H} 128.06 ppm) or by the ^{2}H solvent lock signal[3] unless otherwise noted. For all NMR spectra, multiplets are reported according to their closest first order approximation. Signals referring to ferrocenyl-based C_5H_4 groups are reported as pseudo-triplets (pt). *High-resolution Mass* spectra were recorded on a Waters Liquid 369 Chromatograph Premier Mass Spectrometer, using positive mode electrospray ionization (ESI(+)). Samples were prepared in MeCN and inserted by direct injection via the on-board injector. *Elemental analyses* were performed with a ThermoFlash 2000 device at the London Metropolitan University with acetanilide as the standard.

Single crystal X-ray diffraction analysis. Data were collected with a Rigaku-Oxford Gemini, Xcalibur diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å) and a Rigaku-Oxford Diffraction XtaLAB Synergy-S diffractometer using a micro-focus sealed Cu K_α radiation (λ = 1.54184 Å) X-ray source at 100 K. The molecular structures were solved by direct methods using SHELXS-18[4] and refined by full-matrix least-squares procedures on F^2 using SHELXL-18.[5,6] All non-hydrogen atoms were refined anisotropically and a riding model was employed in the treatment of the hydrogen atom positions, except otherwise noted. Graphics of the molecular structures have been created by using ORTEP.[7]

Further crystallographic data have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data with CCDC numbers 2056667 ([**3b**][BAr^F_4]), 2056668 ([**6a**][BAr^F_4]·$CHCl_3$), 2056669 ([**6b**][BAr^F_4]), 2056670 ([**7**][BAr^F_4]$_2$·2 $CHCl_3$*), 2056671 ([**10**][BAr^F_4]), and 2056672 ([Ru(CO)(dppe)Cp][BAr^F_4]) can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.KCB21EZ, UK (fax +441223336033; email deposit@ccdc.cam.ac.uk). (*Structures have been refined using the SQUEEZE procedure implemented in the PLATON program package, the omitted volume is given below.[8])

Electrochemistry. Cyclic voltammetry was carried out by using a PalmSens Emstat^{3+} potentiostat, with a glassy-carbon working, platinum counter and pseudo-reference electrodes, from solutions in oxygen-free anhydrous dichloromethane containing 0.1 *M* $[NBu_4][BAr^F_4]$ or 0.1 *M* $[NBu_4][PF_6]$ as the electrolyte, scan rate = 100 $mV \cdot s^{-1}$. The presented results are reported against ferrocene as an internal standard as required by IUPAC.[9] Referencing was achieved by addition of decamethylferrocene as an internal standard.[10] The latter has been measured together with ferrocene and its redox potential was set to –626 mV ($\pm$1 mV; E_{step} = 2 mV) for $[NBu_4][BAr^F_4]$ and –565 mV ($\pm$1 mV; E_{step} = 2 mV) for a $[NBu_4][PF_6]$ electrolyte solution. These values represent the average of 5 consecutive measurements, which were all found within the given precision. Data have been processed with the PSTrace 4.8 software and Microsoft Excel to set the formal reduction potentials of the FcH/FcH^+ couple to 0.0 V.[11]

Synthesis of Compounds

$PdCl_2(PPh_3)_2$

The synthesis is based on a published procedure.[12] $PdCl_2$ (1.00 g, 5.64 mmol) and PPh_3 (3.25 g, 12.39 mmol) were dissolved in 30 mL of benzonitrile and degassed for 5 minutes using nitrogen. The mixture was heated to 180 °C and hold at this temperature for 20 min after which is was allowed to cool to ambient temperature. The yellow solid was separated by filtration and the residue washed with dichloromethane until the filtrate is colourless. The product was dried on air or vacuum. Yield: 3.50 g (4.99 mmol, 88 %).

General procedure for the Synthesis of internal alkynes 2a,b and 5a,b via Sonogashira C,C cross-coupling reactions.

Phenylacetylene (0.53 mL, 4.8 mmol), the respective haloarene (4.8 mmol), $PdCl_2(PPh_3)_2$ (84 mg, 0.12 mmol), CuI (23 mg, 0.12 mmol) were stirred in NEt_3 (15 mL) at ambient temperature (iodoarene) or at 75 °C (bromoarenes) for 18 h. The reaction mixture was poured into HCl-acidified water and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were dried over $MgSO_4$. After removal of all volatiles the respective alkynes were purified using column chromatography (silica) using different hexane/CH_2Cl_2 solvent mixtures (see below).

Phenylethynylferrocene (**2a**)[13]

Ethynylferrocene (**9**, 500 mg, 2.38 mmol), iodobenzene (0.27 mL, 2.41 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol) and CuI (15 mg, 0.08 mmol) were reacted at 60 °C according to the general procedure. Column chromatography (silica, 3.5 x 13 cm) with hexane removed iodobenzene. Changing to a 3:7 hexane/dichloromethane mixture eluted the product.

Yield 625 mg (2.18 mmol, 92 %). Spectroscopic data are in agreement with those reported in literature.[14] ^1H NMR ($CDCl_3$, δ): 4.24–4.25 (m, 7 H, C_5H_5, C_5H_4), 4.51 (pt, $J_{H,H}$ = 1.8 Hz, 2H, C_5H_4), 7.30–7.34 (m, 3H, C_6H_5), 7.48–7.50 (m, 2H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 65.4 (^qC), 68.9 (C_5H_4), 70.1 (C_5H_5), 71.6 (C_5H_4), 85.9 (C≡C), 88.4 (C≡C), 124.1 (^qC), 127.8 (*p*-C_6H_5), 128.4 (C_6H_5), 131.5 (C_6H_5) ppm.

1,1'-Bis(phenylethynyl)ferrocene (**2b**)

1,1'-Diiodoferrocenece (300 mg, 0.685 mmol), phenylacetylene (0.3 mL, 2.74 mmol), $PdCl_2(PPh_3)_2$ (48 mg, 0.069 mmol) and CuI (26 mg, 0.137 mmol) were reacted in diisopropylamine (20 mL) at 30 °C for

36 h according to the general procedure. After 1 d, $PdCl_2(PPh_3)_2$ and CuI were added again (same amounts). The work-up follows a very precise procedure[15] using a 4:1 hexane/dichloromethane solvent mixture (silica, 3.5 x 20 cm), which eluted the product as the third orange fraction.

Alternatively: the crude material was extracted twice with small amounts of a 8:2 hexane/diethyl ether mixture, which removed the more soluble starting material and by-products. These solutions could further be purified by column chromatography, as described above. The remaining solid contains the product.

Yield: 214 mg (0.554 mmol, 81 %). Spectroscopic data are in agreement with those reported in literature.[16] ^1H NMR ($CDCl_3$, δ): 4.33 (pt, $J_{H,H}$ = 1.8 Hz, 4H, C_5H_4), 4.55 (pt, $J_{H,H}$ = 1.8 Hz, 4H, C_5H_4), 7.25–7.29 (m, 6H, C_6H_5) , 7.42–7.44 (m, 4H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 67.2 ($^qC_5H_4$), 71.1 (C_5H_4), 73.2 (C_5H_4), 86.7 (C≡C), 87.4 (C≡C), 123.9, 127.8, 128.4, 131.6 ppm.

Diferrocenylacetylene (**5a**)

Ethynylferrocene (**9**, 252 mg, 1.2 mmol), iodoferrocene (338 mg, 1 mmol) $Pd_2(dba)_3$ (7 mg, 1 mol-%), and KO^{t}Bu (224 mg, 2 mmol) were reacted in a 4:1 mL DMF/H_2O solvent mixture at 80 °C for 1 h according to a published procedure.[17] Afterwards, the reaction mixture is poured into ice-cold HCl-acidified water, and extracted with a 1:1 hexane/dichloromethane mixture until the organic phase is colourless. The combined organic phases are filtered through a plug of celite. Column chromatography (silica, 3.5 x 15 cm) using a 1:1 hexane/dichloromethane mixture gave **5a** as an orange solid.

Yield: 150 mg (0.38 mmol, 32 %). ^1H NMR ($CDCl_3$, δ): 4.20 (t, $J_{H,H}$ = 1.9 Hz, 4H, C_5H_4), 4.23 (s, 10H, C_5H_5), 4.45 (t, $J_{H,H}$ = 1.8 Hz, 4H, C_5H_4) ppm.

1,4-Bis(ferrocenylethynyl)benzene (**5b**)

Ethynylferrocene (**9**, 210 mg, 1 mmol), 1,4-diiodobenzene (164 mg, 0.5 mmol), $PdCl_2(PPh_3)_2$ (18 mg, 0.025 mmol), and CuI (10 mg, 0.025 mmol) were reacted in a 1:1 mixture of NEt_3 and THF according to the general procedure. Upon the acidic aqueous work-up dichloromethane was used for extraction. The organic phase was dried over $MgSO_4$, whereby boiling dichloromethane was required to dissolve the product.

Yield: 185 mg (0.352 mmol, 70 %). Spectroscopic data are in agreement with those reported in literature.[18] ^1H NMR ($CDCl_3$, δ): 4.25–4.26 (m, 14H, C_5H_5, C_5H_4), 4.51 (pt, $J_{H,H}$ = 1.8 Hz, 4H, C_5H_4), 7.43 (s, 4H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 13C: 65.2 (^qC), 69.1 (C_5H_4), 70.1 (C_5H_5), 71.6 (C_5H_4), 85.8 (C≡C), 90.3 (C≡C), 123.3 (^qC), 131.4 (C_6H_4) ppm.

Synthesis of Ethynylferrocene (**9**): The synthesis follows published procedures[19]

a) (2-Formyl-1-chlorovinyl)ferrocene

Acetyl ferrocene (7.5 g, 33 mmol) were placed in a 250 mL three-necked round bottom flask, dissolved in 33 mL of *N*,*N*-dimethylformamide (DMF) and cooled to 0 °C. In an additional round bottom flask 10 mL of DMF are cooled to 0 °C followed by dropwise addition of $POCl_3$ (12.5 mL, 137 mmol) to maintain the temperature. After stirring for 1 hour, the yellow solution is transferred into a dropping funnel and slowly added to the mixture containing the ferrocenyl substrate. After complete addition the resulting solution is stirred for additional 2 hours. The dropping funnel is replaced by a reflux condenser through which 30 mL of diethyl ether are added to the blue mixture. A solution of sodium citrate trihydrate (38 g) in 7 mL of water is prepared and carefully added constant cooling to this mixture. After complete addition the mixture is stirred for 48 h, which changes the colour of the solution to red. The mixture is poured into a separatory funnel, the ethereal phase separated and the aqueous phase extracted with diethyl ether (4 times 100 mL). The combined organic phases were washed with a saturated $NaHCO_3$ solution, followed by water and subsequently dried over $MgSO_4$. Removal of all volatiles gave a red solid. (Note: the initial aqueous phase can be treated with further amounts of sodium citrate (half the amount as before) and diethyl ether, stirred overnight and worked-up as above, which gives further product).

Yield: 6.2 g (22.6 mmol, 68 %). ^{1}H NMR ($CDCl_3$, δ): 4.24 (s, 5H), 4.56 (pt, $J_{H,H}$ = 2.0 Hz, 2H), 4.75 (pt, $J_{H,H}$ = 2.0 Hz, 2H), 6.40 (d, $^3J_{H,H}$ = 7.1 Hz, 1H), 10.09 (d, $^3J_{H,H}$ = 7.1 Hz, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 69.0, 70.9, 72.4, 80.2, 120.7, 155.4, 190.9 ppm.

b) Ethynylferrocene

1,4-Dioxane (40 mL) were heated to reflux and (2-Formyl-1-chlorovinyl)ferrocene (6.0 g, 21.9 mmol) was added and refluxed for 5 minutes. A aqueous NaOH solution was prepared (1 *M*, 58 mL) and carefully added through the reflux condenser. (Note: the boiling point of dioxane is higher than of water, which causes a heavy boiling during the beginning of the addition. Slight cooling of the dioxane mixture is recommended). After additional 25 min of reflux the mixture was allowed to cool to ambient conditions where stirring was continued overnight. The reactions mixture is poured into ice-water and carefully neutralized with 1 *M* HCl. The emulsion is extracted several times with hexane (small amounts of diethyl ether can be added). All organic phases are combined washed with $NaHCO_3$ solution, dried over $MgSO_4$ and evaporated to dryness. The crude, purple material is purified using column chromatography (silica, 3.5 x 15 cm column size) with hexane and obtained as an orange solid.

Yield: 3.01 g (14.3 mmol, 65 %). ^{1}H NMR ($CDCl_3$, δ): 2.72 (s, 1H, ≡CH), 4.20 (pt, $J_{H,H}$ = 1.9 Hz, 2H), 4.22 (s, 5H), 4.46 (pt, $J_{H,H}$ = 1.9 Hz, 2H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 64.0, 68.9 (C_5H_4), 70.2 (C_5H_5), 71.9 (C_5H_4), 73.6, 82.7 ppm.

General procedure for the internal alkyne/vinylidene rearrangement

The half-sandwich precursors [RuCl(dppe)Cp] **1** and the respective alkyne were placed in an oven dried Schlenk tube and dissolved in ~5 mL of dried and degassed toluene. Na[BAr$^F{}_4$] was subsequently added and the reaction vessel was placed in an oil bath, preheated to 70 °C (except otherwise noted). The mixture was carefully exposed to vacuum and refilled with nitrogen to remove further dissolved gas, whereby a slight under pressure was set as the final step. The mixture was stirred for 18 h (except otherwise noted). After cooling to ambient temperature, the mixture was transferred onto a hexane silica column, whereby small portions of dichloromethane were used to dissolve solid material. The initial eluent mixture depends on the polarity of the used alkyne, but was usually set to a 6:4 hexane/dichloromethane mixture to remove the excess of the starting material (except otherwise noted). The vinylidene complexes and further by-products were removed using a 3:7 hexane/dichloromethane mixture, except otherwise noted. Afterwards, all volatiles were removed in vacuum.

[Ru(=C=CFcPh)(dppe)Cp][BAr$^F{}_4$] ([**3a**][BAr$^F{}_4$])

[RuCl(dppe)Cp] (**1**, 54 mg, 0.090 mmol), Na[BAr$^F{}_4$] (80 mg, 0.090 mmol), and FcC≡CPh (**2a**, 52 mg, 0.182 mmol) were reacted according to the general procedure, except that the reaction was stopped after 1 hour. During the column chromatographic work-up, **2a** (33 mg, 0.115 mmol, 63 %) was eluted as the first fraction (1:1 hexane/dichloromethane mixture) followed by the title compound [**3a**][BAr$^F{}_4$] (3:7 hexane/dichloromethane mixture), which was obtained as a brown solid after removal of all volatiles. The solid was triturated with pentane and freeze dried in vacuum overnight.

Yield: 155 mg (0.090 mmol, 99 %). EA (%) for $C_{81}H_{55}BF_{24}FeP_2Ru$ (1713.97 g/mol): calcd. C 56.76, H 3.23; found C 56.19, H 3.37 (best match). ^{1}H NMR ($CDCl_3$, *δ*): 2.76–2.93 (m, 4H, CH_2), 3.17 (s, 2H, C_5H_4), 3.87 (s, 2H, C_5H_4), 4.01 (s, 5H, $C_5H_5^{Fc}$), 5.50 (s, 5H, $C_5H_5^{Ru}$), 6.93–6.98 (m, 6H, C_6H_5), 7.06–7.20 (m, 11H), 7.26–7.29 (m, 6H), 7.38–7.42 (m, 2H), 7.51 (s, 4H, BAr^F_4), 7.71 (s, 8H, BAr^F_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, *δ*): 27.9 (dd, $J_{C,P}$ = 25.2, 22.3 Hz, CH_2), 64.8 (br), 91.6 ($C_5H_5^{Ru}$), 117.6 (BAr^F_4), 124.7 (q, $^{1}J_{C,F}$ = 272.6 Hz, CF_3), 128.2–128.9 (m, *m*-BAr^F_4), 129.2–129.3 (m, *m*-dppe), 130.0, 131.4 (dd, $J_{C,P}$ = 5.3, 5.3 Hz, *o*-dppe), 131.7, 131.8–131.9 (m, o-dppe), 134.9 (BAr^F_4), 161.9 (1, $^{1}J_{C,B}$ = 49.8 Hz, C–B) ppm. (The Ru=C carbon could not be resolved). $^{31}P\{^1H\}$ NMR ($CDCl_3$, *δ*): 77. 5 ppm. ESI(+)-HRMS (*m*/*z*): calcd. for $C_{49}H_{43}FeP_2Ru$ 851.1233; found 851.1254 $[M]^+$.

*$[Ru\{=C=C(1'\text{-}(PhC{\equiv}C)C_{10}H_8Fe)Ph\}(dppe)Cp][BAr^F_4]$ (**[3b]**$[BAr^F_4]$) and $[1,1'\text{-}\{Ru(=C=CPh)\ (dppe)Cp\}_2\text{-}C_{10}H_8Fe][BAr^F_4]_2$ (**[4]**$[BAr^F_4]_2$)*

[RuCl(dppe)Cp] (**1**, 108 mg, 0.180 mmol), Na$[BAr^F_4]$ (160 mg 0.180 mmol), and 1,1'-bis(phenylethynyl)ferrocene (**2b**, 91 mg, 0.236 mmol) were reacted according to the general procedure. Upon the column-chromatographic work-up unreacted **2b** (43 mg, 0.111 mmol, 47 %) was recovered while using a 5:5 hexane/dichloromethane solvent mixture. Gradual change towards a 4:6 ratio gave a mixture of both title compounds. The latter was further purified by column chromatography (silica, 3.5 x 20 cm column size) using a 45:55 hexane/dichloromethane solvent mixture, which gave [**3b**]$^+$ followed by [**4**]$^{2+}$.

[**3b**]$[BAr^F_4]$: Orange-red solid. Yield: 202 mg (0.111 mmol, 62 % based on **1**). EA (%) for $C_{89}H_{59}BF_{24}FeP_2Ru$ (1814.09 g/mol): calcd. C 58.93, H 3.28; found C 58.90, H 3.47. ^{1}H NMR ($CDCl_3$, *δ*): 2.67–2.80 (m, 2H, CH_2), 2.82–2.94 (m, 2H, CH_2), 3.21 (s, 2H, C_5H_4), 3.92 (s, 2H, C_5H_4), 4.07 (s, 2H, C_5H_4), 4.34 (s, 2H, C_5H_4), 5.47 (s, 5H, C_5H_5), 6.89–6.94 (m, dppe), 7.05–7.15 (m, 12H), 7.24–7.28 (m, 8H, dppe), 7.33 (d, $^{3}J_{H,H}$ = 6.7 Hz, 2H), 7.38 (t, $^{3}J_{H,H}$ = 7.4 Hz, 2H), 7.47 (dd, $J_{H,H}$ = 6.5, 3.0 Hz, 2H), 7.51 (s, 4H, *p*-BAr^F_4), 7.71 (s, 8H, *o*-BAr^F_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, *δ*): 27.5–27.9 (m, CH_2), 65.8 (C_5H_4), 70.8 (C_5H_4), 71.1 (C_5H_4), 72.8 (C_5H_4), 81.4 (C≡C, HMBC), 91.8 (C_5H_5), 117.6 (*p*-BAr^F_4), 124.7 (q, $^{1}J_{C,F}$ = 272.7 Hz, CF_3), 126.5, 128.3, 128.5, 128.8, 129.1–129.3 (m, dppe), 130.5, 131.4–131.8 (m, dppe), 135.0 (*m*-BAr^F_4), 161.9 (q, $^{1}J_{C,B}$ = 49.9 Hz, C–B), 351 (Ru=C) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, *δ*): 76.4 ppm. ESI(+)-HRMS (*m*/*z*): calcd. for $C_{57}H_{47}P_2Ru$ 951.1564; found 951.1583 $[M]^+$.

Crystal Data for [**3b**]$[BAr^F_4]$: $C_{89}H_{59}BF_{24}FeP_2Ru$, $C_{57}H_{47}FeP_2Ru \cdot C_{32}H_{12}BF_{24}$, M = 1814.03 g·mol^{-1}, orange-red block, 0.185 · 0.177 · 0.114, triclinic, $P\text{–}1$, λ = 1.54184 Å, a = 12.9925(2) Å, b = 17.0979(3) Å, c = 19.4724(3) Å, α = 67.2180(10) °, β = 77.5500(10) °, γ = 89.3470(10) °, V = 3881.93(11) Å^3, Z = 2, ρ_{calcd} = 1.552 Mg·m^{-3}, μ = 4.394 mm^{-1}, F_{000} = 1828, T = 100.0(3) K, θ range 2.528−76.545°, 222031 reflections collected, 15400 independent reflections (R_{int} = 0.1545), 1063 parameters, 1073 restraints, *GooF* = 1.066, $R1$ = 0.0499, $wR2$ = 0.1349 ($I>2\sigma(I)$), $|\Delta\rho|_{\text{max}}$ = 1.613 and –0.905 e·Å^{-3}.

[**4**]$[BAr^F_4]_2$: Orange-red solid. Yield: 35 mg (0.011 mmol, <6 % based on **1**). ^{1}H NMR ($CDCl_3$, *δ*): 2.62–2.72 (m, 8H, CH_2), 2.87 (s, 4H, C_α-C_5H_4), 3.53 (s, 4H, C_β-C_5H_4), 5.28 (s, 10H, C_5H_5), 6.64 (d, $^{3}J_{H,H}$ = 7.3 Hz, 4H, C_6H_5), 6.79–6.84 (m, 8H, dppe), 6.92–6.99 (m, 22H), 7.10–7.14 (m, 4H, dppe), 7.16–7.20 (m, 8H, dppe), 7.31 (t, $^{3}J_{H,H}$ = 7.4 Hz, 4H, dppe), 7.44 (s, 8H, *p*-BAr^F_4), (s, 16H, *o*-BAr^F_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, *δ*): 27.6–27.9 (m, CH_2), 65.7 (br, C_5H_4), 70.6 (br, C_5H_4), 91.4 (C_5H_5), 117.6 (BAr^F_4), 124.7 (q, $^{1}J_{C,F}$ = 272.6 Hz, CF_3), 125.0, 125.3, 126.5, 127.1, 127.7, 128.9 (br), 129.2 (br), 131.2–131.8 (m, dppe), 135.0 (BAr^F_4), 161.9 (q, $^{1}J_{C,B}$ = 49.8 Hz, C–B) ppm. (The Ru=C, and further signals were not unambiguously resolved.) $^{31}P\{^1H\}$ NMR ($CDCl_3$, *δ*): 76.3 ppm. ESI(+)-HRMS (*m*/*z*): calcd. for $C_{88}H_{76}P_4Ru_2/2$ 758.1177; found 758.1156 $[M]^{2+}$.

*[Ru(=C=CFc$_2$)(dppe)Cp][BAr$^F_4$] ([**6a**][BAr$^F_4$])*

[RuCl(dppe)Cp] (**1**, 108 mg, 0.180 mmol), Na[BAr$^F_4$] (160 mg, 0.180 mmol) and diferrocenylacetylene (**5a**, 160 mg, 0.231 mmol) were reacted according to the general procedure. Purification was achieved using column chromatography (silica, 3.5 x 15 cm column size). Starting with a 6:4 hexane/dichloromethane mixture gave unreacted **5a** (61 mg, 0.155 mmol, 67 %). The eluent mixture was gradually changed towards a 4:6 solvent mixture, which gave [**6a**][BAr$^F_4$] (Note: traces of [{Ru(dppe)Cp}$_2$(μ-dppe)][BAr$^F_4$]$_2$ could not be removed.). Removal of all volatiles gave the title compound as brown solid. Single crystals were obtained by layering a CHCl$_3$ solution with hexane at –30 °C.

Yield: 51 mg (0.028 mmol, 16 % based on **1**; and 37 % brsm **5a**). ^{1}H NMR (CDCl$_3$, δ): 2.91–3.10 (m, 4H, CH2), 3.79 (s br, 4H, H2,5-C$_5$H$_4$), 3.87 (pt, $J_{\mathrm{H,H}}$ = 1.9 Hz, 4H, H3,4-C$_5$H$_4$), 4.09 (s, 10H, C$_5$H$_5$), 5.45 (s, 5H, C$_5$H$_5$), 6.99–7.03 (m, 4H, C$_6$H$_5$), 7.16–7.21 (m, 6H, C$_6$H$_5$), 7.25–7.36 (m, 8H, C$_6$H$_5$), 7.45–7.48 (m, 2H, C$_6$H$_5$), 7.51 (s, 4H, BAr$^F_4$), 7.72 (s, 8H, BAr$^F_4$). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 27.4–27.8 (m, CH$_2$), 66.0 (C$_5$H$_4$), 67.9 (C$_5$H$_4$), 69.7 (C$_5$H$_5$$^{\mathrm{Fc}}$), 74.5 ($^{\mathrm{q}}C_{\mathrm{Fc}}$), 91.7 (C$_5H_5$$^{\mathrm{Ru}}$), 117.6 (sept, $^3J_{\mathrm{C,F}}$ = 3.7 Hz, *p*-BAr$^F_4$), 124.7 (q, $^1J_{\mathrm{C,F}}$ = 272.5 Hz, CF$_3$), 125.5 (CH), 127.0, 128.3, 128.4, 128.7–129.4 (m, *m*-BAr$^F_4$, *m*-dppe), 131.7–131.8 (m, *o*-dppe), 131.9 (*p*-dppe), 132.1 (*p*-dppe), 132.6 (m, *o*-dppe), 133.5 (d, $^1J_{\mathrm{C,P}}$ = 58.5 Hz, $^{\mathrm{q}}$dppe), 135.0 (*o*-BAr$^F_4$), 138.0 ($^{\mathrm{q}}$C), 161.9 (q, $^1J_{\mathrm{C,B}}$ = 49.8 Hz, C–B), 363.9 (t, $^2J_{\mathrm{C,P}}$ = 16.3 Hz, Ru=C) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, δ): 77.5 ppm. ESI(+)-HRMS (*m*/*z*): calcd. for C$_{53}$H$_{47}$Fe$_2$P$_2$Ru 959.0890; found 959.0920 [M]$^+$.

Crystal Data for [**6a**][BAr$^F_4$]: C$_{86}$H$_{60}$BCl$_3$F$_{24}$Fe$_2$P$_2$Ru, C$_{32}$H$_{12}$BF$_{24}$ · C$_{53}$H$_{47}$Fe$_2$P$_2$Ru · CHCl$_3$, M = 1941.21 g·mol^{-1}, yellow-brown rod, 0.538 · 0.071 · 0.051, monoclinic, $P2_1/c$, λ = 0.71073 Å, a = 10.4117(4) Å, b = 31.4879(16) Å, c = 24.3673(14) Å, β = 92.969(4) °, V = 7977.9(7) Å^3, Z = 4, ρ_{calcd} = 1.616 Mg·m^{-3}, μ = 0.789 mm^{-1}, F_{000} = 3896, T = 114.95(10) K, θ range 3.173−24.998°, 44170 reflections collected, 14006 independent reflections (R_{int} =0.1155), *GooF* = 1.023, 1102 parameters, 1183 restraints, $R1$ = 0.0832, $wR2$ = 0.1775 ($I>2\sigma(I)$), $|\Delta\rho|_{\max}$ = 0.989 and –1.160 e·Å^{-3}.

*[Ru{=C=CFc(4-(FcC≡C)C$_6$H$_4$)}(dppe)Cp][BAr$^F_4$] ([**6b**][BAr$^F_4$]) and [1,4-{Ru(=C=CFc)(dppe) Cp}$_2$-C$_6$H$_4$][BAr$^F_4$]$_2$ ([**7**][BAr$^F_4$]$_2$)*

A: [RuCl(dppe)Cp] (**1**, 134 mg, 0.223 mmol), Na[BAr$^F_4$] (197 mg 0.223 mmol), and 1,4-bis(ferrocenylethynyl)benzene (**5b**, 45 mg, 0.101 mmol) were reacted according to the general procedure. Column-chromatographic using a 1:1 hexane/chloroform mixture eluted unreacted **5b** (35 mg, 0.071 mmol). Ethyl acetate eluted a green fraction, containing traces of [**7**]$^{2+}$. Single crystals of the latter grew from the CDCl$_3$ solution in the NMR tube within two days.

B: [RuCl(dppe)Cp] (**1**, 108 mg, 0.180 mmol), Na[BAr$^F_4$] (160 mg, 0.180 mmol), and 1,4-bis(ferrocenylethynyl)benzene (**5b**, 111 mg, 0.225 mmol) were reacted according to the general procedure. Column chromatographic purification with a 1:2 hexane/dichloromethane mixture gave unreacted **5b** (52 mg, 0.105 mmol), followed by [**6b**]$^+$ and [**7**]$^{2+}$, respectively. Single crystals of [**6b**][BAr$^F_4$] were grown from a CHCl$_3$ solution layered with hexane at ambient temperature

[**6b**][BAr$^F_4$]: Orange-red solid. Yield: 166 mg (0.086 mmol, 38 % based on **1**; 73 % brsm **5b**). EA (%) for C$_{93}$H$_{63}$BF$_{24}$Fe$_2$P$_2$Ru (1922.01 g/mol): calcd. C 58.12, H 3.30; found C 57.76, H 3.22. In the following, fragments attached to the vinylidene functionality are marked with '$^{\mathrm{V}}$'. ^{1}H NMR (CDCl$_3$, δ): 2.76–2.97 (m, 4H, CH$_2$), 3.17 (s, 2H, C$_5$H$_4$$^{\mathrm{V}}$), 3.88 (s, 2H, C$_5H_4$$^{\mathrm{V}}$), 4.01 (s, 5H, C$_5H_5$$^{\mathrm{V,Fc}}$), 4.29 (s, 5H, C$_5H_5$$^{\mathrm{Fc}}$), 4.32 (pt, $J_{\mathrm{H,H}}$ = 1.8 Hz, 2H, C$_5$H$_4$), 4.56 (pt, $J_{\mathrm{H,H}}$ = 1.7 Hz, 2H, C$_5$H$_4$), 5.52 (s, 5H, C$_5$H$_5$$^{\mathrm{Ru}}$), 6.88 (d, $^3J_{\mathrm{H,H}}$ = 8.1 Hz,

2H, C_6H_4), 6.94–6.99 (m, 4H, dppe), 7.16–7.21 (m, 10H, dppe, C_6H_4), 7.26–7.30 (m, 4H, dppe), 7.24–7.42 (m, 4H, dppe), 7.51 (s, 4H, *p*-BAr$^F_4$), 7.72 (s br, 8H, *o*-BAr$^F_4$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 27.8 (dd, $J_{C,P}$ = 24.6, 22.9 Hz, CH_2), 65.1 (CH), 68.6 (br, CH), 69.4 (CH), 69.5 (br, CH), 70.2 ($C_5H_5^{Fc}$), 71.7 (CH), 85.1 (^{q}C), 88.0 (^{q}C), 90.2 (^{q}C), 91.6 ($C_5H_5^{Ru}$), 117.6 (*p*-BAr$^F_4$), 124.7 (q, $^1J_{C,F}$ = 272.6 Hz, CF_3), 126.5, 128.7–129.3 (m, BAr$^F_4$, dppe), 129.6, 129.4 (CH), 130.6, 131.3–131.9 (m, dppe), 135.0 (m-BAr$^F_4$), 161.9 (q, $^1J_{C,B}$ = 49.8 Hz, C–B) ppm. (The Ru=C and further signals could not be resolved). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 76.3 ppm. ESI(+)-HRMS (*m*/*z*): calcd. for $C_{61}H_{51}Fe_2P_2Ru$ 1059.1230; found 1059.1250 $[M]^+$.

Crystal Data for [**6b**][BAr$^F_4$]: $C_{93}H_{63}BF_{24}Fe_2P_2Ru$, $C_{61}H_{51}Fe_2P_2Ru \cdot C_{32}H_{12}BF_{24}$, M = 1921.92 g·mol^{-1}, orange-pink block, 0.170 · 0.075 · 0.053, monoclinic, *C2/c*, λ = 1.54184 Å, a = 37.1212(10) Å, b = 12.8085(2) Å, c = 36.2792(7) Å, β = 108.987(3), V = 16311.0(7) Å^3, Z = 8, ρ_{calcd} = 1.565 Mg·m^{-3}, μ = 5.574 mm^{-1}, F_{000} = 7744, T = 99.9(4) K, θ range 2.518−66.499°, 73537 reflections collected, 14268 independent reflections (R_{int} = 0.0896), 1194 parameters, 1442 restraints, *GooF* = 1.025, $R1$ = 0.0755, $wR2$ = 0.1834 ($I>2\sigma(I)$), $|\Delta\rho|_{max}$ = 3.631 and –1.594 e·Å^{-3}.

[**7**][BAr$^F_4$]$_2$: Orange crystals. Yield: <21 mg (<0.006 mmol, <3%, <5% brsm; the sample contains unidentifiable by-products.) $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 77.4 ppm. ESI(+)-HRMS (*m*/*z*): calcd. for $C_{92}H_{80}Fe_2P_4Ru_2/2$ 812.1012; found 812.1013 $[M]^{2+}$.

Crystal Data for [**7**][BAr$^F_4$]$_2$: $C_{158}H_{106}B_2Cl_6F_{48}Fe_2P_4Ru$*, $C_{92}H_{80}Fe_2P_4Ru_2 \cdot 2(C_{32}H_{12}BF_{24}) \cdot 2(CHCl_3)$, M = 3588.46 g·mol^{-1}, green-brown block, 0.301 · 0.129 · 0.067, triclinic, *P*–1, λ = 0.71073 Å, a = 14.9101(5) Å, b = 16.8933(5) Å, c = 17.7738(6) Å, α = 115.156(3), β = 92.969(4), γ = 97.565(2) °, V = 3892.9(2) Å^3, Z = 1, ρ_{calcd} = 1.531 Mg·m^{-3}, μ = 0.625 mm^{-1}, F_{000} = 1798, T = 169.9(2) K, θ range 3.269−25.499°, 38044 reflections collected, 14378 independent reflections (R_{int} = 0.0380), *GooF* = 1.049, $R1$ = 0.0532, $wR2$ = 0.1191 ($I>2\sigma(I)$), $|\Delta\rho|_{max}$ = 0.777 and –0.570, 1178 parameters, 1375 restraints e·Å^{-3}. *One further molecule of $CHCl_3$ has been omitted using SQUEEZE (123 e$^-$/cell, 331 Å^3) (Note: Measurements at lower than the reported temperature caused a phase transition, which cracks the crystals.)

*Synthesis of [Ru{=C=C(H)Fc}(dppe)Cp][BAr$^F_4$] ([**8**][BAr$^F_4$])*

In a Schlenk tube, [RuCl(dppe)Cp] (**1**, 100 mg, 0.167 mmol) and ethynylferrocene (**9**, 35 mg, 0.167 mmol) were suspended in dry toluene (5 mL). Na[BAr$^F_4$] (148 mg, 0.167 mmol) was added to the yellow suspension resulting in an immediate clearing. The solution was stirred for 2 hours at 60 °C, resulting in a dark brown solution (Note: the colour of the reaction changed within the first 5 minutes and no change occurred after 30 min). The mixture was purified by column chromatography (silica, 3.5 x 10 cm column size) using a 1:1 hexane/dichloromethane solvent mixture. Removal of all volatiles gave [**4**][BAr$^F_4$] as a brown solid. Single crystals were grown by layering a $CHCl_3$ solution containing [**4**][BAr$^F_4$] with hexane.

Yield: 202 mg (0.123 mmol, 74 % M = 1637.87). EA (%) for $C_{75}H_{51}BF_{24}FeP_2Ru$ (1637.87 g/mol): calcd. C 55.00, H 3.14; found C 53.94, H 2.78 (best match). ^1H NMR ($CDCl_3$, δ): 2.65–2.79 (m, 2H, CH_2), 2.84–2.96 (m, 2H, CH_2), 3.23 (pt, $J_{H,H}$ = 1.8 Hz, 2H, C_5H_4), 3.86 (pt, $J_{H,H}$ = 1.8 Hz, 2H, C_5H_4), 3.95 (s, 5H, $C_5H_5^{Fc}$), 4.37 (s, 1H, $H^{vinylidene}$), 5.44 (s, 5H, $C_5H_5^{Ru}$), 7.07–7.12 (m, 4H, dppe), 7.34–7.47 (m, 16H, dppe), 7.51 (s, 4H, BAr$^F_4$), 7.72 (s, 4H, BAr$^F_4$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 27.5 (dd, $J_{C,P}$ = 25.2, 22.6 Hz, CH_2), 66.3 (C_5H_4), 68.5 (C_5H_4), 69.5 ($C_5H_5^{Fc}$), 70.8 ($^qC_5H_4$), 91.8 ($C_5H_5^{Ru}$), 113.7 (C_β), 117.6 (sept, $^3J_{C,F}$ = 3.9 Hz, *p*-BAr$^F_4$), 124.7 (q, $^1J_{C,F}$ = 272.5 Hz, CF_3), 129.0 (qq, $J_{C,F}$ = 31.5, 3.0 Hz, *m*-BAr$^F_4$), 129.4 (t, $J_{C,P}$ = 5.4 Hz, *m*-dppe), 131.3 (t, $J_{C,P}$ = 5.5 Hz, *o*-dppe), 131.98 (*p*-dppe), 132.04 (*p*-dppe), 132.2 (t, $J_{C,P}$ = 5.4 Hz, dppe), 133.7 (dd, $J_{C,P}$ = 64.1, 5.0 Hz, ^{q}dppe), 135.0 (*o*-BAr$^F_4$), 135.1 (dd, $J_{C,P}$ = 54.4, 8.3 Hz, ^{q}dppe), 161.9 (q, $^1J_{C,B}$ = 49.8 Hz), 355.4 (t, 2JC,P = 16.7 Hz, Ru=C_α) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 77.7 ppm. ^{19}F NMR ($CDCl_3$, δ): –62.3 ppm. ESI(+)-HRMS (*m*/*z*): calcd. for $C_{43}H_{39}FeP_2Ru$ 775.0934; found 775.0927 $[M]^+$.

*Synthesis of [Ru{=C(OMe)CH_2Fc}(dppe)Cp][BAr^F_4] ([**10**][BAr^F_4])*

[RuCl(dppe)Cp] (**1**, 100 mg, 0.167 mmol), ethynylferrocene (**9**, 35 mg, 0.167 mmol) and Na[BAr^F_4] (148 mg, 0.167 mmol) were placed in a Schlenk flask and suspended in 5 mL of methanol and sparged with nitrogen for 5 min. The suspension was heated to reflux for 2 hours. Afterwards, all volatiles were removed in vacuo and the residue was purified by column chromatography (silica, 3.5 x 10 cm column size) using a 2:3 hexane/dichloromethane solvent mixture. Removal of all volatiles gave [**10**][BAr^F_4] as orange-yellow solid. (Note: 3% of [**8**][BAr^F_4] could not be removed completely even by refluxing in MeOH.) Single crystals were grown by layering a $CHCl_3$ solution containing [**10**][BAr^F_4] with hexane.

Yield: 153 mg (0.0916 mmol, 55 % based on **1**). EA (%) for $C_{76}H_{55}BF_{24}FeOP_2Ru \cdot 0.5\ CHCl_3$ (1669.91 · 0.5 119.38 g/mol): calcd. C 53.12, H 3.23; found C 52.94, H 3.76 (best match). ^{1}H NMR ($CDCl_3$, δ): 2.52–2.67 (m, 2H, CH_2^{dppe}), 2.78 (s, 3H, CH_3), 2.78–2.88 (m, 2H, CH_2^{dppe}), 3.81 (s, 2H, CH_2^{Fc}), 3.95 (pt, $J_{H,H}$ = 1.8 Hz, 2H, C_5H_4), 4.11 (s, 5H, $C_5H_5^{Fc}$), 4.16 (pt, $J_{H,H}$ = 1.8 Hz, 2H, C_5H_4), 5.03 (s, 5H, $C_5H_5^{Ru}$), 7.09–7.13 (m, 4H, dppe), 7.32–7.41 (m, 12H, dppe), 7.44–7.49 (m, 4H, dppe), 7.51 (s, 4H, BAr^F_4), 7.72 (s, 8H, BAr^F_4) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 28.0 (dd, $J_{C,P}$ = 24.3, 22.3 Hz, CH_2^{dppe}), 56.5 (CH_2^{Fc}), 60.8 (OCH_3), 68.2 (C_5H_4), 69.5 ($C_5H_5^{Fc}$), 69.6 (C_5H_4), 78.6 ($^qC_5H_4$), 90.7 ($C_5H_5^{Ru}$), 117.6 (sept, $^3J_{C,F}$ = 3.9 Hz, *p*-BAr^F_4), 124.7 (q, $^1J_{C,F}$ = 272.5 Hz, CF_3), 129.0 (qq, $J_{C,F}$ = 31.4, 2.7, *m*-BAr^F_4), 129.3 (t, $J_{C,P}$ = 5.2 Hz, dppe), 129.2 (t, $J_{C,P}$ = 4.9 Hz, dppe), 130.3 (t, $J_{C,P}$ = 5.0 Hz, dppe), 130.9 (*p*-dppe), 131.3 (*p*-dppe), 132.1 (t, $J_{C,P}$ = 5.2 Hz, dppe), 133.5 (dd, $J_{C,P}$ = 60.7, 8.5 Hz, ^{q}dppe), 135.0 (*o*-BAr^F_4), 138.7 (dd, $J_{C,P}$ = 55.9, 10.4 Hz, ^{q}dppe), 161.9 (q, $^1J_{C,B}$ = 49.8 Hz), 302.4 (t, $^2J_{C,P}$ = 12.0 Hz, Ru=C) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 88.6 ppm. ESI(+)-HRMS (*m*/*z*): calcd. for $C_{44}H_{43}FeOP_2Ru$ 807.1196; found 807.1204 $[M]^+$.

Crystal Data for [**10**][BAr^F_4]: $C_{76}H_{55}BF_{24}FeOP_2Ru$, M = 1669.87 g·mol^{-1}, orange block, 0.240 · 0.157· 0.080, triclinic, P–1, λ = 1.54184 Å, a = 15.69410(10) Å, b = 16.96710(10) Å, c = 17.09570(10) Å, α = 103.1660(10) °, β = 114.2720(10) °, γ = 109.2100(10) °, V = 3553.31(5) Å^3, Z = 2, ρ_{calcd} = 1.5561 Mg·m^{-3}, μ = 4.752 mm^{-1}, F_{000} = 1680, T = 99.9(5) K, θ range 3.042−75.587°, 128062 reflections collected, 14115 independent reflections (R_{int} = 0.0626), 1035 parameters, 174 restraints, *GooF* = 1.062, $R1$ = 0.0333, $wR2$ = 0.0854 ($I>2\sigma(I)$), $|\Delta\rho|_{max}$ = 0.750 and –0.883 e·Å^{-3}.

*Reaction of [**8**][BAr^F_4] with Ferrocene*

In a Schlenk tube, [**8**][BAr^F_4] (70 mg, 0.043 mmol) and ferrocene (45 mg, 0.242 mmol) were dissolved in dry, degassed dichloromethane and stirred at ambient temperature for 7 days. Afterwards all volatiles were removed in vacuo. The residue was purified using a plug of silica (5 x 3.5 cm column size). As eluents, hexane was used to remove the excess of ferrocene followed by dichloromethane, which removed a brown band, which gave a brown residue upon removal of all volatiles. Yield 50 mg.

The ^{31}P{^{1}H} NMR spectra showed signals at 75.3 as the dominant species (carbonyl complex $[Ru(CO)(dppe)Cp]^+$) and 77.7 (vinylidene $[\mathbf{8}]^+$). Crystallization of the residue by layering a $CHCl_3$ solution of the mixture with hexane afforded yellow crystals of the carbonyl complex as its $[BAr^F_4]^-$ salt.

ESI(+)-HRMS (*m*/*z*): calcd. for $C_{32}H_{29}OP_2Ru$ 593.0737; found 593.0760 $[M]^+$.

Crystal Data for the carbonyl complex [Ru(CO)(dppe)Cp][BAr^F_4]: $C_{64}H_{41}BF_{24}OP_2Ru$, M = 1455.79 g·mol^{-1}, yellow block, 0.102 · 0.054· 0.032, triclinic, P–1, λ = 1.54184 Å, a = 12.97370(10) Å, b = 14.01970(10) Å, c = 18.0024(2) Å, α = 109.8850(10) °, β = 100.1500(10) °, γ = 94.1850(10) °, V = 2999.58(5) Å^3, Z = 2, ρ_{calcd} = 1.612 Mg·m^{-3}, μ = 3.690 mm^{-1}, F_{000} = 1456, T = 100.2(7) K, θ range 2.672−75.312°, 171312 reflections collected, 11941 independent reflections (R_{int} = 0.0713), 868 parameters, 66 restraints, *GooF* = 1.070, $R1$ = 0.0394, $wR2$ = 0.1013 ($I>2\sigma(I)$), $|\Delta\rho|_{max}$ = 0.907 and –0.951 e·Å^{-3}.

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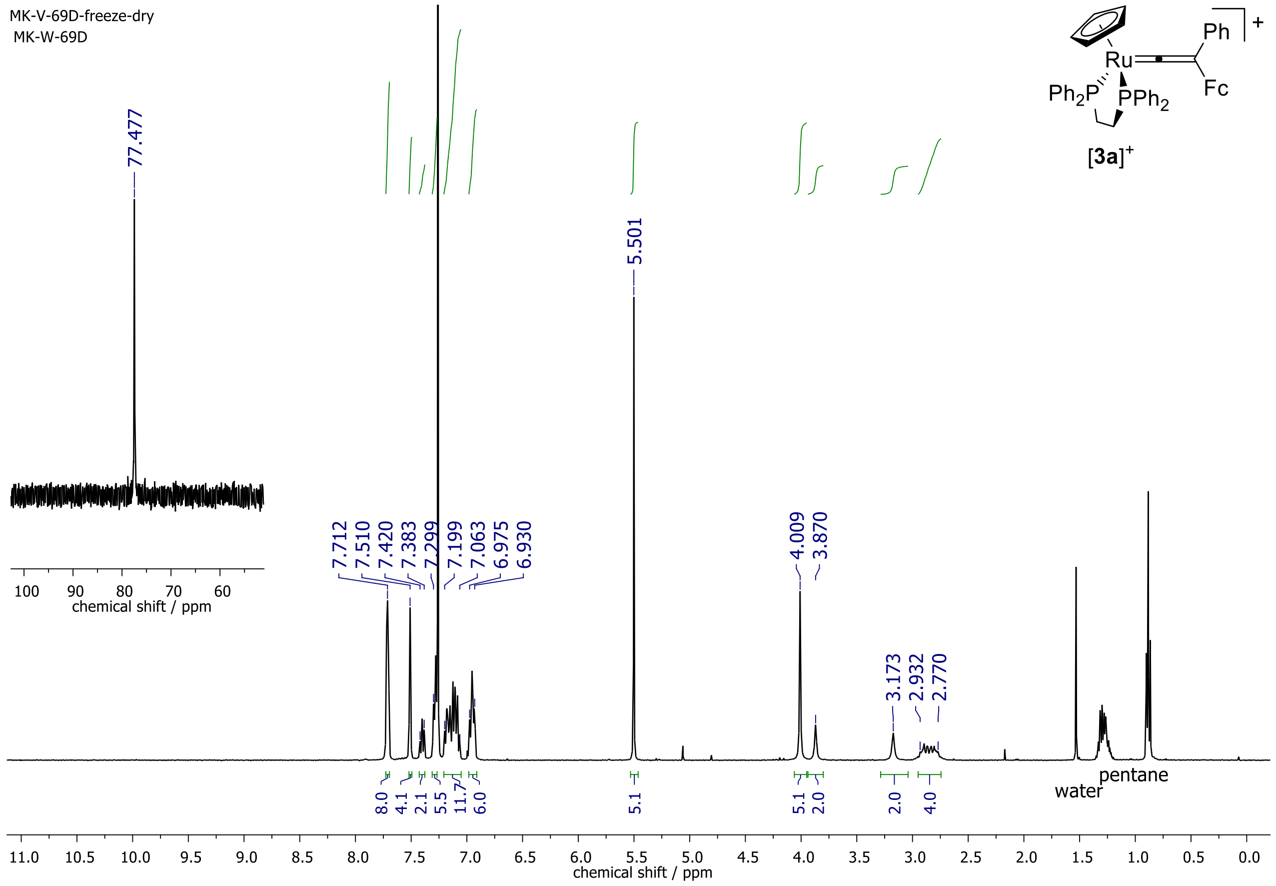
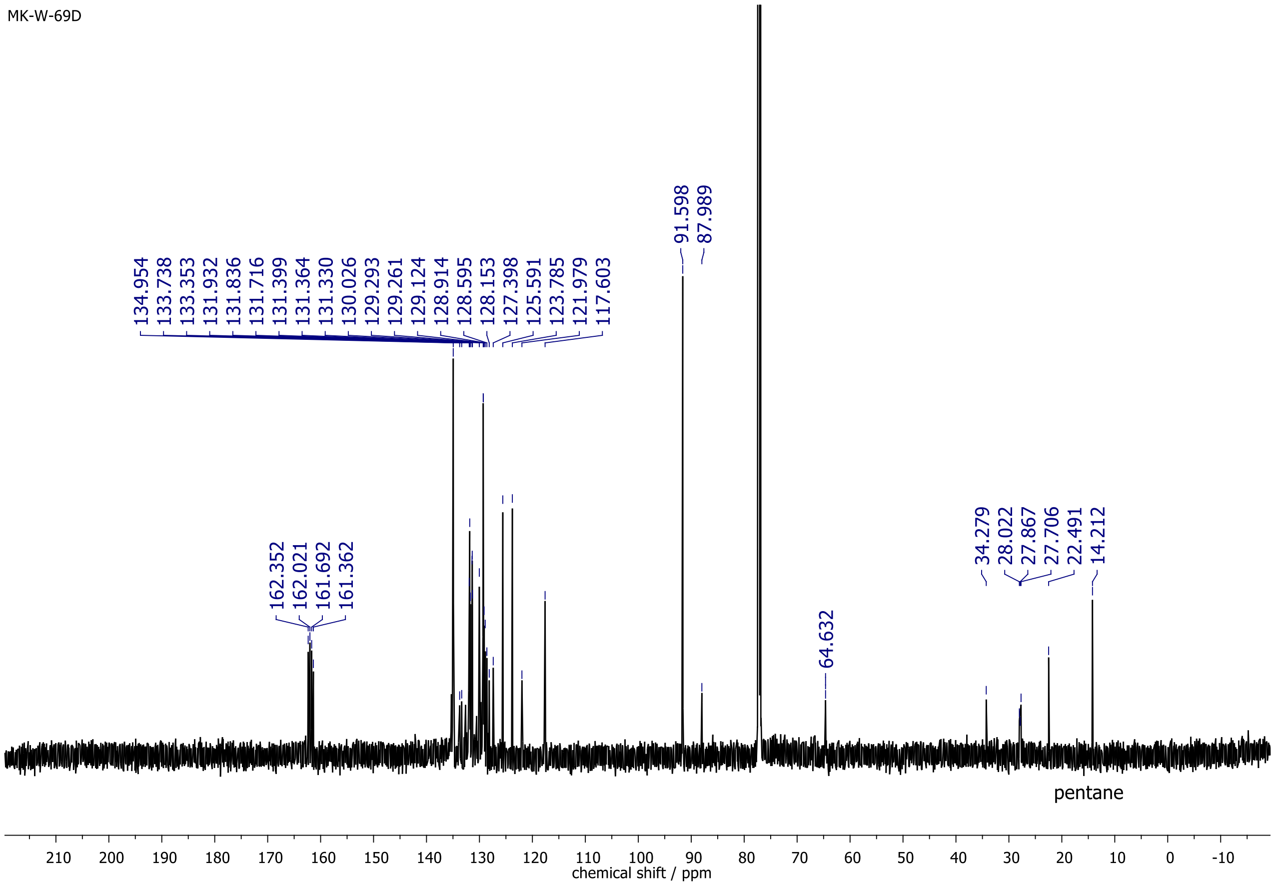
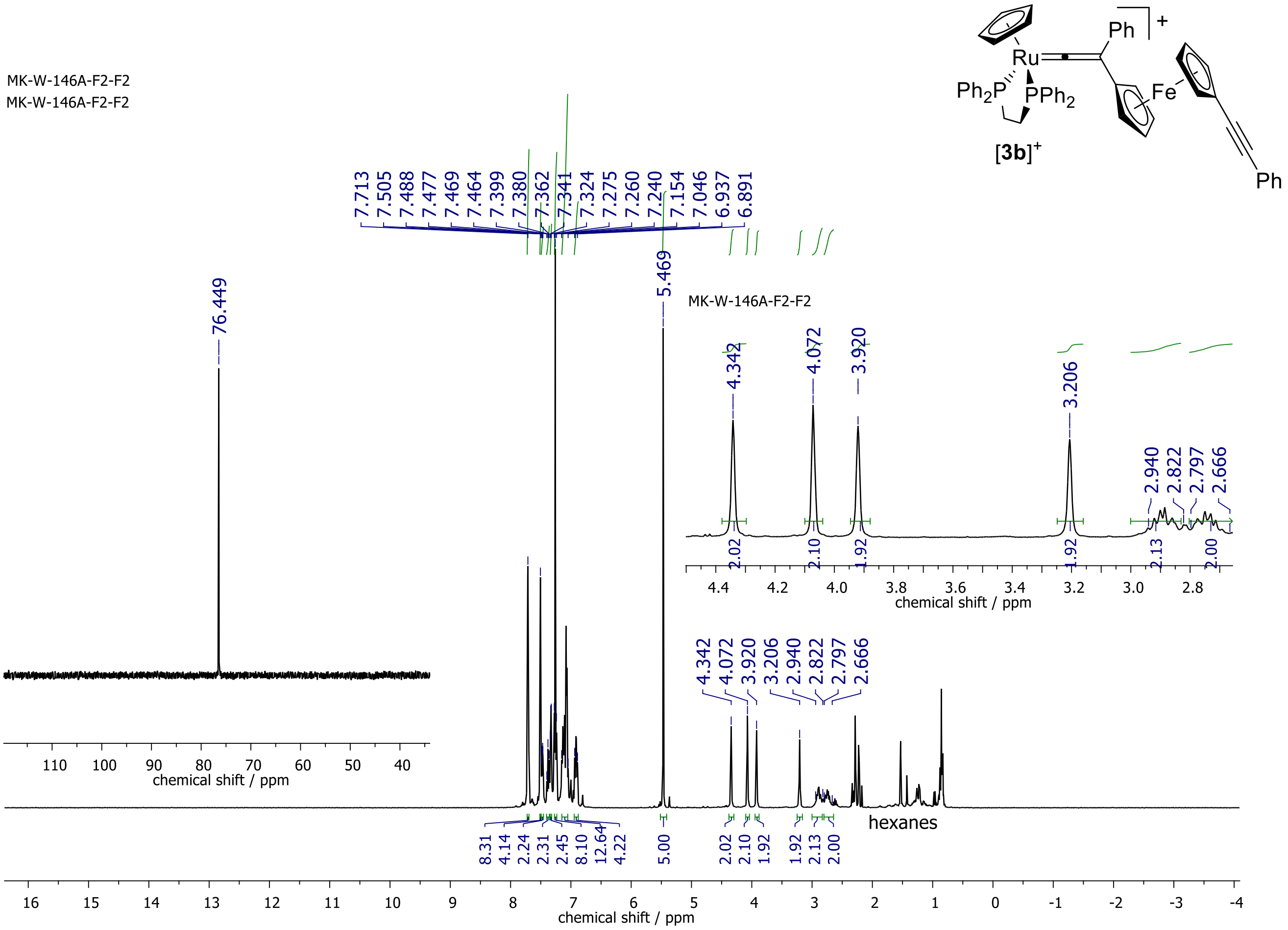
^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} NMR and selected MS spectra of new compounds

^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra of [3a][BAr$^F_4$]

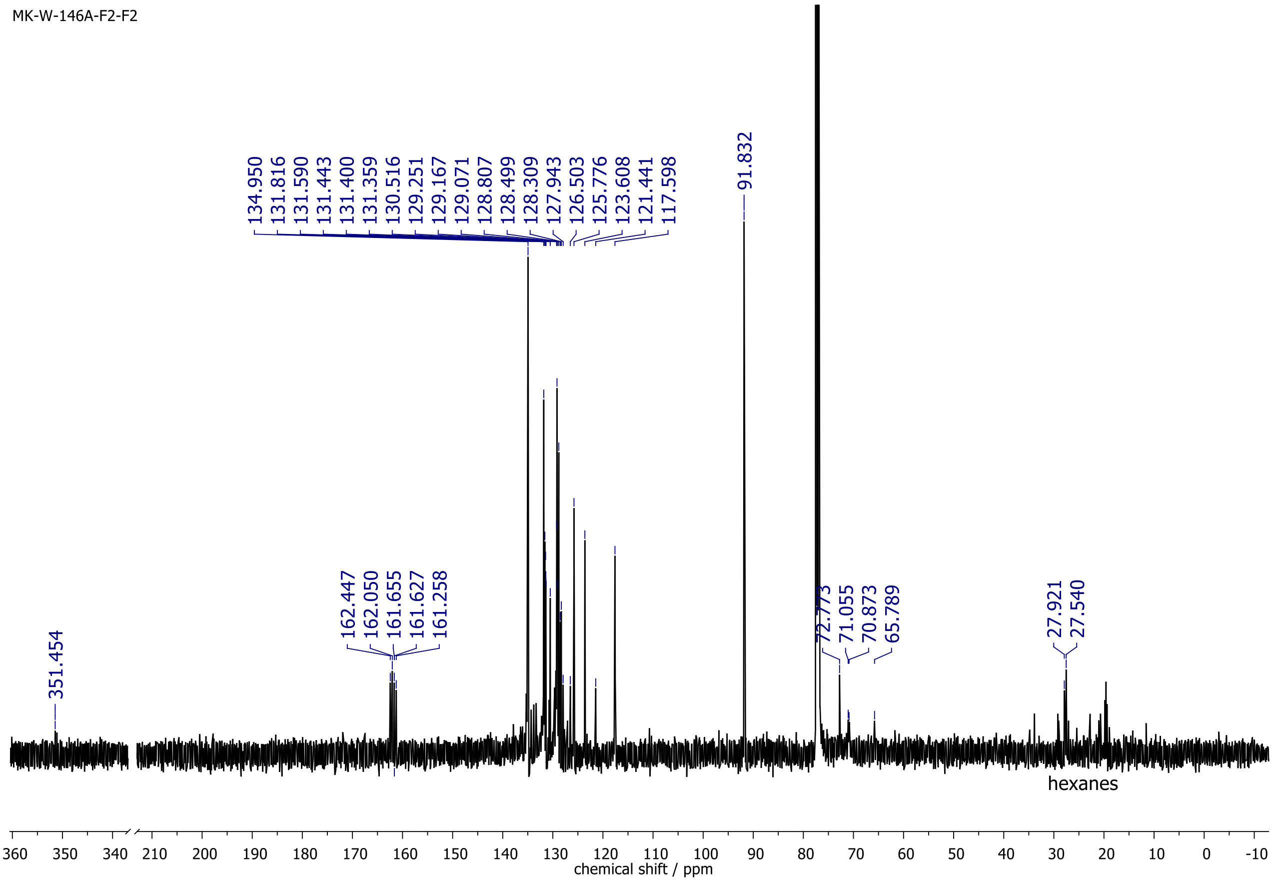




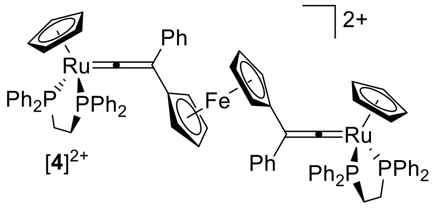
^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra of [3b][BAr$^{F}_{4}$]



[**3b**]$^{+}$



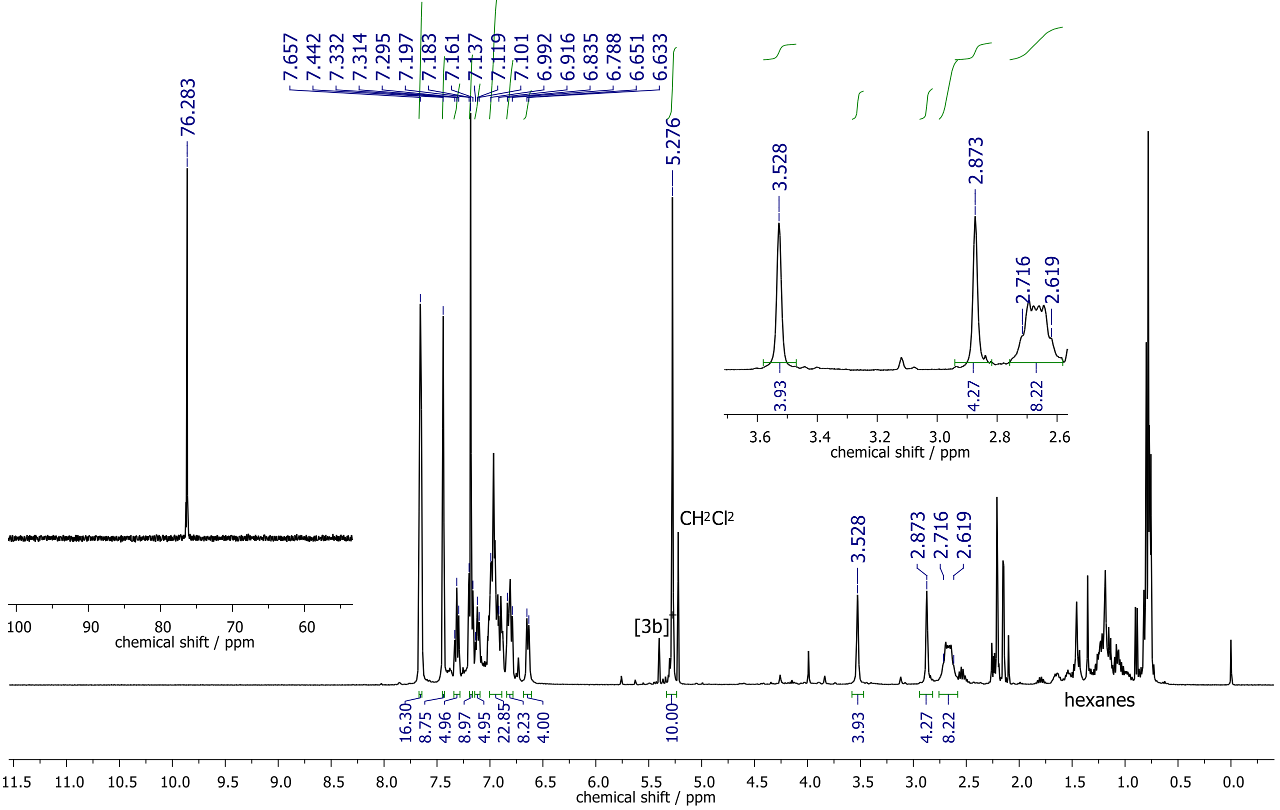
^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra of [4][BAr$^{F}_{4}$]$_2$



[**4**]$^{2+}$

MK-W-146A-F2-F3
MK-W-146A-F2-F3

MK-W-146A-F2-F3



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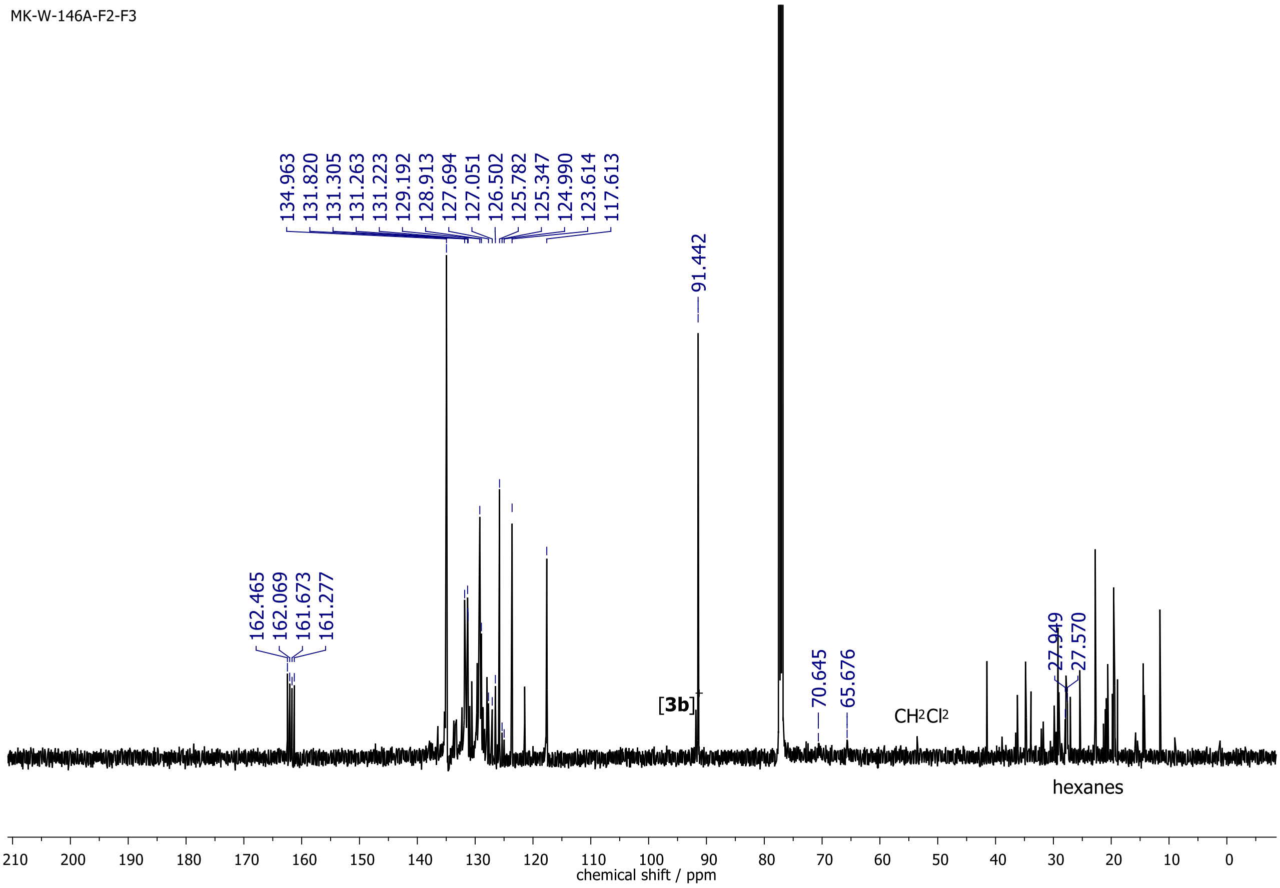
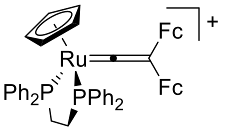
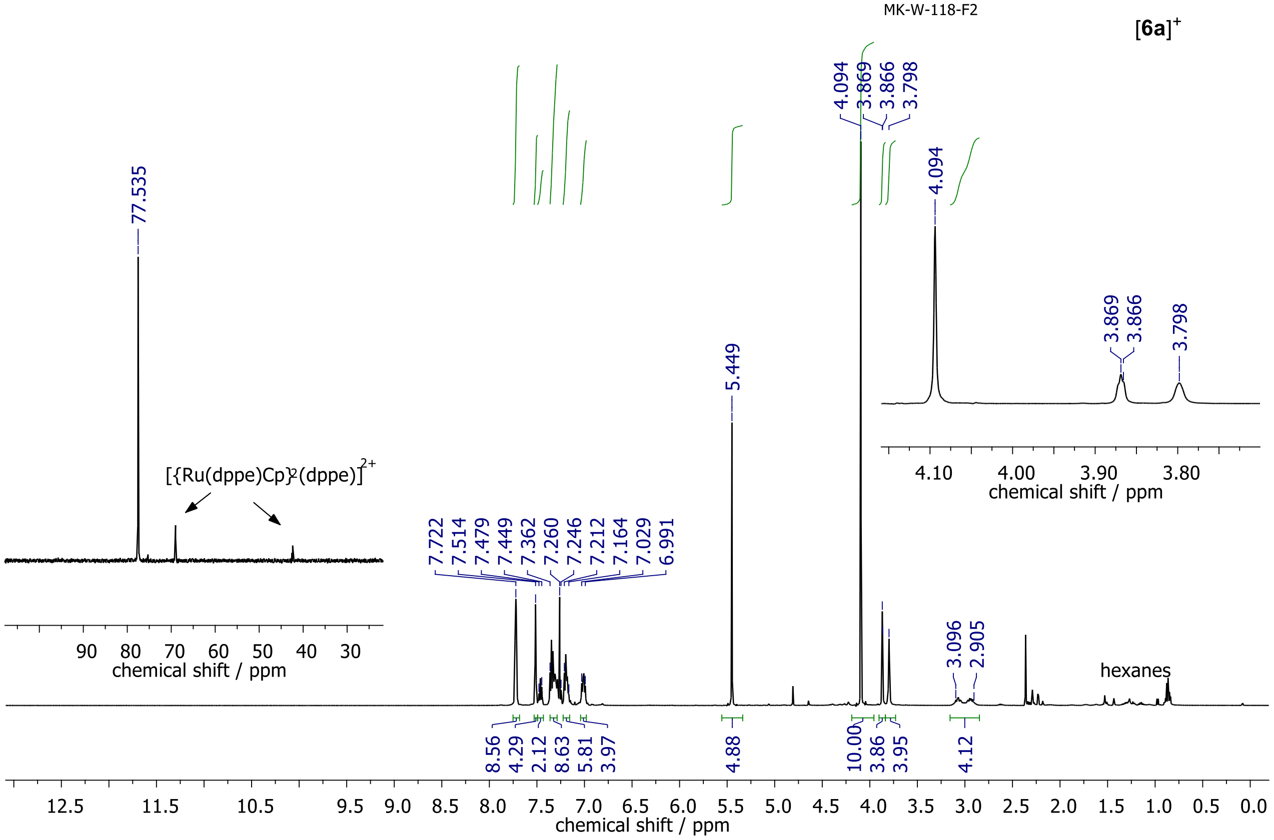
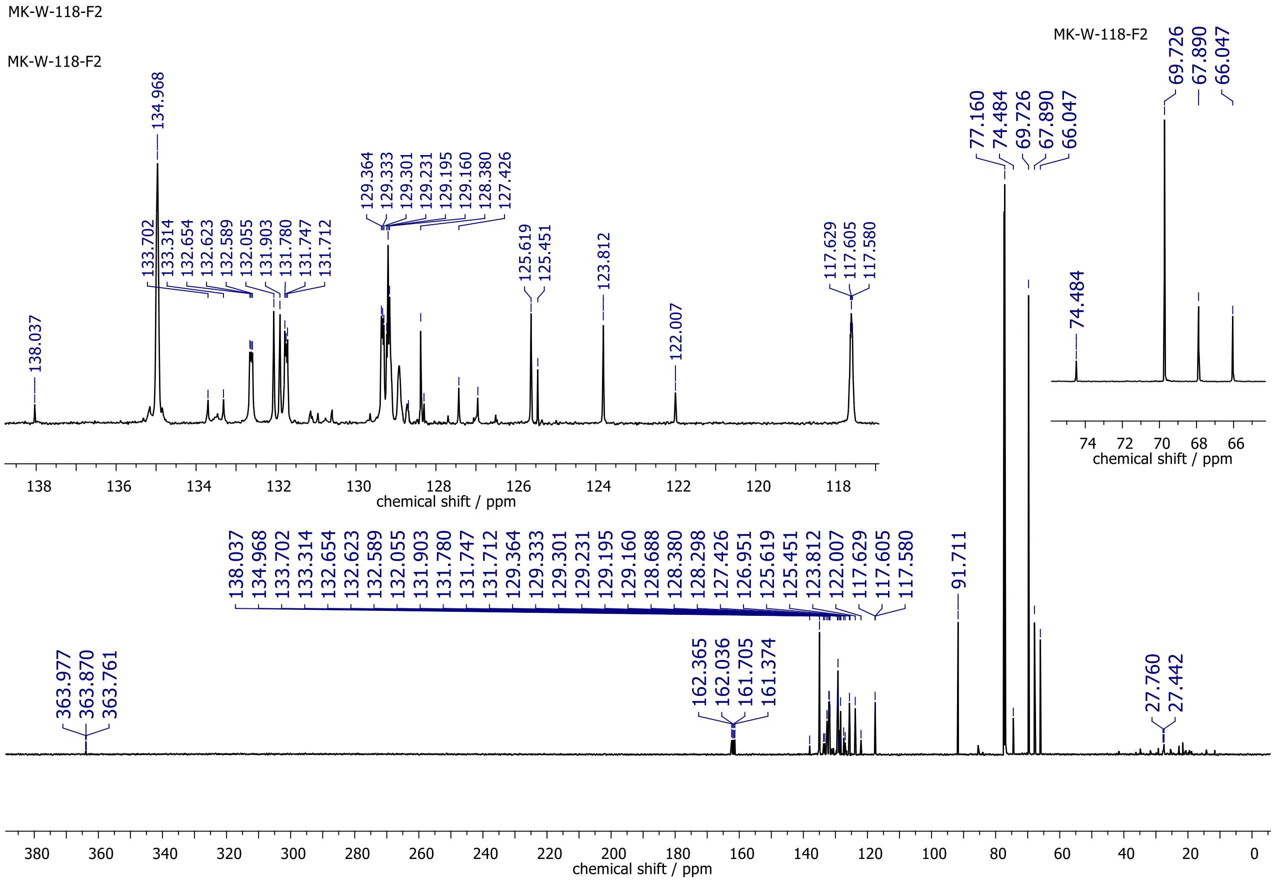


^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra of [6a][BAr$^{F}_{4}$]



[6a]$^{+}$





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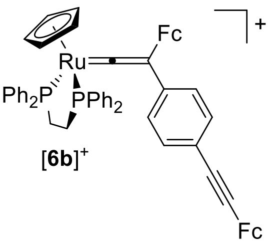

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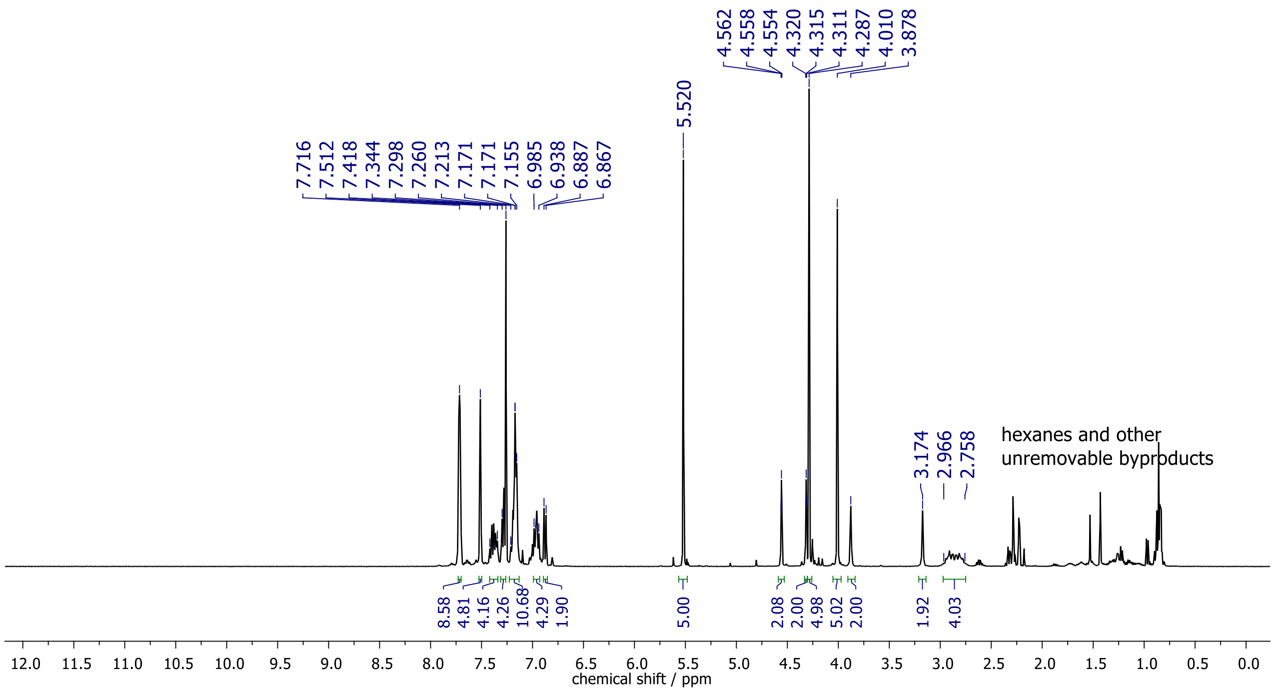
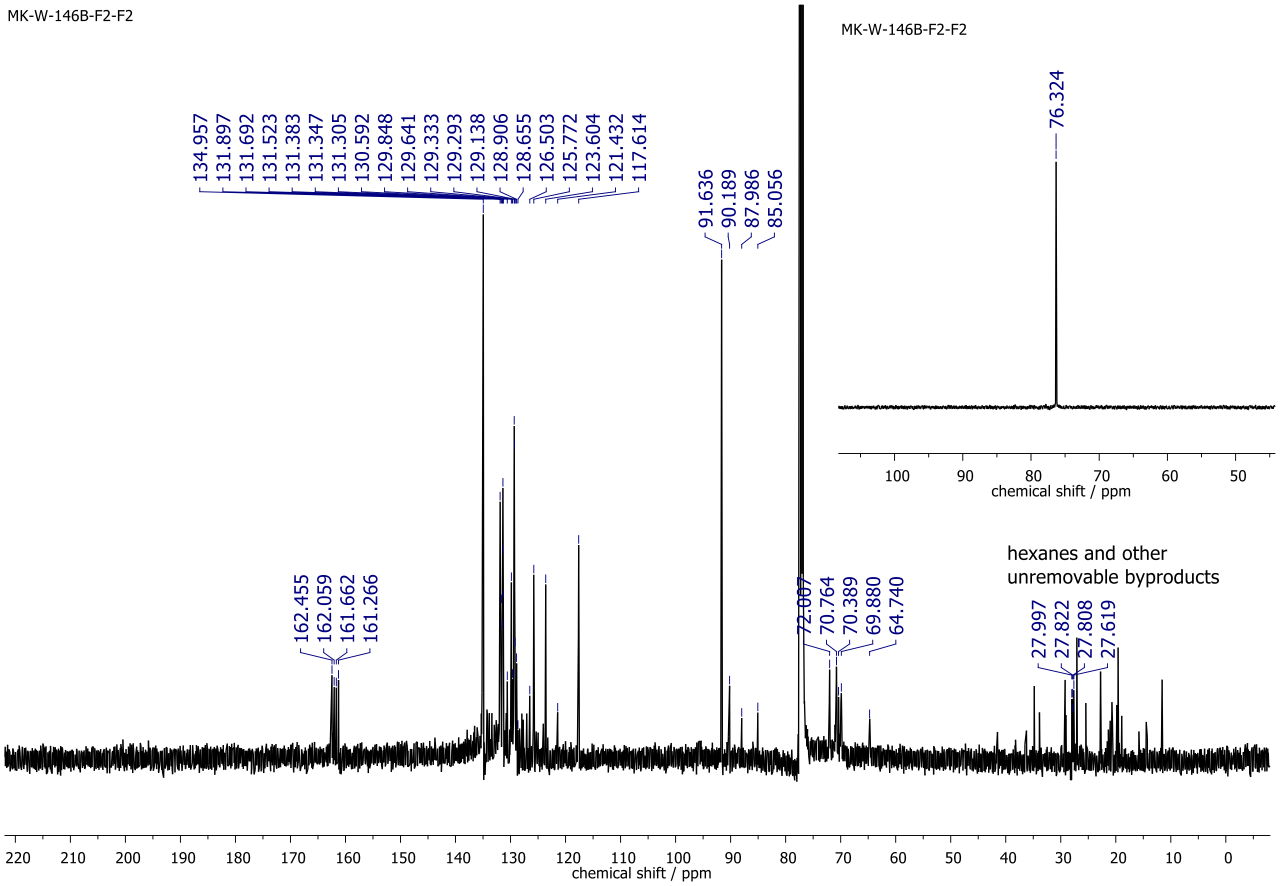
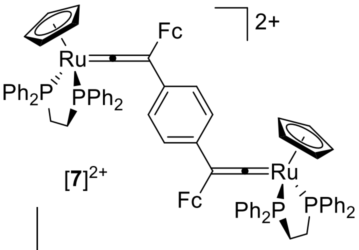


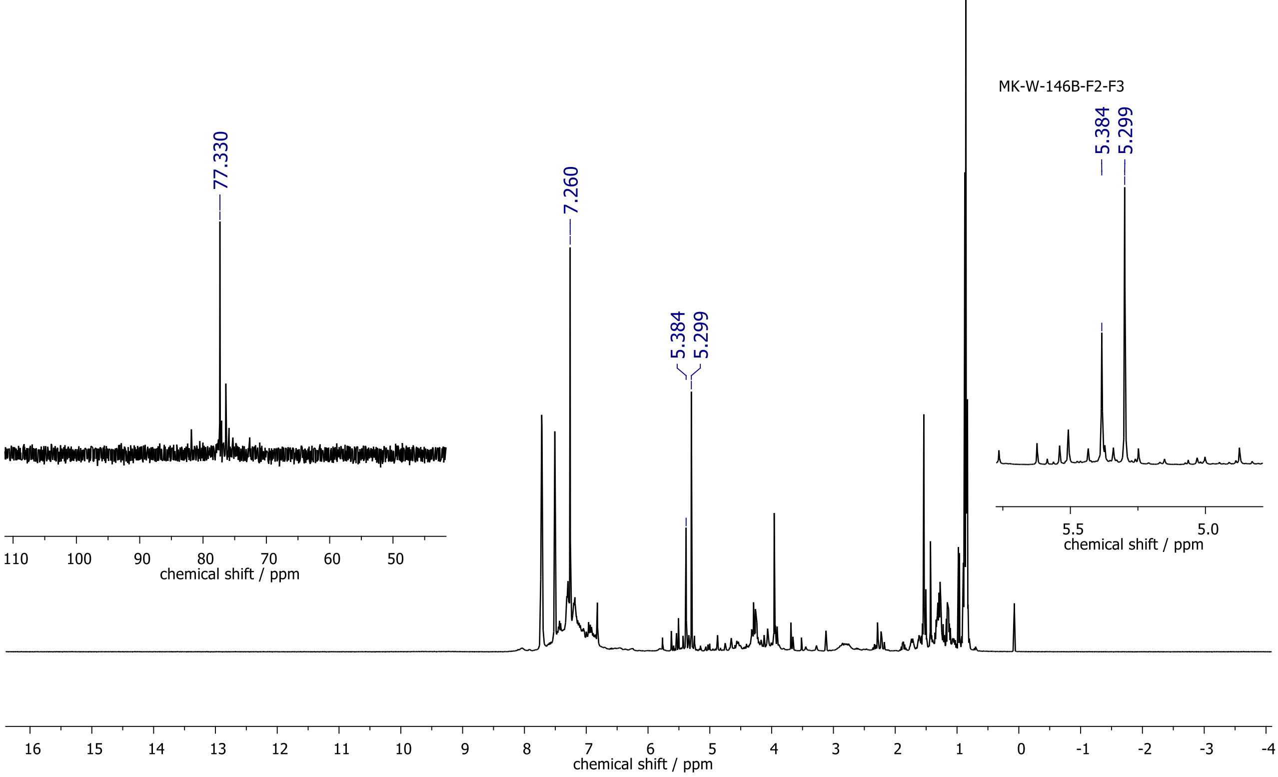


^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of [7][BAr$^{F}_{4}$]$_2$

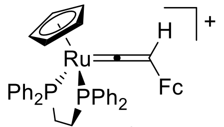
crude mixture of 21 mg



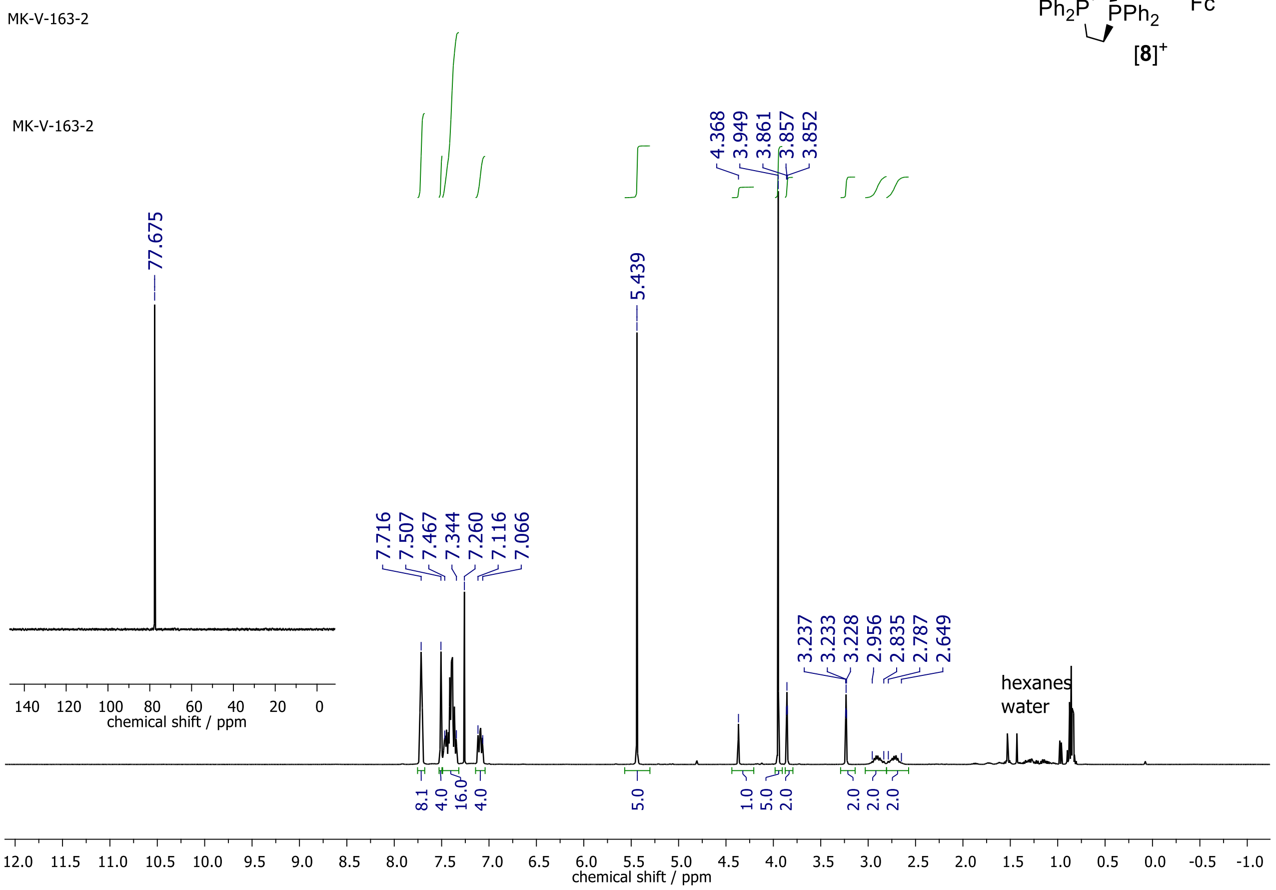
[**7**]$^{2+}$

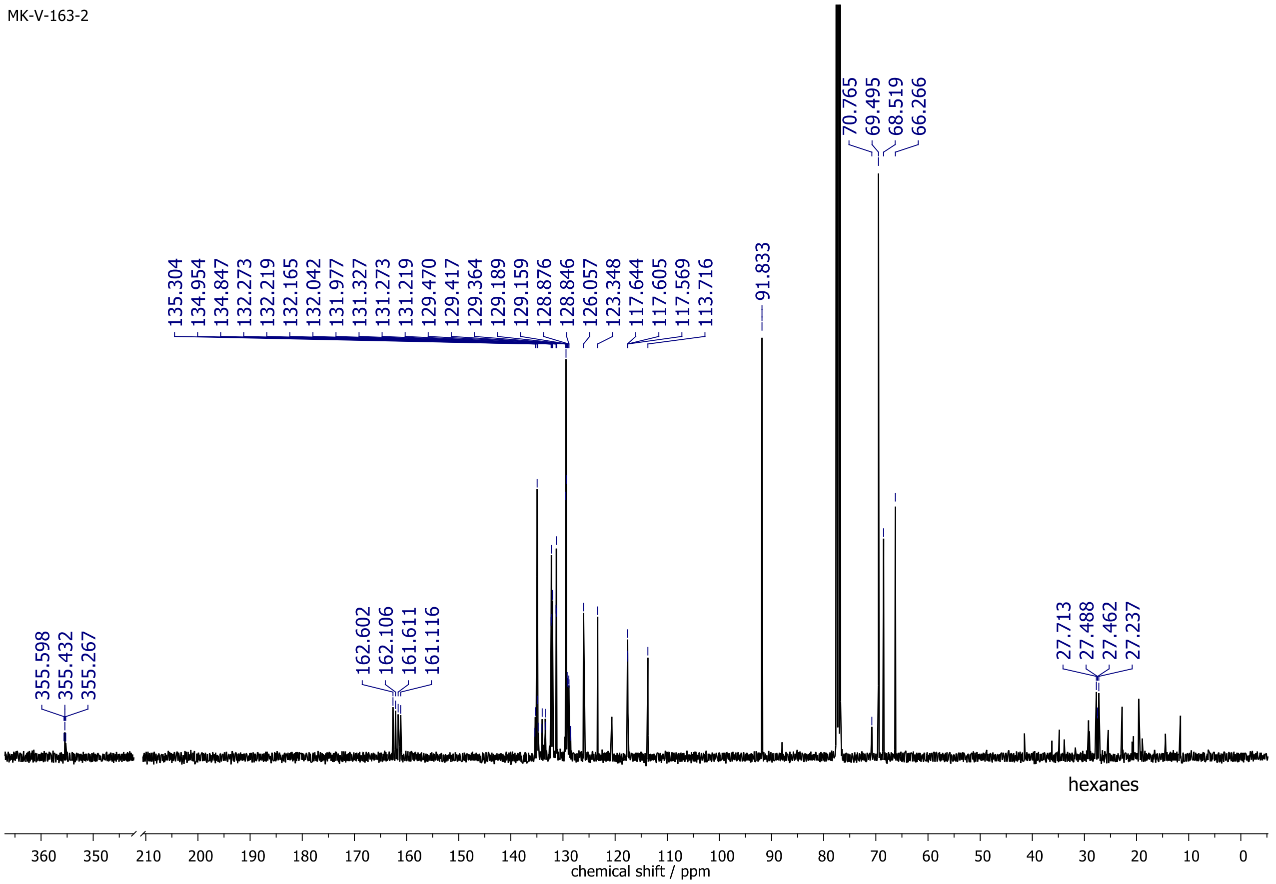


^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra of [8][BAr$^{F}_{4}$]

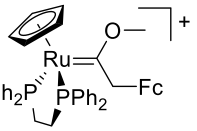


[8]$^{+}$





^{1}H and ^{13}C{^{1}H} NMR spectra of [10][BAr$^F_4$]



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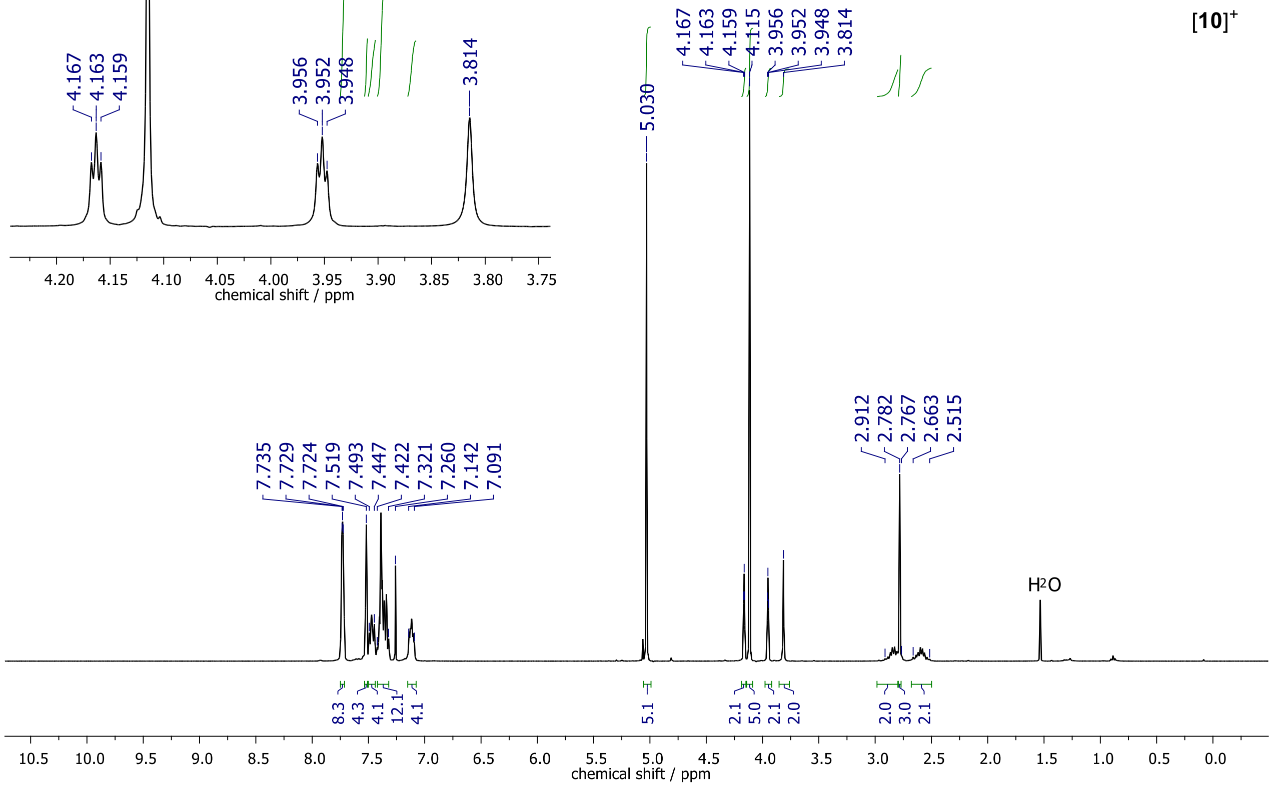
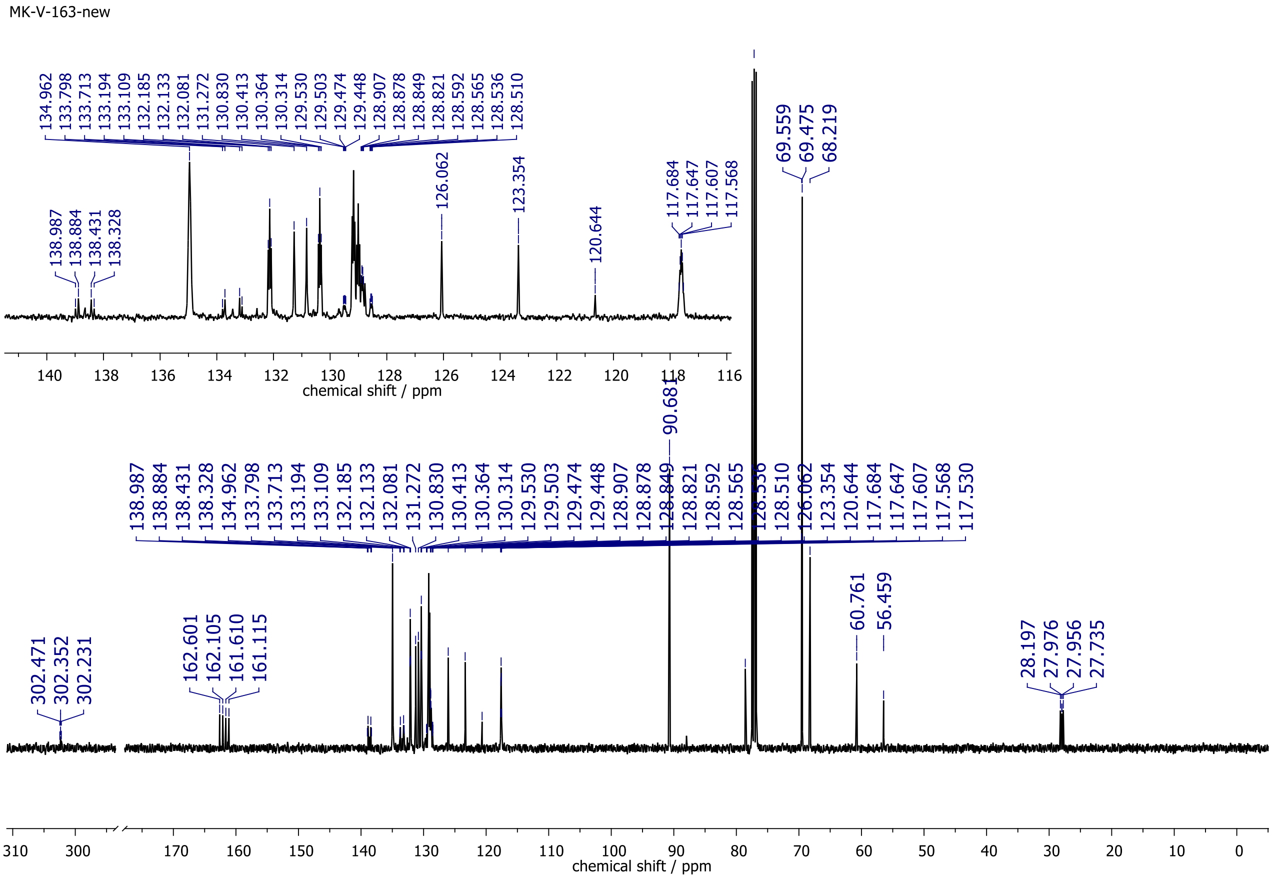
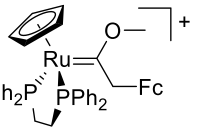




^{31}P{^{1}H} NMR spectra of [**10**][BAr$^{F}_{4}$]



[**10**]$^{+}$