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Synthesis of a diferrocenylvinylidene complex by migration of a ferrocenyl substituent†

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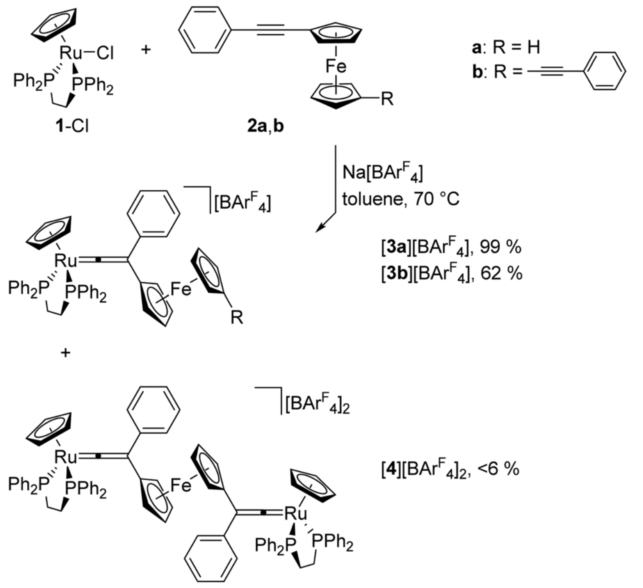
An unusual 1,2-ferrocenyl migration has been observed following reactions of [Ru(dppe)Cp][BAr$^F{}_4$] with diferrocenylacetylene, extending the scope of group rearrangements beyond methyl (Wagner–Meerwein) and phenyl entities. Ferrocene-containing bis(alkynes) RC≡CArC≡CR (R = Fc, Ar = 1,4-phenylene; R = Ph, Ar = 1,1′-ferrocenylene) gave bimetallic bis(vinylidene) complexes following two consecutive rearrangements.

The construction of new molecular scaffolds by controlled intramolecular migration and rearrangement processes is a powerful tool in synthetic chemistry. In the most general possible terms, the course of a rearrangement reaction is governed by the relative migratory aptitude of the possible migrating groups, with migrations of hydrogen, alkyl fragments and substituted aromatic fragments[1] as well as the skeletal bonds of (poly)cyclic frameworks all well known.[2] Examples include the Wagner–Meerwein reaction involving the 1,2-migration of skeletal C–C bonds in carbocations and related methyl substituent migrations observed in the Nametkin and Pinacol rearrangements to name but a few.[2a]

Despite the prevalence of rearrangement reactions and the close synergies in the substitution chemistry of ferrocene and aromatic organic compounds, the migration of ferrocenyl groups is rare and has yet only been observed within a Pinacol rearrangement,[3] whereas methyl migration,[4] Wolff (FcC(O)CHN$_2$ to FcHC=C=O)[5] and Curtius rearrangements (FcC(O)N$_3$ to FcNH$_2$)[6] around the periphery of ferrocenyl backbones are all known. We now report the rearrangement of ferroceneyl-substituted alkynes and diynes to ferrocenyl-substituted vinylidenes within the coordination sphere of a half-sandwich ruthenium fragment.[7–9] The 1,2-ferrocenyl migration occurs in a nucleophilic fashion, similar to those previously reported for rearrangements of internal alkynes.[10]

The coordinatively and electronically unsaturated complex [Ru(dppe)Cp][BAr$^F{}_4$] ([**1**]BAr$^F{}_4$; dppe = 1,2-bis(diphenylphosphino)ethane, Cp = η^5-C$_5$H$_5$, [BAr$^F{}_4$]$^-$ = [B(3,5-(CF$_3$)$_2$–C$_6$H$_3$)$_4$]$^-$) is known to promote rearrangements of internal aromatic alkynes RC≡CR′ under moderate conditions (toluene, 70 °C, 0.5–12 h) to vinylidenes: C=CR(R′) *via* 1,2-migration reactions within the metal coordination sphere.[7–9] Scoping reactions of ferrocenylphenylacetylene (**2a**) with [**1**][BAr$^F{}_4$] (generated *in situ* from RuCl(dppe)Cp (**1-Cl**)[11] and Na[BAr$^F{}_4$])[12] gave the vinylidene complex [**3a**][BAr$^F{}_4$] in quantitative yield (Scheme 1).

Given the results of computational studies on related systems, showing migration of the less electron-rich substituent,[10] it is likely that the phenyl group migrates in the formation of



Scheme 1 Internal alkyne/vinylidene rearrangement reactions of alkyne **2a** and bis(alkyne) **2b** for the synthesis of ferrocenyl phenyl vinylidene complexes.

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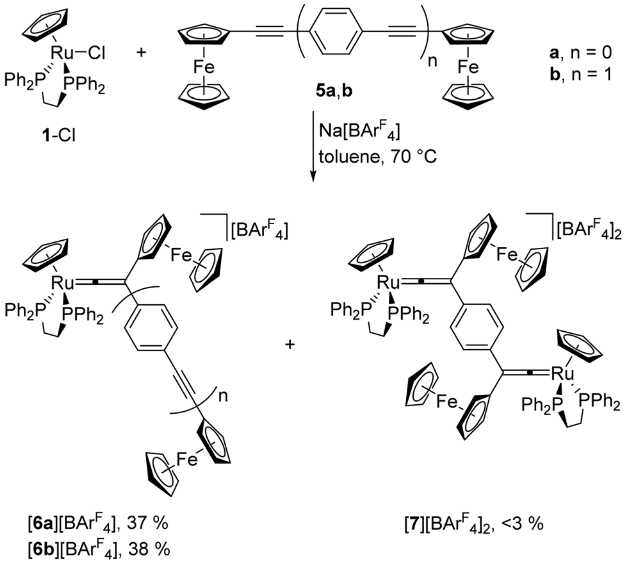


Scheme 2 Internal alkyne/vinylidene rearrangement of diferrocenyl(bis) alkynes **5a**,**b** for the synthesis of diferrocenyl vinylidene complexes.

[**3a**]$^+$. A similar reaction of [**1**][BAr$^F_4$] with **2b**, bearing an additional phenylethynyl substituent in the 1′-position, gave [**3b**][BAr$^F_4$] in good (62%) yield together with a double-rearrangement product, the bimetallic bis(vinylidene) complex [**4**][BAr$^F_4$]$_2$ in low yield over 18 h.

With ferrocenyl alkynes clearly demonstrated to be compatible with the rearrangement processes within the coordination sphere of [Ru(dppe)Cp]$^+$, attention was turned to the exploration of the ferrocenyl migration processes (Scheme 2). Reaction of a mixture of **1-Cl** and Na[BAr$^F_4$] with 1,2-diferrocenylacetylene (**5a**) gave the diferrocenylvinylidene complex [**6a**][BAr$^F_4$], which although only isolated in moderate (37%) yield, unambiguously evidenced the migration of a ferrocenyl moiety (Fig. 1).

Mechanistically, half-sandwich species such as [Ru(dppe)Cp]$^+$ are known to stabilise the vinylidene product relative to the η^2-alkyne tautomer upon reaction with terminal and internal alkynes.[13] Asymmetrically-substituted alkyne substrates bearing Ph and *p*-OMe-C_6H_4 groups show the highest rates of reaction (typically being adjudged complete within 0.5 h at 70 °C in dichloroethane), driven by migration of the less-electron-rich substituent.[10] Notably, symmetric alkynes, *e.g.* PhC≡CPh, and aliphatic, (*i.e.* electron rich) substrates rearrange less quickly, taking 1 h and 10 d, respectively to reach completion.[8] This general pattern of reactivity is reflected in the high yield of [**3a**]$^+$ and its relatively rapid formation (2 h) from **2a**, combining an electron-rich ferrocenyl group and a phenyl ring. Although 1,2-diferrocenylacetylene (**5a**) combines both aspects above mentioned that potentially lower the migration rate, it may also be that the coordination of the alkyne substrate towards the metal centre is less effective, due to the increased bulkiness of a ferrocenyl compared to a phenyl substituent.

The reaction of the bis(alkyne), 1,4-bis(ferrocenylethynyl)benzene (**5b**) with [**1**][BAr$^F_4$] gave products arising from mono ([**6b**][BAr$^F_4$], 38%) and double ([**7**][BAr$^F_4$]$_2$, <3%) rearrangement reactions (Scheme 2). Although the double rearrangement product was only isolated in trace quantities, the structure was confirmed by single crystal X-ray diffraction (Fig. 2). Although we cannot definitively rule out the formation of [**7**][BAr$^F_4$]$_2$ by migration of the vinylidene-functionalised phenylene group {Ru(C=C(Fc)C_6H_4–)(dppe)Cp}$^+$ (which would also be unprecedented), we suggest that in this case it is more likely that the smaller ferrocenyl moiety acts as the migrating group.

The procedure outlined in Schemes 1 and 2 provides access to ferrocenyl-substituted vinylidene complexes that are otherwise only accessible by either protonation[14] or S_N2-type reactions of ferrocenylacetylide complexes with *e.g.* MeI[15] and other alkyl halides,[16] whereas products bearing arene entities were inaccessible. Attempts to obtain [**6a**]$^+$ by reacting the ferrocenyl vinylidene [Ru{C=C(H)Fc}(dppe)Cp]$^+$ ([**8**]$^+$) and ferrocene (FcH) in accordance to an intramolecular S_EAr-type cyclization,[17] were not successful (Scheme 3).

As an aside, we note that attempts to synthesise complex [**8**]$^+$ from **1**, Na[BAr$^F_4$] and ferrocenylacetylene FcC≡CH (**9**) in methanol, the common solvent for such reactions with terminal alkynes,[18] resulted in formation of the carbene [**10**]$^+$ within 2 h. This is somewhat unusual, the formation of Fischer carbenes by

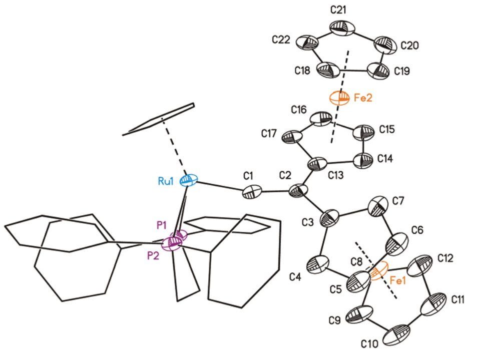


Fig. 1 ORTEP/wireframe model (50% probability level) of **[6a]$^+$** showing the labelling of the vinylidene ligand. Hydrogen atoms and the [BAr$^F_4$]$^-$ counter ion are omitted for clarity. Selected bond distances (Å): Ru=C1 1.840(3), C1=C2 1.337(11), C2–C3 1.482(11), C2–C13 1.468(11), C3–C2–C13 121.6(7).

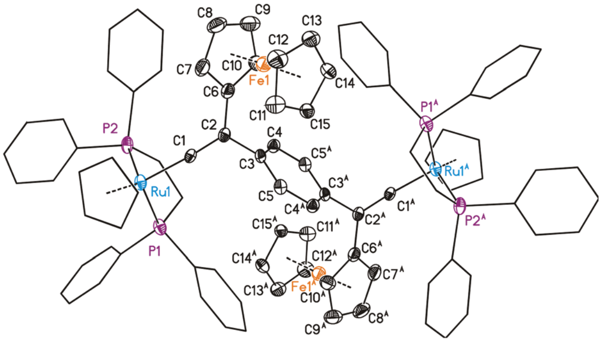
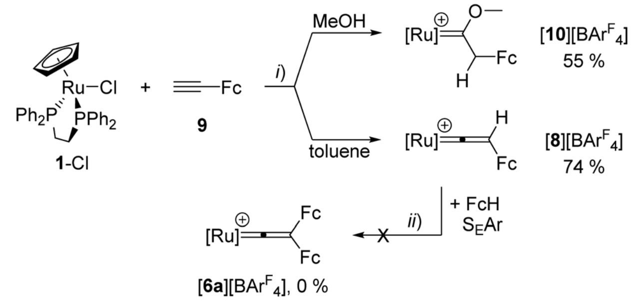


Fig. 2 ORTEP/wireframe model (30% probability level) of [**7**]$^{2+}$ showing the labelling of the vinylidene ligand. Hydrogen atoms, the [BAr$^F_4$]$^-$ counter ions and two disordered molecules of $CHCl_3$ are omitted for clarity. Selected bond distances: Ru=C1 1.843(3), C1=C2 1.311(4), C2–C3 1.498(5), C2–C6 1.475(5), Ru···Ru 10.4738(6), C_5H_5···C_5H_5 11.407(16), C3–C2–C6 118.6(3). (Symmetry codes for generating equivalent atoms: −*x*, −*y*, −*z*.)



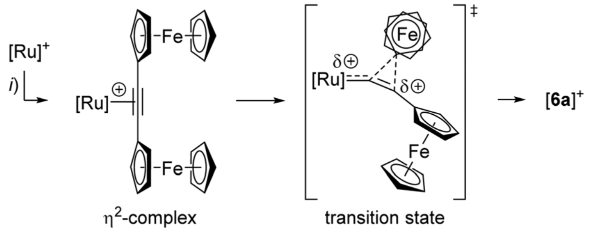
Scheme 3 Reaction of **1** with ethynylferrocene (**9**) and attempted synthesis of diferrocenyl vinylidene [**6a**]$^+$ by S$_E$Ar from vinylidene [**8**]$^+$. (i) Na[BAr$^F_4$], reflux, 2 h, solvent; (ii) CH$_2$Cl$_2$, 25 °C, 7 d.

addition of MeOH to sterically encumbered vinylidene complexes usually requiring reaction periods of 2 days.[19] To avoid this issue, the synthesis of [**8**]$^+$ was carried out in toluene.

The vinylidene complexes [**3a,b**]$^+$, [**4**]$^{2+}$, [**6a,b**]$^+$, [**7**]$^{2+}$, [**8**]$^+$, and carbene [**10**]$^+$ were characterised by various NMR techniques, in addition to mass spectrometry and IR spectroscopy. The ^{31}P{^{1}H} NMR resonances of the dppe ligands appear at ~77 ppm for vinylidene complexes and at 89 ppm for carbene [**10**]$^+$. Resonances of the α carbon of the vinylidene ligand were observed between 352 and 364 ppm in the ^{13}C{^{1}H} NMR spectra (see ESI†). The carbene carbon in [**10**]$^+$ is significantly more shielded and resonates at 302 ppm.

Vinylidene complexes [**3a**][BAr$^F_4$], [**6a**][BAr$^F_4$], [**6b**][BAr$^F_4$], [**7**][BAr$^F_4$]$_2$ and carbene [**10**][BAr$^F_4$] could further be analysed by single crystal X-ray diffraction (Fig. 1, 2 and Fig. S2, S3, ESI†). The vinylidene complexes display Ru=C$_\alpha$ (1.840(3)–1.857(5) Å) and C$_\alpha$=C$_\beta$ (1.31 Å) bond lengths entirely consistent with the description as vinylidene structures (Table S1, ESI†).[20] The Ru=C bond length in carbene [**10**]$^+$ is elongated to 1.948(2) Å. The C$_\beta$–R1/R2 distances in vinylidene complexes are consistent with the C–C single bond nature of these connections. Especially in [**7b**]$^{2+}$, the similarity of the C2–C6 (1.475(5) Å) and C2–C3 (1.498(5) Å) distance confirms the absence of a cumulene character of the bridging phenylene. Together with a rather perpendicular vinylidene/phenylene plane intersection (68.3(3)°) delocalisation over the entire π-system, and hence communication between both metal centres, can be excluded.

Based on the observations described here and elsewhere[10] the rearrangement of 1,2-diferrocenylacetylene (**5a**) within the coordination sphere of [**1**]$^+$ can be envisioned in a series of simple steps (Scheme 4). Coordination of the alkyne results in a η^2-complex from which a subsequent 1,2-sigmatropic shift of a ferrcenyl group takes place. Migration of one of the ferrocenyl groups from the alpha towards the beta carbon is the first of its kind and results in the diferrocenylvinylidene complex [**6a**][BAr$^F_4$]. The formation of the bimetallic, dicationic bis(vinylidene) complexes [**4**]$^{2+}$ and [**7**]$^{2+}$ requires coordination of [Ru(dppe)Cp]$^+$ ([**1**]$^+$) to the positively charged alkynes [**3b**]$^+$ and [**6b**]$^+$ prior to the second rearrangement. The low yields of [**4**]$^{2+}$ and [**7**]$^{2+}$ might therefore be reasonably explained by the electrostatic repulsion that must be overcome to form the initial π-complex intermediates.



Scheme 4 Schematic representation of the mechanism for the synthesis of diferrocenylvinylidene complex [**6a**]$^+$. ([Ru] = [Ru(dppe)Cp]; the [BAr$^F_4$]$^-$ counter ions are omitted.)

Analysis of the electrochemical properties showed (electro)-chemically reversible ferrocenyl-related redox events for [**3a,b**]$^+$, [**4**]$^{2+}$, [**6a,b**]$^+$ and [**10**]$^+$, whereas [**8**]$^+$ slowly decomposed (Table 1 and Fig. S1; for more information see the ESI†). The *gem*-diferrocenyl vinylidene [**6a**]$^+$ reveals the lowest (most thermodynamically favourable) redox potentials. Replacement of one Fc by a phenyl group increases $E_1^{\circ\prime}$ from 31 ([**6a**]$^+$) to 55 mV ([**3a**]$^+$). Additional FcC≡C groups in *para* position of the phenyl moiety ([**6b**]$^+$) resulted in essentially no change in the first oxidation potential.

In contrast, functionalization of the ferrocene moiety with an electron-withdrawing PhC≡C fragment in the 1′-position (Fc′, [**3b**]$^+$) shifts the redox potential to 121 mV, whereas a cationic vinylidene fragment (Fc″, [**4**]$^{2+}$) is less electron withdrawing ($E_1^{\circ\prime}$ = 93 mV). The relative oxidation potentials of [**3a**]$^+$ (55 mV) and [**4**]$^{2+}$ (93 mV) are readily attributed to the differences in charge on the complex, but surprisingly small. All told, inspection of the trends in the first oxidation potential indicate that the ferrocene moiety is the redox site, that the formal complex charge is predominantly located at ruthenium, and that conjugation between the vinylidene entity and the ferrocenyl group is of minor importance. Carbene [**10**]$^+$ shows

Table 1 Ferrocenyl-related redox events ($E^{\circ\prime}$) in vinylidene complexes [**3a,b**]$^+$, [**4**]$^{2+}$, [**6a,b**]$^+$, and [**8**]$^+$ (general substitution pattern [Ru{=C=CR^{1}R^2}(dppe)Cp]$^+$), and carbene [**10**]$^{+\,a}$

Compd.	R^1	R^2	$E_1^{\circ\prime}$	$E_2^{\circ\prime}$	$\Delta E_{1,2}^{\circ\prime}$
Vinylidene					
[3a]$^+$	Ph	Fc	55	—	
[3b]$^+$	Ph	Fc‴(Ph)	121	—	
[4]$^{2+}$	Ph	Fc″(Ph)	93	—	
[6a]$^+$	Fc	Fc	31	476	445
[6a]$^{+\,b}$	Fc	Fc	−40	110	150
[6b]$^{+\,c}$	Fc	Ph‴(Fc)	60	174	114
[8]$^+$	Fc	H	14	—	—
Carbene					
[10]$^+$	CH$_2$Fc	OMe	172	—	—

Potentials *vs.* FcH/FcH$^+$ except otherwise noted, scan rate of 100 mV s^{-1}; glassy carbon (GC) working electrode; anhydrous dichloromethane solutions containing 0.1 mol L^{-1} of [NBu$_4$][BAr$^F_4$] as supporting electrolyte at 25 °C; ‴ – featuring an alkynyl substituent; ″ – featuring a vinylidene substituent. ^{a} All potentials are given in mV. ^{b} In 0.1 mol L^{-1} [NBu$_4$][PF$_6$]. ^{c} Obtained *via* square wave voltammetry (fitted voltammogram).

the most anodically shifted redox process, although being well-separated from the cationic carbene entity.

As expected, the diferrocenyl functionalized complexes [**6a,b**]$^+$ showed an additional redox process at higher potential. In *gem*-diferrocenyl vinylidene [**6a**]$^+$ these two processes are separated by $\Delta E^{\circ\prime}_{1,2} = 445$ mV in the $[\mathrm{NBu_4}][\mathrm{BAr^F}_4]$ electrolyte featuring a bulky and weakly-coordinating anion. Measurement of the voltammetry in a 0.1 M $[\mathrm{NBu_4}][\mathrm{PF_6}]$ electrolyte solution reduces the redox separation to $\Delta E^{\circ\prime}_{1,2} = 150$ mV, due to a better ion-pairing in solution and consequent shielding of the developing positive charge by the $[\mathrm{PF_6}]^-$ counter ion. The change in the separation of these two redox processes, $\Delta\Delta E^{\circ\prime}_{1,2} = 295$ mV, can thus be ascribed to a compensation of electrostatic repulsion. The redox separation of 150 mV is similar to *gem*-diferrocenyl alkenes bearing H[21] and alkyl groups,[22] as well as tetraferrocenyl allene.[23] Although the magnitude of ΔE is a result of the sum of a number of factors,[24] the residual redox separation of 150 mV in [**6a**]$^+$ in $[\mathrm{NBu_4}][\mathrm{PF_6}]$ electrolyte is also likely dominated by electrostatic interactions rather than electronic communication, as shown recently in a study of cross-conjugated diferrocenyl imines.[25] Insertion of a phenylethynyl spacer ([**6b**]$^+$) further reduced $\Delta E^{\circ\prime}_{1,2}$ to 114 mV even if measured in $[\mathrm{NBu_4}][\mathrm{BAr^F}_4]$.

In summary reaction of $[\mathrm{Ru(dppe)Cp}]^+$ ([**1**]$^+$) and $\mathrm{FcC{\equiv}CFc}$ (**5a**) resulted in an internal alkyne/vinylidene rearrangement affording complex $[\mathrm{Ru}\{{=}\mathrm{C}{=}\mathrm{CFc_2}\}(\mathrm{dppe})\mathrm{Cp}]^+$ ([**6a**]$^+$) clearly demonstrating that ferrocenyl groups are able to migrate along a carbon–carbon bond in a 1,2-fashion similar to methyl (Wagner–Meerwein) and phenyl group rearrangements. Substrates bearing two alkynyl functionalities and multiple ferrocenyl fragments underwent two subsequent rearrangements forming bimetallic bis(vinylidene) complexes. Electrochemical investigations of the vinylidene complexes revealed a redox separation of up to 445 mV for a $={\mathrm{C}}{=}\mathrm{CFc_2}$ substitution pattern caused by electrostatic interactions.

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Conflicts of interest

There are no conflicts to declare.

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