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The synthesis and characterisation of 1′-ethynyl-2,5-dimethylazaferrocene and derivatives

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Abstract

The synthesis of 1′-ethynyl-2,5-dimethylazaferrocene is reported along with its cyclic voltammetry measurements and the X-ray structure determination of its $W(CO)_5$-complex. Basic coordination and organic chemistry of 1′-ethynyl-2,5-dimethylazaferrocene is also presented via derivatives incorporating *cis*-Pt(dppe) and $Si(Et)_3$ units.

Keywords: Azaferrocenes; Alkynes; Cyclic voltammetry

1. Introduction

Conjugated molecules linked to redox active ferrocene fragments represent promising candidates for the design of ‘molecular wires’, carbon rich compounds, nonlinear optical materials or biochemically useful compounds. Ethynylferrocene (**1**) (Fig. 1) is an important example of a redox active molecule successfully used as a building block in materials and coordination chemistry. Electrochemical study of diferrocenylacetylene has been reported [1] and reveals a mixed-valence state of its monocation. Detailed spectroscopic and diffraction studies have been reported featuring ethynylferrocene (**1**) linked to a (η^6-arene)tricarbonylmanganese fragment [2]. **1** has also been built into redox active polymers, oligomers and highly conductive molecular wires [3a,3b,3c], organometallic dehydroannulenes and other carbon rich compounds [4a,4b,4c]. Ethynylferrocene (**1**) exhibits a very rich coordination chemistry towards metals and metalloids i.e. complexes with Pt [5], Mn [6], Ru [6,7a,7b,7c], Os [6,7b], Ti [8a,8b], Co [9], Ni [8b,10] Si [8a,9] have been reported. Additionally, **1** has been described as a building block in more structurally sophisticated complexes [11] i.e. via metal-catalysed cross-coupling reactions and the synthesis of 1,3,5-tris(ferrocenyl)benzene [12]. The third order nonlinear optical properties of alkynes and polyynes containing **1** have been reported [13] and ethynylferrocene (**1**) modified estrogens have been demonstrated as possessing an estrogenic effect *in vitro* [14] and as substrates for the synthesis of its $^{99(m)}Tc(CO)_3$ derivatives [15]. In contrast, progress in the synthetic chemistry of azaferrocene and its more stable derivative 2,5-dimethylazaferrocene – the closest heteroanalogues of ferrocene – has been limited due to its instability and the lack of efficient functionalisation methods. In recent years however, the chemistry of azaferrocenes has been revitalised. Lateral lithiation opens access to wide variety of derivatives [16a,16b,16c], and the classical Friedel–Crafts reaction has also recently been reported for azaferrocenes some 40 years after its discovery

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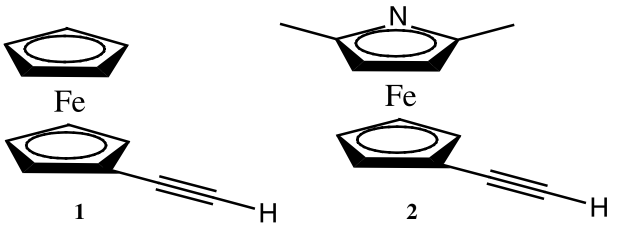


Fig. 1. The structures of compounds **1** and **2**.

[17]. Some azaferrocene derivatives show moderate anticancer activity [18] and interesting electrochemical behaviour for aryl capped ethenylazaferrocenes have been recently described [19]. Application of azaferrocenes in catalysis [20a,20b] and as a redox active nitrogen ligand enabling novel photoinduced redox processes of metalloporphyrins and metallophthalocyanines [21] are known.

In this paper, we report the synthesis and electrochemistry of 1′-ethynyl-2,5-dimethylazaferrocene (**2**) (Fig. 1), a direct nitrogen heteroanalogue of **1**. We also report here the crystallographic structure of $W(CO)_5$-**2** complex and synthesis of Pt and Si derivatives of **2**. Progress in coordination and materials chemistry strongly demands the design and synthesis of new ligands and building blocks, and in this respect we believe that **2** has a real role to play.

2. Results and discussion

2.1. Synthesis of 2

High yielding syntheses of ethynylferrocene (**1**) have been described [22a,22b]. However, to synthesise **2** we adopted methods based on dimethyl-1-diazo-2-oxopropylphosphonate **3** (Fig. 2), a reagent that transforms a variety of aliphatic, aromatic and organometallic aldehydes into terminal alkynes under mild conditions [23a,23b]. Utilisation of **3** in ferrocenyl alkyne synthesis has also been described [4a,4b]. In a first attempt to make **2** we followed a one-pot procedure described by Bestmann et al. [23a]. Dimethyl-1-diazo-2-oxopropylphosphonate **3** was generated *in situ* by addition of dimethyl-2-oxopropylphosphonate to a suspension of K_2CO_3 and *p*-toluenesulfonylazide and was then reacted with 1′-formylo-2,5-dimethyloazaferrocene (**4**) at room temperature for 6 h. After workup and purification by column chromatography **2** was isolated as an orange oil in 6% yield. A trace of starting aldehyde **4** was also isolated. It should be noted that isolation of **2** *via* column chromatography and the removal of some organic impurities suffers from difficulties. We assume that the low product yield in this experiment is due to the complex character of the reaction mixture that can trigger decomposition of the rather unstable 1′-formylo-2,5-dimethyloazaferrocene (**4**) or the product **2**. Another factor that should be considered is the electron rich character of the formyl group in **4** that deactivates aldehydes towards reaction with moderately nucleophilic reagents generated during the course of the reaction from dimethyl-1-diazo-2-oxopropylphosphonate **3**.

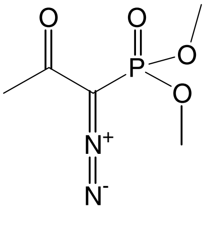
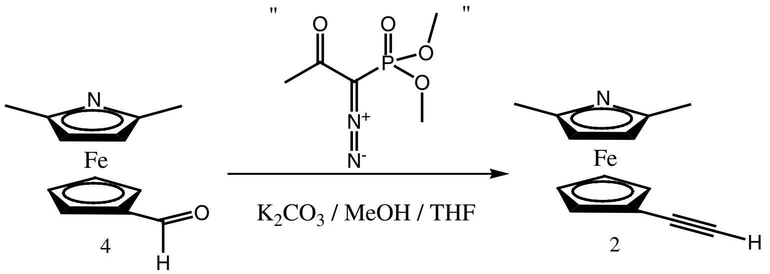


Fig. 2. The structure of compound **3**.

In a second attempt we applied diazotransfer reaction to the synthesis of dimethyl-1-diazo-2-oxopropylphosphonate **3** according to the procedure reported by Vanderwalle et al. [24]. According to the procedure, the crude reaction mixture was filtered through a Celite pad and the solvent evaporated. ^{1}H and ^{31}P NMR examination of this material revealed its very high level of purity. The ^{31}P NMR spectrum exhibited only signals at 22.98 ppm and 14.71 ppm. The first signal was attributed to dimethyl-2-oxopropylphosphonate (the starting material in the synthesis of **3**) and the second signal was assigned to **3**. The ratio of signals was 1:8.5, so an enhanced amount of **3** was clearly achieved. We decided to use this mixture as the reactant in the next experiment.

To a suspension of **4** and K_2CO_3 in methanol, a THF solution of reactant was added and allowed to react overnight (Scheme 1). After simple workup, product **2** was isolated by column chromatography as an air-stable orange oil in analytically pure form. The procedure was repeated several times, with differing amounts of reactant, and it was found that even when an increased amount of reactant (see Section 4) was used, traces of starting material **4** were still isolated. However, using a mixture of dimethyl-2-oxopropylphosphonate and dimethyl-1-diazo-2-oxopropylphosphonate in place of the one-pot method previously applied gave an excellent yield of 75%. Our method is operationally simple (it is not necessary to isolate **3** in pure form) and gave a pure product, easily separable by chromatography in reproducible yields. The ^{1}H NMR spectrum of **2** shows a singlet (4.36 ppm) for β-pyrrolyl protons, two two-proton triplets (4.34 and 4.19 ppm) from the substituted cyclopentadienyl ligand, a singlet (2.82 ppm) from the ethynyl group and a singlet (2.24 ppm) from the two α-pyrrolyl methyl groups. Accumulated for comparison (on the same 270 MHz spectrometer) the ^{1}H NMR spectrum of ethynylferrocene (**1**) shows a singlet corresponding to the ethynyl proton at 2.71 ppm. The ^{13}C NMR spectrum of **2** shows signals for ethynyl group carbons at 80.8 ppm ($C{\equiv}CH$) and 75.0 ppm ($C{\equiv}CH$). Analogous signals for the ethynyl group of **1** are present at 82.5 ppm ($C{\equiv}CH$) and 73.5 ppm ($C{\equiv}CH$). The IR spectrum of **2** shows characteristic ethynyl absorption bands at 2109 cm^{-1} (2103 cm^{-1} for **1**). The high resolution mass spectrum (HRMS, EI, 70 eV) of **2** indicates a peak at *m*/*e* 239.0403 with the calculated value for $C_{13}H_{13}NFe$ being 239.0397.



Scheme 1. The formation of compound **2**.

2.2. Cyclic voltammetry of 2

The measurements were carried out in dichloromethane solutions at room temperature on a standard three-electrode system (platinum working electrode, saturated calomel electrode as a reference and platinum gauze counter electrode) using 0.1 M Bu_4NClO_4/CH_2Cl_2 as supporting electrolyte. All potentials were recalculated and given vs. $FeCp_2^+/FeCp_2$ redox couple. Electrochemical data are given in Table 1. Ethynylferrocene (**1**), ferrocene (**5**), 2,5-dimethylazaferrocene (**6**) were also investigated as reference compounds. Compounds **2** and **6** displayed (Fig. 3) a single partially chemically reversible and electrochemically irreversible oxidation process. The ratio $i_{pc}/i_{pa} \approx 0.5$ for 2,5-dimethylazaferrocene and ≈ 0.3 for **2**, indicates the lower stability (i.e. a higher reactivity) of the radical cation of the latter compound. The instability of the azaferrocenium cation was attributed to the localisation of the unpaired electron on nitrogen rather than at iron [25]. The higher reactivity of the ethynyl-substituted azaferrocenium cation is in keeping with the higher oxidation potential of **2** in comparison with 2,5-dimethylazaferrocene ($\mathbf{2}^{+\cdot}$ is therefore a stronger oxidant than the 2,5-dimethylazaferrocenium ion). Under the same conditions, ferrocene and ethynylferrocene displayed chemically reversible oxidation processes ($i_{pc}/i_{pa} = 0.95$–0.96). Comparison of the data in Table 1 shows that introduction of the ethynyl group to ferrocene and to 2,5-dimethylazaferrocene brings about approximately the same anodic shift of the $E_{1/2}$ values (0.16 V). This contrasts with the effect of the styryl group which behaves as an electron withdrawing group in styrylferrocene and as an electron donating group in 1′-styryl-2,5-dimethylazaferrocene [19]. Apparently, further comparative studies are needed to understand differences in electronic properties of these metallocenes.

Table 1
Electrochemical data on **1**, **2**, **6** and **5**

Compound	$E_{1/2}$/V	ΔE/V	i_{pc}/i_{pa}
2	0.400	0.230	0.31
6	0.240	0.160	0.69
1	0.160	0.230	0.96
5	0	0.090	0.95

The reported i_{pc}/i_{pa} ratios have been calculated at scan rate: 0.1 V s^{-1}.

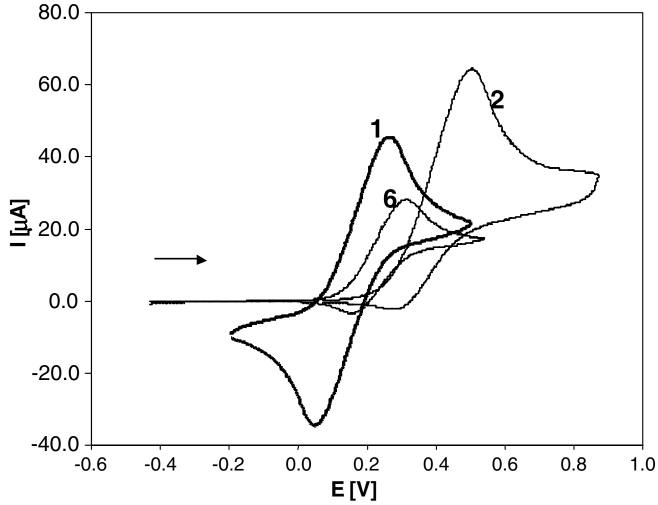


Fig. 3. Cyclic voltammograms of **1**, **2** and **6** in CH_2Cl_2 with 0.1 M Bu_4NClO_4 on Pt vs. $\mathbf{5}^+/\mathbf{5}$, scan rate: 0.1 V s^{-1}.

2.3. X-ray structure of W(CO)$_5$-2

In pure isolated form **2** is an air-stable, orange oil. The oily character, which is common for 2,5-dimethylazaferrocene and its derivatives at room temperatures, makes it impossible for any crystallographic measurements for this class of molecules. To overcome these difficulties, oily **2** can be transformed *via* reaction with photochemically generated $W(CO)_5$-THF into its $W(CO)_5$-**2** crystalline derivative. Compound $W(CO)_5$-**2** was characterised by IR, ^1H NMR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography. X-ray quality crystals of $W(CO)_5$-**2** were grown from *n*-pentane. The structure revealed the 2,5-dimethylazaferrocene unit to have an eclipsed conformation (*ca.* 3° stagger, rings inclined by *ca.* 3°) with the alkynyl substituent lying directly underneath the C(11) methyl group (Fig. 4), a conformation stabilised by a C–H···π contact from one of the methyl protons to the centre of the C(13)≡C(14) triple bond [H···π 2.93 Å, C–H···π 129°, H···π vector inclined by *ca.* 82° to the C(13)≡C(14) bond]. The geometry of the coordination of the tungsten-pentacarbonyl unit to the

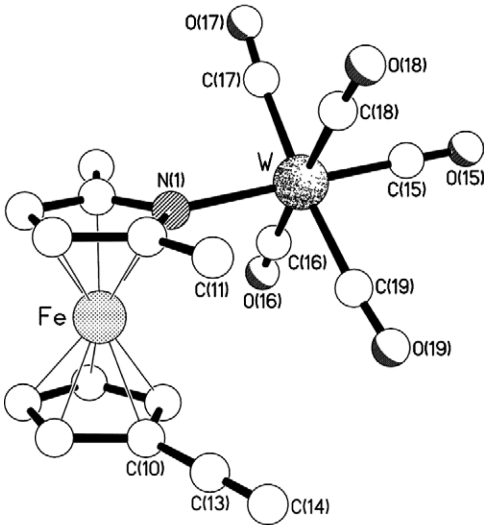


Fig. 4. The molecular structure of W(CO)$_5$-**2**.

nitrogen of the aza-ferrocenyl moiety is very similar to those seen previously in related structures [16b,17,26]. The tungsten centre has a distorted octahedral geometry with *cis* angles in the range 86.42(9)–93.52(7)°, and *trans* angles between 174.36(9)° and 179.20(7)° (Table 2). The W–CO bond *trans* to the nitrogen [1.966(2) Å] is noticeably shorter than the others [which range between 2.039(2) and 2.044(2) Å] reflecting the relative donor abilities of carbonyl and pyrrole. The coordination of the tungsten to the pyrrole ring is markedly distorted, the metal lying *ca.* 0.27 Å out of the C$_4$N plane. The W(CO)$_5$ moiety adopts a staggered conformation with respect to the pyrrole ring, the {W, C(15), C(17), C(19), N(1)} and {W, C(15), C(16), C(18), N(1)} planes being inclined by *ca.* 44° and 42°, respectively to the plane of the pyrrole ring. Adjacent molecules are linked by a C–H···π interaction between a proton on the pyrrole ring in one molecule and the cyclopentadienyl ring in a screw-related counterpart with an H···π separation of *ca.* 2.73 Å and a C–H···π angle of *ca.* 143° [the H···π vector is inclined by *ca.* 81° to the ring plane] forming a chain of molecules along the crystallographic *b* axis direction (see Fig. S2 in the supporting information). The closest approach to the pyrrole ring is from the O(18) carbonyl oxygen atom in a C_i-related molecule at *ca.* 3.34 Å [the C–O···π angle is *ca.* 123°].

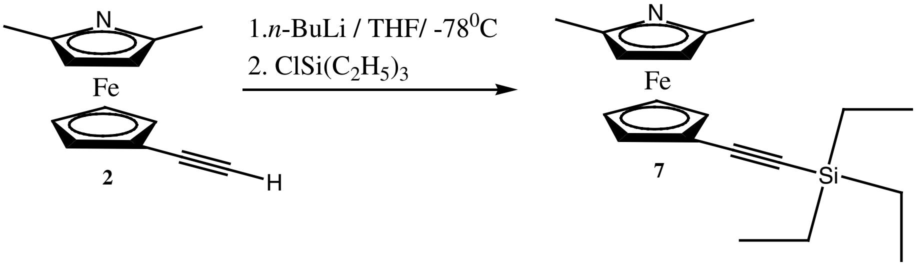
Table 2
Selected bond lengths (Å) and bond angles (°) for W(CO)$_5$-**2**

W–N(1)	2.2870(16)	W–C(15)	1.966(2)
W–C(16)	2.044(2)	W–C(17)	2.042(2)
W–C(18)	2.039(2)	W–C(19)	2.039(2)
C(13)–C(14)	1.184(3)		
N(1)–W–C(15)	179.20(7)	N(1)–W–C(16)	91.13(7)
N(1)–W–C(17)	92.10(8)	N(1)–W–C(18)	92.50(8)
N(1)–W–C(19)	93.52(7)	C(15)–W–C(16)	88.07(9)
C(15)–W–C(17)	87.96(10)	C(15)–W–C(18)	88.31(9)
C(15)–W–C(19)	86.42(9)	C(16)–W–C(17)	90.95(9)
C(16)–W–C(18)	176.21(8)	C(16)–W–C(19)	89.27(9)
C(17)–W–C(18)	87.84(10)	C(17)–W–C(19)	174.36(9)
C(18)–W–C(19)	91.59(9)	C(10)–C(13)–C(14)	177.4(3)

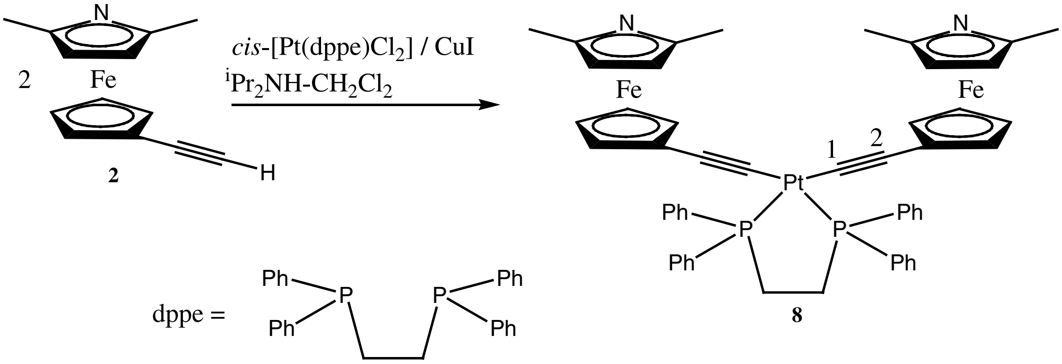
2.4. Reactivity of **2** – the synthesis of 7, **8**, **9**

We examined the chemical properties of **2** towards lithiation, silylation and coordination to Pt centres *via* the *cis*-[Pt(dppe)Cl$_2$] complex. 1′-Ethynyl-2,5-dimethylazaferrocene (**2**) was treated with *n*-BuLi in THF at −78 °C for 1 h and then chlorotriethylsilane in THF was added (Scheme 2). After 1 h, the reaction was quenched by addition of water. The separation of 1′-(triethylsilyl)ethynyl-2,5-dimethylazaferrocene (**7**) was easily achieved *via* column chromatography on silica and the product was isolated as an air stable red-orange oil. Substitution of the hydrogen atom of the ethynyl group is confirmed by the ^{1}H NMR spectrum of **7**. The ethynyl proton signal is not present but the characteristic nine protons triplet (1.04 ppm) and six proton quartet (0.66 ppm) of the ethyl groups are present. In the ^{13}C NMR spectrum signals of the ethynyl carbons are shifted downfield (103.2 ppm and 89.5 ppm) in comparison to **2** (80.8 ppm and 75.0 ppm). The IR spectrum of **7** shows ethynyl absorption bands at 2149 cm^{-1}. The high resolution mass spectrum (HRMS, EI, 70 eV) of **7** indicates a peak at *m*/*e* 353.1246 with the calculated value for $C_{19}H_{27}NSiFe$ being 353.1262.

For the synthesis of the bis(1′-ethynyl-2,5-dimethyloazaferrocenyl) complex of platinum (II) **8**, a literature procedure was followed (Scheme 3) [27]. 1′-Ethynyl-2,5-dimethylazaferrocene (**2**) was reacted overnight at room temperature with *cis*-[Pt(dppe)Cl$_2$] in the presence of a catalytic amount of copper iodide in the solvent mixture diisopropylamine and methylene chloride. Product **8** was isolated as an orange-red highly viscous oil *via* column chromatography on neutral alumina. Compound **8** was characterised by IR, ^{1}H, ^{13}C, ^{31}P NMR spectroscopy and mass spectrometry. The *cis*-geometry of complex **8** was confirmed by comparison of ^{13}C and ^{31}P NMR spectra with those previously reported for the analogous *cis*-ethynylferrocene platinum (II) complex [5a]. Carbon 1 (directly linked to the Pt centre) generates a doublet of doublets pattern of signals due to large (152 Hz) *trans*-$^2J_{PC}$ and small (15 Hz) *cis*-$^2J_{PC}$ coupling constants. For the *cis*-ethynylferrocene analogue of **8** such coupling constants were reported as 145 and 13 Hz [5a]. The doublet assigned to carbon 2 has *trans*-$^3J_{PC}$ coupling constants equal to 35 Hz but the *cis*- signals were not detected. This same doublet in the *cis*-ethynylferrocene counterpart was reported to be 33 Hz but the *cis*-coupling constant was also not detected. The ^{31}P NMR spectrum of **8** shows a single phosphorus signal with the platinum-phosphorus coupling constant equal to 2283 Hz (cf. 2281 Hz reported for the *cis*-ethynylferrocene analogue). Again, the oily **8** was transformed by formation of the crystalline W(CO)$_5$-**8** species. The structure of W(CO)$_5$-**8** was confirmed by IR, ^{1}H, ^{13}C, ^{31}P NMR spectroscopy and elemental analysis.



Scheme 2. The formation of compound **7**.



Scheme 3. The formation of compound **8**.

3. Conclusions

1′-Ethynyl-2,5-dimethylazaferrocene (**2**), a new air-stable heterometallocene has been prepared and characterised. Spectroscopy of **2** (IR, ^{1}H, ^{13}C NMR) indicates a similar triple bond character compared to ethynylferrocene (**1**). Cyclic voltammetry of **2** reveals an anodic shift of the oxidation potential in comparison to the parent 2,5-dimethylazaferrocene. The W(CO)$_5$-**2** crystal structure indicates intramolecular hydrogen contacts between the α-methyl groups of the pyrrolyl ring and triple bond. The synthetic potential of **2** was explored in a preliminary fashion via the synthesis of two Si and Pt derivatives. These results, in our opinion, support further study into the organic and coordination chemistry of **2** as a new potential heterometallocene building block in coordination, materials and medicinal chemistry. The advantage that **2** offers is in the tuning of electrochemical or optical properties by nitrogen atom protonation, methylation or coordination of additional metal centres.

4. Experimental

4.1. General remarks

All preparations were carried out using standard Schlenk techniques. All solvents were distilled over standard drying agents under nitrogen directly before use, and all reactions were carried out under an atmosphere of nitrogen. NMR spectra were recorded using a Delta upgrade on JEOL EX270 MHz, Bruker DRX400 MHz, Bruker AV500 spectrometers. Chemical shifts are reported in δ (ppm) using CDCl$_3$ (^{1}H δ 7.26 ppm), or external 85% aqueous H$_3$PO$_4$ (^{31}P) as the reference solvents. Mass spectra were recorded using positive FAB and EI methods on a micromass Autospec Q spectrometer. Infrared spectra were recorded as KBr disks on a Perkin–Elmer Spectrum RX FTIR spectrometer. Microanalyses were carried out by Mr. S Boyer at SACS (Scientific Analysis and Consultancy Services) at the University of North London. 2,5-Dimethylazaferrocene [28], 1′-formylo-2,5-dimethylazaferrocene [16b], *p*-toluenesulfonylazide [29] and *cis*-[Pt(dppe)Cl$_2$] [30] were prepared according to literature methods. All other chemicals were purchased from the Aldrich Chemical Co. The cyclic voltammetry measurements of **1**–**4**, 2,5-dimethylazaferrocene and ferrocene derivatives were carried out in CH$_2$Cl$_2$ with 0.1 M Bu$_4$NClO$_4$ under an Ar atmosphere on AUTOLAB (Eco Chemie BV) in three electrode system, where the working electrode was Pt (ϕ = 1.5 mm), the reference was a saturated calomel electrode, and the counter electrode was cylindrical platinum gauze. All potentials were recalculated and given vs. $\mathrm{FeCp_2^+/FeCp_2}$ redox couple.

4.1.1. Synthesis of 2

To a stirred suspension of 1′-formyl-2,5-dimethylazaferrocene (115 mg, 0.47 mmol) and finely powdered K$_2$CO$_3$ (194 mg, 1.4 mmol) in dry methanol (4 ml), a mixture of dimethyl-1-diazo-2-oxopropylphosphonate and dimethyl-2-oxopropylphosphonate (540 mg, 8.5:1 by ^{31}P NMR) in dry THF (1 ml) were added. The mixture was allowed to react overnight at room temperature and protected against light. A water saturated solution of $\mathrm{NaHCO_3}$ was added and the mixture was extracted with chloroform. The combined organic layers were dried over $\mathrm{MgSO_4}$ and the solvent was evaporated. The resultant oily, orange residue was subjected to column chromatography ($\mathrm{SiO_2}$, eluent: chloroform). The second (orange) fraction was collected and after evaporation of solvent furnished **2** as an orange oil in 75% yield (84 mg). ^{1}H NMR δ ($\mathrm{CDCl_3}$) 270 MHz: 4.36 (s, 2H, β-pyrrolyl), 4.34 (t, $J = 1.7$ Hz, 2H, $\mathrm{C_5H_4}$), 4.19 (t, $J = 1.7$ Hz, 2H, $\mathrm{C_5H_4}$), 2.82 (s, 1H, $\mathrm{C{\equiv}C}\mathit{H}$), 2.24 (s, 6H, $\mathrm{CH_3}$-pyrrolyl). ^{13}C {^{1}H}NMR δ ($\mathrm{CDCl_3}$) 100 MHz: 102.7 (α-pyrrolyl), 80.8 ($\mathit{C}\mathrm{{\equiv}CH}$), 75.0 ($\mathrm{C{\equiv}}\mathit{C}\mathrm{H}$), 72.7 ($\mathrm{C_5H_4}$), 72.2 (β-pyrrolyl), 70.9 ($\mathrm{C_5H_4}$), 65.6 (*ipso*-$\mathrm{C_5H_4}$), 14.7 ($\mathrm{CH_3}$ groups). MS (EI, 70 eV) $m/e = 239$ [$\mathrm{M^+}$], 89 [$\mathrm{C_5H_4C{\equiv}CH^+}$] HRMS: $m/e = 239.0403$ (Calc. for $\mathrm{C_{13}H_{13}NFe}$: 239.0397). IR (KBr, $\mathrm{cm^{-1}}$): $\nu_{\mathrm{C{\equiv}CH}}$ 2109. Anal. Calc. for $\mathrm{C_{13}H_{13}NFe}$: C, 65.30; H, 5.48; N, 5.86. Found: C, 65.24; H, 5.42; N, 5.86%.

4.1.2. Synthesis of $\mathrm{W(CO)_5}$-**2**

$\mathrm{W(CO)_5}$ (211 mg, 0.6 mmol) dissolved in THF (40 ml) was photolysed with a 400 W high-pressure mercury lamp for 25 min. The photolyte was treated with **2** (136 mg, 0.56 mmol) and the resulting solution was protected against light and stirred at room temperature for 5 h. Removal of solvent, followed by column chromatography ($\mathrm{SiO_2}$, eluent:chloroform:*n*-hexane 1:1) and evaporation of solvents gave $\mathrm{W(CO)_5}$-**2** as orange crystals. Yield 252 mg (80%). ^{1}H NMR δ ($\mathrm{CDCl_3}$) 270 MHz: 4.62 (s, 2H, β-pyrrolyl), 4.38 (m, 4H, $\mathrm{C_5H_4}$), 2.93 (s, 1H, $\mathrm{C{\equiv}C}\mathit{H}$), 2.59 (s, 6H, $\mathrm{CH_3}$-pyrrolyl) MS (EI, 70 eV) $m/e = 563$ [$\mathrm{M^+}$], 479 [$\mathrm{M^+}$–3CO], 423 [$\mathrm{M^+}$–5CO], 239 [$\mathrm{M^+}$–$\mathrm{W(CO)_5}$] IR (KBr, $\mathrm{cm^{-1}}$): $\nu_{\mathrm{C{\equiv}CH}}$ 2068, $\nu_{\mathrm{C{\equiv}O}}$ 1905, 1862. Anal. Calc. for $\mathrm{C_{18}H_{13}NO_5WFe}$: C, 38.40; H, 2.33; N, 2.49. Found: C, 38.46; H, 2.21; N, 2.46%.

4.1.3. Synthesis of 7

n-BuLi (1.6 M in hexane, 0.3 ml, 0.45 mmol) was added to a nitrogen-saturated solution of 1′-ethynyl-2,5-dimethyloazaferrocene (**2**) (100 mg, 0.41 mmol) in THF (10 ml) at −78 °C. The orange solution darkened and the mixture was stirred for 1 h at −78 °C. Chlorotriethylsilane (50 µl, 0.3 mmol) in 1 ml of THF was added and the stirring was continued for 1 h. The reaction was then quenched by water, extracted with chloroform, dried over $\mathrm{MgSO_4}$ and the solvent evaporated to give a dark brown-orange oil which was subjected to column chromatography ($\mathrm{SiO_2}$, eluent:ethyl acetate). After evaporation of the solvent, **7** was isolated as a red-orange oil. Yield 67 mg (46%). ^{1}H NMR δ ($\mathrm{CDCl_3}$) 400 MHz: 4.36 (s, 2H, β-pyrrolyl), 4.33 (s, 2H, $\mathrm{C_5H_4}$), 4.19 (s, 2H, $\mathrm{C_5H_4}$), 2.25 (s, 6H, $\mathrm{CH_3}$-pyrrolyl), 1.04 (t, $J = 7.8$ Hz, $\mathrm{CH_2C}\mathit{H}_3$), 0.66 (q, $J = 7.8$ Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$) ^{13}C {^{1}H}NMR δ ($\mathrm{CDCl_3}$) 100 MHz: 103.2 ($\mathrm{C{\equiv}C}$), 102.5 (α-pyrrolyl), 89.5 ($\mathrm{C{\equiv}C}$), 72.5 ($\mathrm{C_5H_4}$), 72.3 (β-pyrrolyl), 70.9 ($\mathrm{C_5H_4}$), 67.1 (*ipso*-$\mathrm{C_5H_4}$), 14.6 (α-$\mathrm{CH_3}$ pyrrolyl groups), 7.4 ($\mathrm{C_2H_5}$), 4.4 ($\mathrm{C_2H_5}$) MS (EI, 70 eV) $m/e = 353$ [$\mathrm{M^+}$], HRMS: $m/e = 353.1246$ (Calc. for $\mathrm{C_{19}H_{27}NSiFe}$: 353.1262) IR (KBr, $\mathrm{cm^{-1}}$): $\nu_{\mathrm{C{\equiv}CH}}$ 2149. Anal. Calc. for $\mathrm{C_{19}H_{27}NSiFe}$: C, 64.58; H, 7.70; N, 3.96. Found: C, 64.68; H, 7.78; N, 3.89%.

4.1.4. Synthesis of 8

A mixture of **2** (110 mg, 0.5 mmol) and *cis*-[$\mathrm{Pt(dppe)Cl_2}$] (166 mg, 0.25 mmol) in a 1:2 volume ratio in $^{i}\mathrm{Pr_2NH}$–$\mathrm{CH_2Cl_2}$ (5 ml:10 ml) was allowed to react in the presence of CuI (4 mg) at room temperature overnight. The resulting solution was evaporated to dryness. The residue was re-dissolved in chloroform and the solution was subjected to column chromatography on neutral $\mathrm{Al_2O_3}$ (eluent:chloroform). One orange fraction was eluted and after removal of the solvent, **8** was isolated as an orange-red high viscosity oil. Yield 232 mg (43%). ^{1}H NMR δ ($\mathrm{CDCl_3}$) 400 MHz: 8.03–7.98 (m, 8H, *meta*-Ph), 7.46–7.44 (m, 12H, *ortho* and *para*-Ph), 4.06 (t, $J = 1.7$ Hz, 2H, $\mathrm{C_5H_4}$), 4.04 (s, 2H, β-pyrrolyl), 3.97 (t, $J = 1.7$ Hz, 2H, $\mathrm{C_5H_4}$), 2.44–2.34 (m, 4H, –$\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2$–), 2.09 (s, 6H, $\mathrm{CH_3}$-pyrrolyl). ^{13}C {^{1}H}NMR δ ($\mathrm{CDCl_3}$) 125 MHz: 134.0–133.2 (m, *meta*-Ph), 131.2 (s, *para*-Ph), 129.7 (d, $^{1}J_{\mathrm{PC}} = 54$ Hz, *ipso*-Ph), 128.7–128.5 (m, *ortho*-Ph), 106.4 (d, $^{3}J_{\mathrm{PC}} = 35$ Hz Pt–$\mathrm{C{\equiv}}\mathit{C}$), 101.7 (s, α-pyrrolyl), 101.2 (dd, $^{2}J_{\mathrm{PC}}(\mathit{trans}) = 152$ Hz, $^{2}J_{\mathrm{PC}}(\mathit{cis}) = 15$ Hz, Pt–$\mathit{C}\mathrm{{\equiv}C}$), 73.2 (s, β-pyrrolyl), 72.6 (s, *ipso*-$\mathrm{C_5H_4}$), 71.6 (s, α or β $\mathrm{C_5H_4}$), 69.8 (s, α or β $\mathrm{C_5H_4}$), 28.7–28.2 (m, –$\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2}$–), 15.3 (s, $\mathit{C}\mathrm{H_3}$-pyrrolyl). ^{31}P {^{1}H}NMR δ ($\mathrm{CDCl_3}$) 162 MHz: 40.75 ($^{1}J_{\mathrm{PtP}} = 2283$ Hz). IR (KBr, $\mathrm{cm^{-1}}$): 2122; 2107; 533 FAB MS (+ve): $m/e = 1070$ $[\mathrm{M + H}]^+$, 975 $[\mathrm{M + H{-}C_6H_9N}]^+$, 832 $[\mathrm{M + H{-}C_{13}H_{12}NFe}]^+$.

4.1.5. Synthesis of $\mathrm{W(CO)_5}$-**8**

$\mathrm{W(CO)_5}$ (140 mg, 0.4 mmol) dissolved in THF (40 ml) was photolysed with a 400 W high-pressure mercury lamp for 25 min. The photolyte was treated with **8** (154 mg, 0.14 mmol) and the resulting solution was stirred at room temperature for 6 h. Removal of the solvent, followed by column chromatography (neutral $\mathrm{Al_2O_3}$, eluent:chloroform:*n*-pentane 1:1) and evaporation of the solvents gave $\mathrm{W(CO)_5}$-**8** as an orange crystalline solid. Yield 167 mg (70%). ^{1}H NMR δ ($\mathrm{CDCl_3}$) 270 MHz: 8.05–7.95 (m, 8H, *meta*-Ph), 7.59–7.46 (m, 12H, *ortho* and *para*-Ph), 4.17 (s, 2H, β-pyrrolyl), 4.12 (s, 4H, $\mathrm{C_5H_4}$), 2.42–2.34 (m, 4H, –$\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2$–), 2.34 (s, 6H, $\mathrm{CH_3}$-pyrrolyl). ^{13}C {^{1}H}NMR δ ($\mathrm{CDCl_3}$) 125 MHz: 198.6 *trans*-*C*O, 191.1 *cis*-*C*O, 134.0–133.0 (m, *meta*-Ph), 131.6 (s, *para*-Ph), 129.8–128.2 (m, *ipso*-Ph and *ortho*-Ph), 105.31 (d, $^{3}J_{\mathrm{PC}} = 35$ Hz Pt–$\mathrm{C{\equiv}}\mathit{C}$), 105.0 (s, α-pyrrolyl), 103.7 (dd, $^{2}J_{\mathrm{PC}}(\mathit{trans}) = 145$ Hz, $^{2}J_{\mathrm{PC}}(\mathit{cis}) = 15$ Hz, Pt–$\mathit{C}\mathrm{{\equiv}C}$), 75.9 (s, β-pyrrolyl), 73.6 (s, *ipso*-$\mathrm{C_5H_4}$), 73.5 (s, α or β $\mathrm{C_5H_4}$), 71.7 (s, α or β $\mathrm{C_5H_4}$), 29.3–28.7 (m, –$\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2}$–), 18.8 (s, $\mathit{C}\mathrm{H_3}$-pyrrolyl). ^{31}P {^{1}H}NMR δ ($\mathrm{CDCl_3}$) 109 MHz: 41.70 ($^{1}J_{\mathrm{PtP}} = 2294$ Hz) IR (KBr, $\mathrm{cm^{-1}}$): 2065, 1907, 532. Anal. Calc. for $\mathrm{C_{62}H_{48}N_2P_2O_{10}PtW_2Fe_2}$: C, 43.36; H, 2.82; N, 1.63. Found: C, 43.27; H, 2.82; N, 1.63%.

4.2. Crystallography

*Crystal data for [W(CO)$_5$-**2**]*: $C_{18}H_{13}FeNO_5W$, $M = 562.99$, monoclinic, $P2_1/c$ (no. 14), $a = 9.4161(12)$ Å, $b = 12.345(3)$ Å, $c = 16.1457(15)$ Å, $\beta = 100.786(9)°$, $V = 1843.6(5)$ Å^3, $Z = 4$, $D_c = 2.028$ g cm^{-3}, μ(Mo Kα) = 7.049 mm^{-1}, $T = 173$ K, orange/brown blocks, Oxford Diffraction Xcalibur 3 diffractometer; 6061 independent measured reflections, F^2 refinement, $R_1 = 0.022$, $wR_2 = 0.054$, 4758 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 64°$], 238 parameters. CCDC 603274.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.043.

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