

Electron-rich Fe(II) and Fe(III) organoiron σ -alkynyl complexes bearing a functional aryl group. Vibrational spectroscopic investigations of the substituent effect on the C \equiv C triple bond †

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Solid state Raman and IR spectra of $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-X})^{n+}][\text{PF}_6^-]_n$ ($n = 0, 1$; dppe = 1,2-(diphenylphosphino)ethane; X = NO₂, CN, CF₃, F, Br, H, Me, ^tBu, OMe, NH₂) complexes (**1a–j**)/[**1a–j**]⁺[PF₆[−]]) were recorded. The Raman spectra are discussed in connection with the corresponding solid state IR spectra. In the present set of compounds, Raman allows a firm identification of $\nu_{\text{C}\equiv\text{C}}$ stretching modes and confirms the occurrence of Fermi coupling with some substituents in a given oxidation state. Linear correlations between the IR frequencies or between the square roots of the intensities of the alkynyl stretch and the electronic substituent parameters (ESPs) allow establishment of the electronic origin of the substituent influence on the strength and polarization of the triple bond.

Introduction

In the field of molecular-based materials, transition metal–acetylide complexes attract considerable attention for various applications since it has been realized that very interesting properties could emerge from the synergy between metal centres and triple bonds.^{2–18} Often, the stretching motion of the acetylide linkage in the “M–C \equiv C” fragment absorbs in a spectral region devoid of other transitions and constitutes an interesting probe to study the electronic structure of this organometallic motif. Accordingly, IR spectroscopy has been advantageously used to investigate the bonding within M–C \equiv C units in very different architectures, from the infinite organometallic polymers¹⁹ to discrete mono- or polynuclear redox-active complexes.^{20–22}

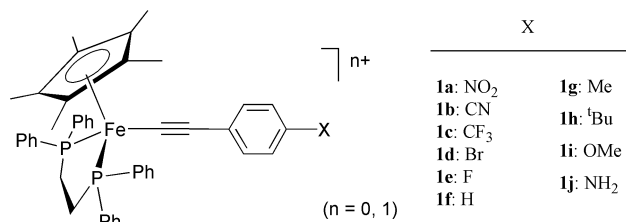
We have recently synthesised and characterized the family of mononuclear Fe(II) and Fe(III) iron acetylides $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-X})^{n+}][\text{PF}_6^-]_n$ ($n = 0, 1$; dppe = 1,2-bis(diphenylphosphino)ethane; X = NO₂, CN, CF₃, F, Br, H, Me, ^tBu, OMe, NH₂) (**1a–j**)/[**1a–j**]⁺[PF₆[−]]. See Scheme 1).¹ The stretching frequency of the triple bond ($\nu_{\text{C}\equiv\text{C}}$) was apparently dependant on the electronic nature of the appended substituent and its evolution could be qualitatively rationalized using a val-

ence bond (VB) formalism (Scheme 2), considering that respectively electron-withdrawing substituents in Fe(II) acetylides (**1a–j**) or electron-releasing substituents in the Fe(III) congeners [b1a–j]⁺[PF₆[−]] favour the cumulenic character of the alkynyl bridge.²³ In the present work we wanted first to confirm the previous results by recording the corresponding solid state Raman spectra. These two spectroscopies are very complimentary since strong IR intensities are expected for large dipole moment changes, while Raman transitions are connected to changes in polarisability of the electronic cloud.²⁵ We will also try to demonstrate the purely electronic nature of this substituent effect by investigating the frequency dependence as well as the intensity dependence of the alkynyl stretch on various sets of electronic substituent parameters (ESPs) characterizing the substituent X. The signification of these results regarding the structure of the metal–alkynyl unit in $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-X})^{n+}][\text{PF}_6^-]_n$ will be discussed.

Experimental

Raman spectra of the solid samples in sealed glass tubes were obtained by diffuse scattering and recorded in the 100–3300 cm^{−1} range (Stokes emission) using a Bruker RFS 100 spectrometer with a laser excitation source at 1064 nm. For some samples like **1d** (X = Br), a strong fluorescence precluded the observation of the Raman spectrum. In other cases such as, for instance, **1f** (X = H) or [b1d]⁺[PF₆[−]], only part of the spectrum was obtained.

Transmittance-FTIR spectra were recorded using a Bruker IFS28 spectrometer, equipped with a Nernst Globar source, a KBr separator and a DTGS detector (400–7500 cm^{−1}). Solid samples spectra were obtained from Nujol mulls in KBr windows. IR intensity measurements were performed with 0.005–0.018 M solutions of the complexes in distilled and degassed dichloromethane, under argon, using a 0.1 mm thick liquid cell with KBr windows. Typically, the spectrum for the neutral complex was recorded first. The spectrum for the corresponding Fe(III) congener was recorded next, after *in situ* oxidation



Scheme 1

† Electronic supplementary information (ESI) available: Figs. S1–3: solution IR correlations. See <http://www.rsc.org/suppdata/dt/b1/b108723c/>

For the preceding article on Fe(II) and Fe(III) alkynyls, see: ref. 1.

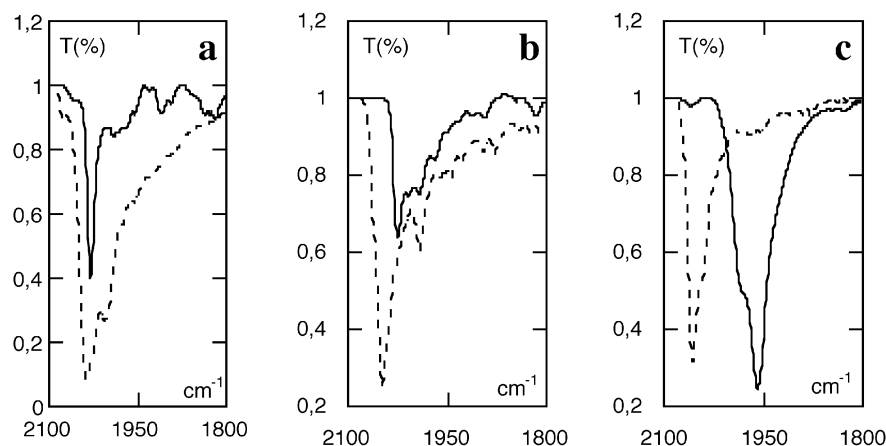
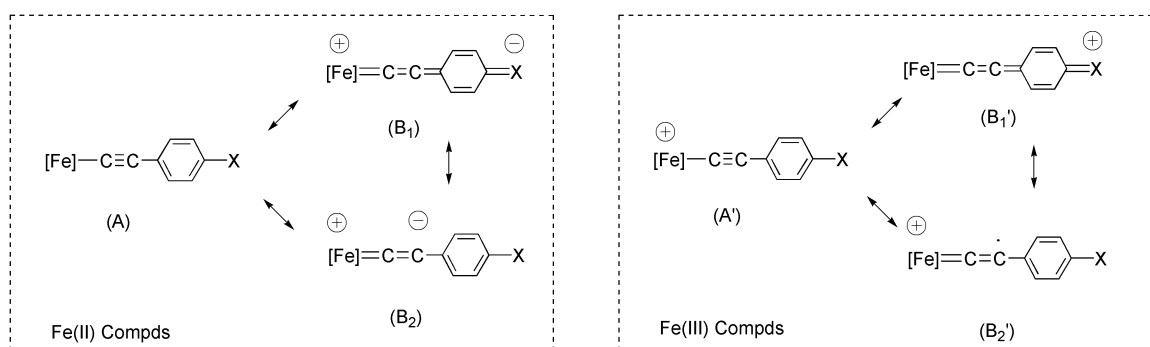


Fig. 1 IR $\nu_{\text{C}\equiv\text{C}}$ absorptions for $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C}(\text{C}_6\text{H}_4)\text{X}]^+[\text{PF}_6^-]_n$ complexes for $n = 0$ (broken lines) and $n = 1$ (full lines) with $\text{X} = \text{NO}_2$ (a); $\text{X} = \text{H}$ (b) or $\text{X} = \text{NH}_2$ (c).



Scheme 2

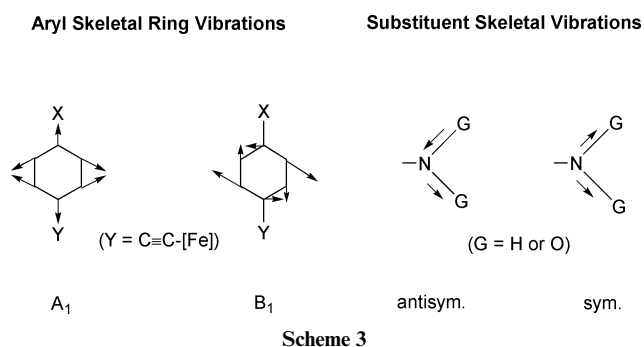
using ferrocenium hexafluorophosphate.¹ Integration was performed on the absorption peak expressed in absorbance mode, taking into account only the regions above the background. For very weak absorptions, rather large experimental uncertainties were stated (*ca.* 50%), mostly owing to the difficulty to properly define the integration area. In such cases, the spectra were recorded twice with solutions of different concentrations. Double checks using solutions made from isolated Fe(III) alkynyl complexes were also performed in some cases. The frequencies were expressed in wavenumbers (cm^{-1}) as usual, while for the intensities the IUPAC practical units ($\text{cm}^{-2} \text{M}^{-1}$) were retained. Data fitting and computation of linear regression coefficients was achieved by use of the Kaleidagraph™ program. The synthesis of **1a–j** and $[\mathbf{1a-j}]^+[\text{PF}_6^-]$ was previously reported.¹

Results and discussion

Solid state Raman and IR spectrometry of $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-X})]^+[\text{PF}_6^-]_n$ ($n = 0, 1$)

The solid state IR spectra of **1a–j** and $[\mathbf{1a-j}]^+[\text{PF}_6^-]$ were recorded along with the corresponding Raman spectra. The wavenumbers of most of the Raman transitions observed in the Stokes region for these compounds match closely these obtained by IR spectroscopy (Figs. 1 and 2). However, depending on the compound, most transitions exhibit different relative magnitudes in the Raman and IR. Moreover, for most compounds, the Raman spectrum exhibits fewer transitions than the IR. For compounds belonging to the C_1 symmetry group in the solid state,¹ selection rules can not be advanced here, since all vibrational modes should be equally Raman and IR active. Thus, only the few vibronic motions detected in Raman result in large polarisability changes. Among these, some selected Raman transitions for the present Fe(II) and Fe(III) alkynyls are compared to the corresponding IR absorptions in Table 1.

In Raman, two transitions dominate the spectrum of most complexes regardless the substituent present and the oxidation state of the iron centre. These are (i) the triple bond stretching mode ($2100\text{--}1950 \text{ cm}^{-1}$) and (ii) a second transition in the aromatic region ($1650\text{--}1590 \text{ cm}^{-1}$). Since the aryl bearing the X substituent experiences a C_{2v} local symmetry, we attribute the latter to the A_1 stretching mode of the aromatic ring. Another third strong peak is also often present below 1590 cm^{-1} . In this spectral range however, the stretching modes expected for the substituted phenyl ring are undistinguishable from vibrational modes involving other parts of the molecule.³⁰ Accordingly, several assignments can be proposed for this third absorption which could either correspond to the B_1 skeletal deformation of the substituted aryl ring (Scheme 3),^{26,27} to a Fermi resonance



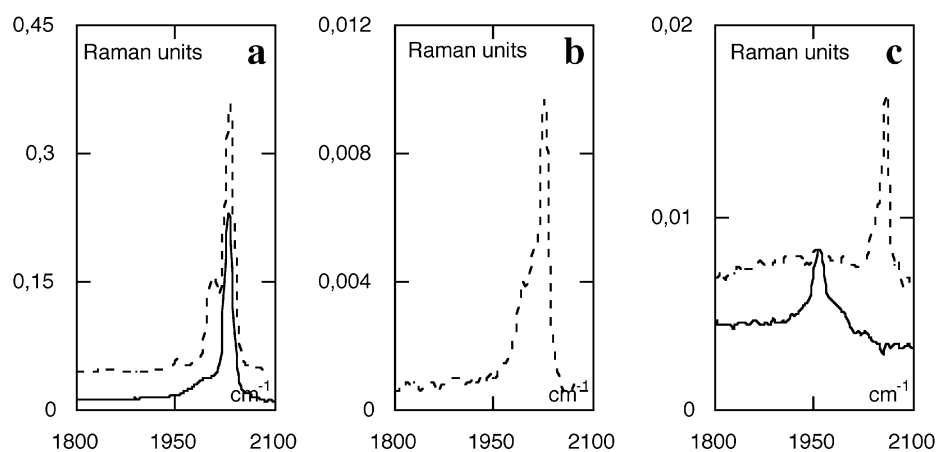
Scheme 3

involving the A_1 mode and modes of lower energy²⁸ or to a skeletal deformation of the phenyl groups of the dppe ligand.³⁰ In addition to these features in common, Raman peaks corresponding to characteristic stretching motions of the substituent also sometimes show up very intensely such as, for instance, the symmetric and antisymmetric motions of NO_2 or NH_2 (Scheme 3). Finally, all Raman spectra exhibit several

Table 1 Selected Raman ($\pm 4 \text{ cm}^{-1}$) vs. IR ($\pm 2 \text{ cm}^{-1}$) data for $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C}(\text{C}_6\text{H}_4)\text{X}^{n+}][\text{PF}_6^-]_n$ in the solid state

X	Stretching vibration	$n = 0$		$n = 1$	
		Raman ^a (%)	IR ^b (%)	Raman ^a (%)	IR ^b (%)
NO ₂	C≡C	2032 (80)	2037 (100)	2030 (100)	2030 (40)
		2007 (20)	2006 (80)	—	—
	Ar (A ₁)	1578 (100)	1578 (100)	1581 (100)	1582 (80)
	NO ₂ (antisym) ^c	1505 (2)	1499 (80)	1515 (2)	1513 (80)
	NO ₂ (sym)	1322 (400)	1324 (100)	1337 (140)	1337 (90)
CN	C≡C	2045 (40)	2047 (100)	2036 (60)	2042 (≤ 5)
		2026 (60)	2028 (100)	2021 (60)	2021 (≤ 5)
	Ar (A ₁)	1590 (100)	1590 (100)	1593 (100)	1594 (40)
	C≡N	2217 (40)	2218 (80)	2224 (40)	2224 (20)
		2050 (sh, ^d 100)	2053 (100)	2040 (100)	2041 (br, ^d ≤ 5)
CF ₃	C≡C	2031 (40)	2022 (60)	—	—
	Ar (A ₁)	1600 (80)	1600 (80)	1605 (60)	1606 (30)
	Ar (2nd mode)	—	—	1587 (40)	—
CF ₃ (antisym) ^c		1321 (60)	1319 (100)	1323 (60)	1324 (80)
Br	C≡C	—	2053 (100)	— ^e	2021 (15)
				— ^e	1993 (15)
	Ar (A ₁)	—	1599 (40) ^c	1574 (100)	1624 (20) ^c
F	C≡C	2056 (100)	2056 (90)	2021 (90)	2021 (40)
	Ar (A ₁)	1588 (100)	1599 (20)	1592 (100)	1594 (50)
	Ar (2nd mode)	1560 (20)	—	—	1575 (15)
H	C≡C	— ^e	2049 (95)	2026 (100)	2025 (30)
				1994 (40)	1993 (sh, ^d 20)
	Ar (A ₁)	1587 (100)	1589 (60)	1593 (80)	1597 (20) ^c
Me	C≡C	2060 (100)	2060 (80) ^{c,e}	2027 (100) ^c	2022 (br, ^d 20) ^c
	Ar (A ₁)	1603 (60)	1600 (15)	1603 (100)	1600 (20)
	Ar (2nd mode)	1586 (40)	1586 (15)	1589 (20)	—
^t Bu	C≡C	2060 (100)	2055 (90)	— ^e	1995 (br, ^d 50)
	Ar (A ₁)	1601 (60)	1592 (40) ^c	1593 (40)	1595 (30)
	Ar (2nd mode)	1587 (20)	—	1549 (100)	—
OMe	C≡C	2062 (100)	2063 (90)	2022 (80)	2019 (br, ^d 20)
	Ar (A ₁)	1600 (60)	1590 (10) ^c	1596 (5)	1596 (50)
	Ar (2nd mode)	1586 (20)	—	—	1566 (20)
NH ₂	C≡C	2058 (100)	2056 (85)	1980 (sh, ^d 5)	1983 (sh, ^d 50)
				1957 (20)	1959 (90)
	Ar (A ₁)	1602 (60)	1615 (40)	1591 (100)	1627 (75)
	Ar (2nd mode)	1587 (40)	1602 (40) ^c	—	1589 (90)
	NH ₂ (antisym)	— ^f	3435 (40)	— ^f	3489 (15)
	NH ₂ (sym)	— ^f	3358 (40)	— ^f	3391 (70)

^a Relative intensity (%) calibrated on the most intense peak among $\nu_{\text{C}\equiv\text{C}}$ and $\nu_{\text{Ar}(A_1)}$. ^b Relative transmission (%) calibrated on the most intense peaks ($[\text{PF}_6^-]$ absorption peak at *ca.* 840 cm^{-1} for Fe(III) acetylides). ^c Tentative assignment. ^d Abbreviations: sh = shoulder, br = broad peak. ^e Strong fluorescence of the sample. ^f Out of spectrometer range.

**Fig. 2** Raman $\nu_{\text{C}\equiv\text{C}}$ transition for $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C}(\text{C}_6\text{H}_4)\text{X}^{n+}][\text{PF}_6^-]_n$ complexes for $n = 0$ (broken lines) and $n = 1$ (full lines) with X = NO₂ (a); X = H (b) or X = NH₂ (c). The $\nu_{\text{C}\equiv\text{C}}$ transition was not observed for **1f** (b), owing to fluorescence of the sample (see Experimental section).

moderate-to-strong absorptions in the range $950\text{--}1200 \text{ cm}^{-1}$, which have not been assigned.

In comparison, the intensities of the corresponding IR absorptions are much more variable from one complex to the other. First, the triple bond stretch for most Fe(III) complexes appears weaker than in the corresponding Fe(II) parents. Within Fe(II) complexes, a slight decrease seems to take place

with the increasing electron-releasing power of the substituent X *i.e.* from **1a** to **1j**. Oppositely, within Fe(III) complexes, the $\nu_{\text{C}\equiv\text{C}}$ intensity clearly decreases with the increasing electron-withdrawing power of X, from **1j**⁺ $[\text{PF}_6^-]$ to a minimum for **1b**⁺ $[\text{PF}_6^-]$, and then slightly increases again for **1a**⁺ $[\text{PF}_6^-]$. The intensity of the “A₁” aryl stretch exhibits roughly similar variations with X. Relative to the triple bond stretch, its

intensity remains weaker in Fe(II) acetylides while larger or comparable in Fe(III) acetylides.

As exemplified in Figs. 1(a) and 2(a), Raman spectrometry clearly reveals the $\nu_{\text{C}\equiv\text{C}}$ fundamental mode with Fe(III) alkynyls presenting electron-withdrawing substituents like [**1a-c**]⁺[PF₆⁻]. This is a very interesting observation since this important vibrational motion is often quite weak in the corresponding IR spectra and might be confused with an harmonic or combination mode. Additionally, for **1a** (Fig. 1 and 2(a)), **1b**, **1c**, [**1b**]⁺[PF₆⁻], [**1d**]⁺[PF₆⁻], [**1f**]⁺[PF₆⁻] (Fig. 1 and 2(b)) and [**1j**]⁺[PF₆⁻] (Fig. 1 and 2(c)), a splitting of the $\nu_{\text{C}\equiv\text{C}}$ absorption is observed. This feature, also previously reported on the corresponding IR spectra, had been attributed to Fermi coupling.¹ Raman spectrometry provides here an alternative means to evidence the occurrence of Fermi coupling.³¹ Often observed in the case of organic alkynes,^{18,32-35} such a coupling is unpredictable, and results from interaction of the C≡C stretching fundamental with another mode of very close energy and same symmetry, corresponding to an harmonic or to a combination of fundamentals of lower energy. Most often, stretching or swinging motions of the single bonds connecting the substituents to the triple bond are involved in the (harmonic or combination) mode that couples with the alkynyl stretch.³² The latter presents usually a negligible intensity and is not detected in absence of Fermi coupling.²⁵ However, when coupling is operative, this mode benefits from the intensity of the $\nu_{\text{C}\equiv\text{C}}$ fundamental and is observed as the second (unexpected) band. In a *crude approximation*, the energy (in cm⁻¹) of the unperturbed $\nu_{\text{C}\equiv\text{C}}$ stretch and also of the other mode is given by the centre of the Fermi doublet.^{36,37} Thus, both must be in the 2040–2020 cm⁻¹ range for **1a-c** or [**1b**]⁺[PF₆⁻] and are probably located in the 1900–1970 cm⁻¹ range for [**1d**]⁺[PF₆⁻], [**1f**]⁺[PF₆⁻] and [**1j**]⁺[PF₆⁻]. In these narrow spectral regions, very weak IR absorptions can be detected as shoulders on the tail of the $\nu_{\text{C}\equiv\text{C}}$ absorptions for the other Fe(II) and Fe(III) complexes (see for instance Fig. 1(a)–(c)). These could typically correspond to the unperturbed harmonic or combination mode that couples with the $\nu_{\text{C}\equiv\text{C}}$ fundamental. Due to the complexity of the resulting IR spectra, a precise identification of the low energy fundamental(s) responsible for the coupling is not possible.³⁸ Except for **1b**, oxidation of the complex constitute a means to “switch” on (X = Br, H, NH₂) and off (X = NO₂, CF₃) the Fermi coupling. This phenomenon can easily be understood considering that the redox process will change the energies of at least one of the fundamentals involved in the coupling, mismatching thereby the energy of the $\nu_{\text{C}\equiv\text{C}}$ fundamental and of the other mode. A similar behaviour was recently reported with redox-active isonitrile ruthenium clusters.³⁹ Conversely for **1b**/[**1b**]⁺[PF₆⁻], where the Fermi splitting is observed in both oxidation states, we have to conclude that the oxidation/reduction process does not affect any of the modes involved in the coupling process.

Correlation of $\nu_{\text{C}\equiv\text{C}}$ frequencies with ESPs for [(η^2 -dppe)-(η^5 -C₅Me₅)Fe(C≡C-C₆H₄-X)]ⁿ⁺[PF₆⁻]_n (n = 0, 1) complexes

In compounds bearing a functional aryl ring where one of the substituent is systematically varied, correlations with electronic substituent parameters (ESPs) constitute an interesting method to probe the nature of the substituent influence.⁴⁰⁻⁴³ Typically, a good linear correlation with a spectroscopic variable reveals the dependence of the latter on the substituent and also its electronic origin. Additionally, the nature of the ESP set used provides information about the “way” this influence is transmitted.⁴⁴ Wavenumber values are usually considered as reflecting the change in bond order within a given vibrator. Thus, in order to investigate further the substituent influence on the alkynyl structure in **1a-j**/[**1a-j**]⁺[PF₆⁻], we have looked for linear correlations between the ($\nu_{\text{C}\equiv\text{C}}$)_X recorded in dichloromethane solutions and various sets of ESPs.^{46,47}

For the Fe(II) acetylides **1a-j**, the linear fit with usual Hammett ESPs (σ_p) is rather poor ($R = 0.88$) unless two lines are used to fit the data (see electronic supplementary material (ESI[†])).⁴⁸ A better linear fit can be obtained by use of σ^- values, (Fig. 3(a) and eqn. 1(a); $R = 0.96$). With Fe(III) acetylides, a good fit is obtained with the regular Hammett set ($R = 0.97$; see ESI), but a comparable fit ($R = 0.95$) can also be achieved with σ^+ values (Fig. 3(b) and eqn. 2(b)).

$$(\nu_{\text{C}\equiv\text{C}})_X \text{ (cm}^{-1}\text{)} = -21.5 (\sigma^-)_X + 2055 \quad (1a)$$

$$(\nu_{\text{C}\equiv\text{C}})_X \text{ (cm}^{-1}\text{)} = 28.1 (\sigma^+)_X + 2006 \quad (1b)$$

For Fe(II) complexes, the correlation (Fig. 3(a); eqn. 1(a)) suggests that a diminution in the alkynyl bond order takes place with strongly electron withdrawing substituents. In contrast, for Fe(III) complexes, the positive slope of eqn. 1(b) suggests that electron withdrawing substituents reinforce the alkynyl bond order. The magnitudes of the slopes indicate that these changes are more marked for Fe(III) than for Fe(II) acetylides.

For Fe(II) complexes, better correlations were obtained with the σ^- set than with the more common σ_p set. In contrast, for Fe(III), comparable fits were obtained in correlations with both the σ_p and the σ^+ sets.⁴⁹ Thus, at least for Fe(II) acetylides, the substituent effect is not “classical”, but resembles somewhat to the effect operative when a negative (positive) charge develops at the *para*-X-position of the aryl ring.^{24,46} A non-negligible “inductive” contribution is present, as evidenced by the failure to obtain a good correlations with the σ_R^0 set ($R = 0.83$), but also certainly a larger resonant contribution.⁴⁹ Analysed from a VB standpoint and considering only the VB structures depicted in Scheme 2, this analysis suggest that with the present Fe(II) alkynyl complexes, the weight of a VB structure like (B₁) is dominant over (B₂) in the bonding description. A similar reasoning would also support the predominance of VB structures such as (B₃) or (B₄) (see Scheme 4), over (B₂).



Scheme 4

Notably, a VB structure such as (B₄) finds support in recent NBO calculations conducted by Jiao and Gladysz.⁵⁰ Importantly, while both (B₁) and (B₂) correspond to retrodonation of the metal d orbitals into the vacant π^* orbitals of the alkynyl ligand, (B₃) or (B₄) do not. Given the controversy that actually exists about the importance of back-donation for electron-rich metal alkynyl complexes,⁵¹⁻⁵³ the balance between VB structures like (B₁) and (B₃) or (B₄) in the bonding description is of importance. Unfortunately, the present spectroscopic investigation alone cannot help to decide whether canonical forms such as (B₃) or (B₄) have to be included in the bonding description of electron-rich Fe(II) acetylides such as **1a-1j**. We are currently trying to get more insight in this important question by performing DFT computations on model complexes.

Correlations of IR intensities $A_{\text{C}\equiv\text{C}}$ for [(η^2 -dppe)(η^5 -C₅Me₅)Fe(C≡C-C₆H₄-X)]ⁿ⁺[PF₆⁻]_n (n = 0, 1) complexes

An alternative means to investigate the electronic substituent influence on IR data for an alkynyl vibrator is to correlate the square root of the intensity of its stretching motion with ESPs.^{35,54,55} According to theory (eqn. (2)), the intensity of

$$A = (N\pi/2.303 \times 3000c^2)(\partial\mu/\partial Q)_X^2 \quad (2)$$

a given IR absorption is essentially determined by the $\partial\mu/\partial Q$ term, where μ is the molecular dipolar moment and Q represents the normal coordinate of the vibrating mode.⁵⁶

Table 2 IR data for $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C}(\text{C}_6\text{H}_4)\text{X}^{n+}][\text{PF}_6^-]_n$ in CH_2Cl_2 solution

X	$n = 0$		$n = 1$	
	$\nu_{\text{C}\equiv\text{C}}/\text{cm}^{-1}$	$A_{\text{C}\equiv\text{C}}/10^3 \text{ cm}^{-2} \text{ M}^{-1}$	$\nu_{\text{C}\equiv\text{C}}/\text{cm}^{-1}$	$A_{\text{C}\equiv\text{C}}/10^3 \text{ cm}^{-2} \text{ M}^{-1}$
NO ₂	2036, 2008(sh)	81.2 ± 4.0	2038	0.6 ± 0.1
CN	2050(sh), 2025	57.0 ± 2.5	— ^b	0.0 ± 0.0
CF ₃	2050, 2030(sh)	36.0 ± 0.8	2013 ^c (br ^d)	0.3 ± 0.3
Br	2054	25.0 ± 4.0	2017, 1991	1.7 ± 1.0
F	2057	20.3 ± 1.0	2005 (br ^d)	3.7 ± 0.7
H	2053	16.5 ± 2.0	2021, 1988	3.5 ± 2.0
Me	2056	22.0 ± 1.1	1994	7.5 ± 1.0
^t Bu	2053	28.3 ± 1.5	1996	8.7 ± 1.0
OMe	2058	15.4 ± 0.8	1988	12.2 ± 0.6
NH ₂	2060	16.5 ± 0.8	1962(sh ^d), 1937	46.3 ± 2.0

^a Intensities in practical IUPAC units.⁵⁹ ^b 2041 and 2021 cm^{-1} in the solid (see Table 1). ^c Previously not detected.¹ ^d Abbreviations: sh = shoulder, br = broad peak.

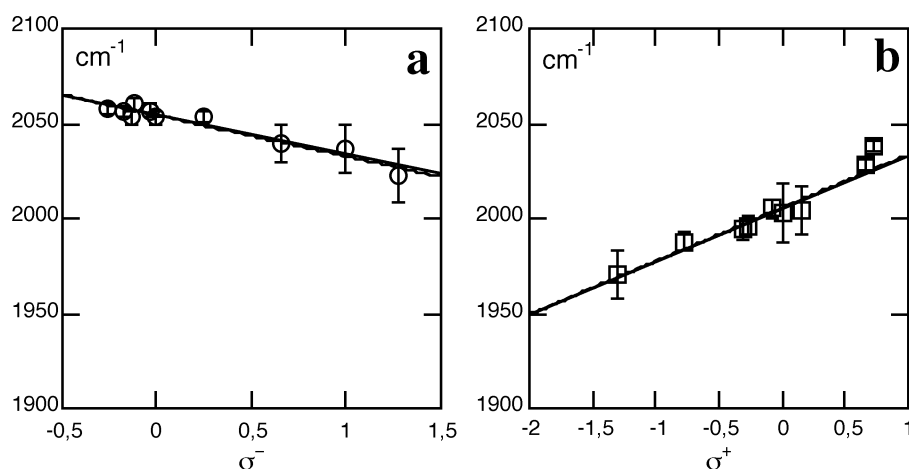


Fig. 3 Plot of the alkyne bond stretching energy (cm^{-1}) of $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C}(\text{C}_6\text{H}_4)\text{X}^{n+}][\text{PF}_6^-]_n$ complexes ($X = \text{NO}_2, \text{CN}, \text{CF}_3, \text{F}, \text{Br}, \text{H}, \text{Me}, \text{}^t\text{Bu}, \text{OMe}, \text{NH}_2$) vs. various ESP sets. (a) $n = 0$ and σ^- ; (b) $n = 1$ and σ^+ . For several points in the graphs, the large uncertainties on the wavenumbers originate from the Fermi coupling. In these cases, half of the frequency separation of the Fermi doublet was taken as the experimental uncertainty.

The observed linear dependence of $(A_{\text{C}\equiv\text{C}})^{1/2}$ on relevant ESP sets originates from the linear dependence of the $\partial\mu/\partial Q$ term, which has been theoretically rationalized.^{57,58} Thus, correlations of ESPs with square roots of IR intensities corresponding to a given mode result from the electronic substituent influence on the changes in the dipole moment during the vibrational motion ($\partial\mu/\partial Q$ term). Of note, the sign of $[(A_{\text{C}\equiv\text{C}})_X]^{1/2}$ which corresponds to the sign of $(\partial\mu/\partial Q)_X$ is actually indeterminate from intensity measurements. Only an absolute value for $[(A_{\text{C}\equiv\text{C}})_X]^{1/2}$ is accessible.

$$A = (1/Cl) \int \ln(I_0/I) dv = 2.303 \int \epsilon(v) dv \quad (3)$$

We have experimentally measured the IR intensities (eqn. (3))^{59,60} of $\nu_{\text{C}\equiv\text{C}}$ for **1a–j** and **[1a–j]⁺[PF₆[−]]** in dichloromethane solutions⁶¹ and attempted to correlate their square roots with the various ESPs previously tested.⁶² Reasonable and reproducible values could be obtained with **1a–j** and **[1a–j]⁺[PF₆[−]]** by the use of routine integration procedures implemented in the spectrometer (Table 2). These values confirm the trends observed with solid samples (Table 1).

We next have looked for linear correlations between $[(A_{\text{C}\equiv\text{C}})_X]^{1/2}$ and several ESP sets. With Fe(II) acetylides, the best linear fit was obtained with σ^- parameters (Fig. 4(a) and eqn. 4(a); $R = 0.94$), while poorer fits were obtained with σ_{R}^0 ESPs ($R = 0.78$) or with the regular Hammett set ($R = 0.84$).⁴⁷ For Fe(III) acetylides, the best fit was achieved the σ^+ set (Fig. 4(b) and eqn. 4(b); $R = 0.97$). Here also, poorer fits were obtained with σ_{R}^0 ($R = 0.85$) or σ_{p} ($R = 0.96$).⁶⁴

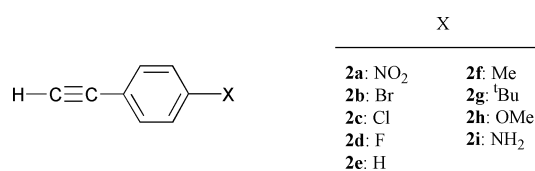
$$[(A_{\text{C}\equiv\text{C}})_X]^{1/2} = 92.8 (\sigma^-)_X + 148.3 \quad (4a)$$

$$[(A_{\text{C}\equiv\text{C}})_X]^{1/2} = -101.3 (\sigma^+)_X + 60.2 \quad (4b)$$

As mentioned earlier, $[A_{\text{C}\equiv\text{C}}]^{1/2}$ vs. ESP correlations are not unprecedented for alkynes. Linear correlations with σ_{R}^0 parameters have been reported for mono- or di-substituted organic representatives.^{35,55,65} More specifically, in the case of *para*-substituted aryl ethynyls **2a–h**, with the substituent X appended the phenyl group rather than directly to the alkyne core, linear correlations with σ^+ were evidenced.^{54,58} The following dependence (eqn. (5)) was notably reported for **2a–h** ($R = 0.997$).⁵⁴

$$[(A_{\text{C}\equiv\text{C}})_X]^{1/2} = -17.6 (\sigma^+)_X + 12.9 \quad (5)$$

To our knowledge, the present work constitutes the first extension of such an approach to organometallic alkynes. At odds with many correlations found for directly substituted organic alkynes, the best correlations for Fe(II) and Fe(III) acetylides are respectively obtained with the σ^- and σ^+ sets and not with the σ_{R}^0 set. The correlation obtained for the Fe(III) complexes resembles that (eqn. (5)) reported for **2a–h** (see Scheme 5), but in **[1a–j]⁺[PF₆[−]]** the substituent influence appears



Scheme 5

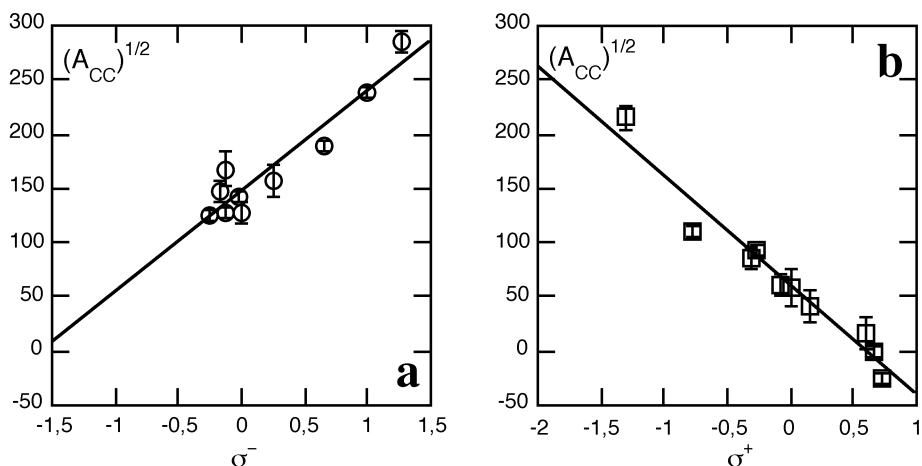
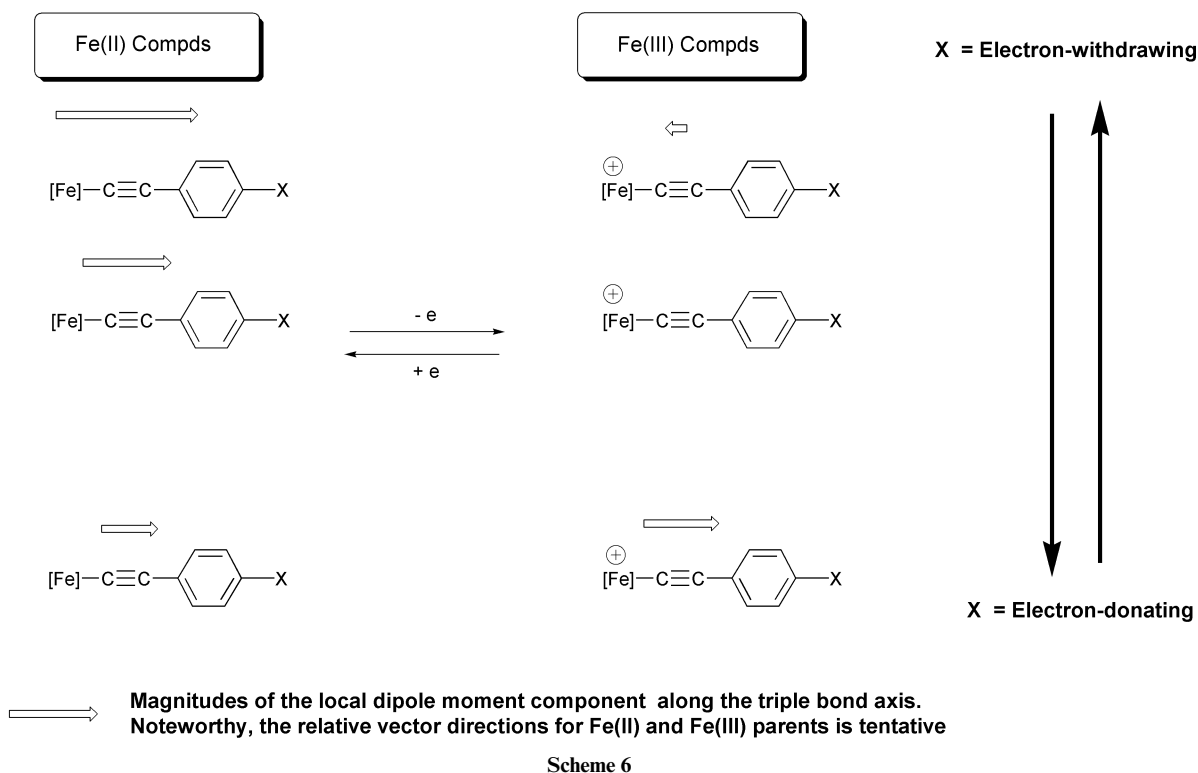


Fig. 4 Solution IR $[A_{\text{CC}}]^{1/2}/10$ vs. ESP correlations for $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C}(\text{C}_6\text{H}_4)\text{X}^{n+}][\text{PF}_6^-]_n$ complexes ($\text{X} = \text{NO}_2, \text{CN}, \text{CF}_2, \text{Br}, \text{F}, \text{H}, \text{Me}, \text{tBu}, \text{OMe}, \text{NH}_2$) for $n = 0$ (a) or $n = 1$ (b).



much more pronounced, as evidenced by the larger negative slope in eqn. 4(b) (-101.3 vs. -17.6). This can be taken as an experimental evidence for the larger polarisability of the triple bond in $\text{X}-(\text{C}_6\text{H}_4)-\text{C}\equiv\text{C}-\text{Y}$, when Y is an organometallic substituent such as “ $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}]^+$ ” rather than an hydrogen atom.

In a simple approach, Egorochkin *et al.* have proposed that within sets of very similar alkynes, changes in $[(A_{\text{CC}})_X]^{1/2}$ might primarily reflect changes in the magnitude of the local dipole moment $(\mu_{\text{CC}})_X$ associated with the vibrating unit (here the alkynyl linker).⁶⁵ In this respect, the present correlations obtained with **1a-j** and **[1a-j]⁺[PF₆⁻]** would indicate that $[(\mu_{\text{CC}})_X]$ (*i.e.* the polarisation of the alkynyl unit) increases with increasing electron-withdrawing character of the substituent in Fe(II) acetylides, while the reverse trend would take place in Fe(III) acetylides.^{66,67} Of note, in eqn. 4(b), we have considered a negative value of $[(A_{\text{CC}})_X]^{1/2}$ for compound **[1a⁺][PF₆⁻]** and positive signs for all other values. This improves greatly the quality of the fit, regardless the ESP sets considered and would be related to change of sign of $(\partial\mu/\partial Q)_X$ in eqn. (2), which in turn would be related to a reversal of the local μ_{CC} dipole moment in the

Fe(III) series for very electron withdrawing substituents. Thus, while the relative orientations of the local dipole moments along the alkynyl axis in Fe(II) and Fe(III) complexes cannot be derived from the available intensity data, an “umpolung” of the local μ_{CC} for very electron-withdrawing substituents is strongly suggested by the correlation obtained in the Fe(III) series (Fig. 4(b) and eqn. 4(b)).⁶⁸ Moreover, analysis of the relative magnitudes of $(A_{\text{CC}})_X$ (Table 2) suggests also that the alkynyl linker in Fe(III) acetylides is less polarized than in the corresponding Fe(II) parents (Scheme 6). Indeed, oxidation of **1a-j** greatly decreases the intensities of the corresponding ν_{CC} and can even lead to the complete disappearance of this IR absorption in dichloromethane solution, as for **1b/[1b][PF₆⁻]**.⁶⁷ Such redox-triggered bleaching of the ν_{CC} has already been reported for related transition metal acetylides.^{69,70}

The decrease in $[(\mu_{\text{CC}})_X]$ upon oxidation when electron withdrawing substituents are appended to the aryl ring makes sense. We know from Mössbauer spectra,^{1,2} that the electronic vacancy remains mostly centred on the iron atom in the Fe(III) complexes, and this regardless the nature of X . Accordingly, the σ - π -Lewis acidity of the electronically depleted aryl ring

towards the triple bond appears more efficiently counteracted by the improved Lewis acidity of the metal centre in Fe(III) acetylides.

Finally, having evidenced correlations between resp. σ^- and σ^+ and the $(\nu_{\text{C=C}})_X$ or $[(A_{\text{C=C}})_X]^{1/2}$ for **1a-j** and **[1a-j]⁺[PF₆⁻]**, we have looked for a cross-relation between $(\nu_{\text{C=C}})_X$ (in cm^{-1}) and $[(A_{\text{C=C}})_X]^{1/2}$ (in $\text{cm}^{-1} \text{M}^{-1/2}$). Rather good fits were obtained for both Fe(II) and Fe(III) alkynyls with $R = 0.96$ (see ESI). This suggests that a similar electronic influence of the substituent X underlies the evolution of $(\nu_{\text{C=C}})_X$ and $[(A_{\text{C=C}})_X]^{1/2}$ in the present series of $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-X})^{n+}][\text{PF}_6^-]_n$ complexes. As a corollary, σ^- and σ^+ , respectively, appear therefore as the best sets of ESPs for correlating the IR data with such Fe(II) and Fe(III) electron-rich alkynyls.

Conclusion

With metal acetylides such as **1a-j** and **[1a-j]⁺[PF₆⁻]**, we have shown that the classic IR investigation of the triple bond structure based on wavenumber values can usefully be complemented by solid state Raman and IR intensity measurements. Regarding the alkynyl bridge, Raman constitutes a convenient non-destructive means to confirm the solid state IR data. This spectrometry proves particularly interesting when the triple bond is only slightly polarized and allows firm identification of $\nu_{\text{C=C}}$ stretching modes. Also of note, it constitutes a straightforward alternative means to evidence Fermi coupling with the alkynyl stretch.

In IR, linear correlations between $(\nu_{\text{C=C}})_X$ or $[(A_{\text{C=C}})_X]^{1/2}$ and σ^- and σ^+ ESPs, respectively, were evidenced. Qualitatively, this indicates that the substituent dependence of these IR data in **1a-j** and **[1a-j]⁺[PF₆⁻]** is essentially electronic in origin. Such correlations, which are unprecedented for metalla-alkynes, also allow a quantitative insight into the substituent effect. The ESP sets used, which incorporate a strong mesomeric contribution to the substituent influence, are in line with a simple VB description of the bonding in the Fe–C≡C core (Scheme 2). Analysed from a “molecular device” perspective, this contribution reveals that, depending on the redox state of the complex, both the alkynyl bond order and the polarizations of the alkynyl unit in $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-X})^{n+}][\text{PF}_6^-]_n$ complexes can be fine-tuned by judicious choice of the substituent X. In addition, redox-switching of the triple bond polarization can be performed.

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$$\sigma = \sigma_I + \sigma_R = a\sigma_I^0 + \beta\sigma_R^0 \quad (1)$$

The classical Hammett set (σ_p) implies a equivalent balance of the mesomeric and inductive effect regardless the nature of the substituent ($a = \beta$ in eqn. (1)), while σ^+ or σ^- sets originate from a

- different blend of these contributions for each substituent. They emphasize the mesomeric contribution of electro-attracting substituents in the σ^- set and of electron donating substituents in the σ^+ set.⁴⁶
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