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Redox-Switchable Second-Order Molecular Polarizabilities with Electron-Rich Iron σ-Aryl Acetylides[†]

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$\mu\cdot\beta$ products were experimentally derived by EFISH for several Fe(II) and Fe(III) σ-aryl acetylides of formula $[(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)Fe(C{\equiv}C{-}Ar)]^{n+}$, $n(PF_6)^-$ (dppe = 1,2-bis(diphenylphosphino)ethane; $n = 0, 1$), where Ar = *p*-Py, *m*-Py, *o*-Py (**1a**−**c**/**1a**$^+$); Ar = *p*-C_5H_4-$N(CH_3)^+$, *o*-C_5H_4-$N(CH_3)^+$ (**2a**,**b**$^+$); Ar = *p*-C_6H_4X with X = NO_2, CN, CF_3, H, OMe, NH_2 (**3a**−**f**/**3a**−**f** $^+$). For comparison purposes, EFISH data were also gathered on the Ru(II) analogues (**4a**,**b**) of **3a**,**b**. Significant figures for $\mu\cdot\beta$ were determined, with the Fe(II) complexes **2a**$^+$ and **3a**,**b** possessing the most electron-deficient aryl rings opposed to the metal center, indicating good second-order molecular polarizabilities. For most representatives among **3a**−**f**/**3a**−**f**$^+$ and **4a**,**b**, β and β_0 values could be derived using DFT-computed dipole moments. The substituent influence on β and β_0 is especially marked in the neutral complexes and follows the electron-accepting properties of X: $NO_2 > CN > H > OMe \approx NH_2$. The comparison between **4a**,**b** and **3a**,**b** indicates that the Fe(II) center is more efficient than Ru(II) as an organometallic donor group when opposed to strong acceptors. In addition, we also show with (**3a**−**f**/**3a**−**f**$^+$) that the NLO response can be fine-tuned by variation of the X substituent in each redox state. Thus, given the facile and reversible oxidation to the corresponding Fe(III) parents, Fe(II) acetylides might conveniently be used for switching purposes in molecular devices for NLO.

Introduction

This past decade, the study of various classes of polynuclear complexes featuring *electron-rich* transition metal-acetylides as endgroups has revealed that the M−C≡C fragments constitute particularly attractive building blocks for the realization of various molecular devices,[3−5] especially when these are stable under several redox states.[6] By combination of such organometallic fragments with various unsaturated organic spacers, interesting properties can be achieved in supernuclear assemblies, with respect to intramolecular electron transfer or magnetic superexchange.[6−12] Recent investigations concerned with the exploitation of such

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(1) (a) Denis, R.; Toupet, L.; Paul, F.; Lapinte, C. *Organometallics* **2000**, *19*, 4240−4251. (b) Paul, F.; Mevellec, J.-Y.; Lapinte, C. *J. Chem. Soc., Dalton Trans.* **2002**, 1783−1790.

(2) Weyland, T.; Ledoux, I.; Brasselet, S.; Zyss, J.; Lapinte, C. *Organometallics* **2000**, *19*, 5235−5237.

(3) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 80−154.

(4) (a) Chisholm, M. H. *Acc. Chem. Res.* **2000**, *33*, 53−61. (b) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1351−1377. (c) Ziessel, R. *Synthesis* **1999**, 1839−1865. (d) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863−1933. (e) Yam, V. W.-W.; Lo, K. K.-W.; Wong, K. M.-C. *J. Organomet. Chem.* **1999**, *578*, 3−30. (f) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797−2858. (g) Stang, P. J. *Chem. Eur. J.* **1998**, *4*, 19−27. (h) Akita, M.; Chung, M.-C.; Sakurai, A.; Sugimoto, S.; Terada, M.; Tanaka, M.; Moro-Oka, Y. *Organometallics* **1997**, *16*, 4882−4888. (i) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547−550.

(5) (a) Peters, T. B.; Bohling, J. C.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1999**, *18*, 3261−3263, and references cited. (b) Touchard, D.; Haquette, P.; Guesmi, S.; Le Pichon, L.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 3640−3648. (c) Markwell, R. D.; Butler, I. S.; Kakkar, A. K.; Khan, M. S.; Al-Zahkawani, Z. H.; Lewis, J. *Organometallics* **1996**, *15*, 2331−2337, and references cited.

(6) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178/180*, 427−505.

(7) Paul, F.; Lapinte, C. In *Unusual Structures and Physical Properties in Organometallic Chemistry*; Gielen, M., Willem, R., Wrackmeyer, B., Eds.; Wiley & Sons, Ldt: Chichester, 2002; 219−295.

(8) (a) Paul, F.; Meyer, W.; Jiao, H.; Toupet, L.; Gladysz, J. A.; Lapinte, C. *J. Am. Chem. Soc.* **2000**, *122*, 9405−9414. (b) Weyland, T.; Costuas, K.; Toupet, L.; Halet, J.-F.; Lapinte, C. *Organometallics* **2000**, *19*, 4228−4239. (c) Le Stang, S.; Paul, F.; Lapinte, C. *Organometallics* **2000**, *19*, 1035−1043. (d) Weyland, T.; Costuas, K.; Mari, A.; Halet, J.-F.; Lapinte, C. *Organometallics* **1998**, *17*, 5569−5579. (e) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129−7138.

(9) Bruce, M. I.; Low, P. J.; Costuas, K.; Halet, J.-F.; Best, S. P.; Heath, G. H. *J. Am. Chem. Soc.* **2000**, *122*, 1949−1962.

(10) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810−822, and references therein.

(11) Kheradmandan, S.; Heinze, K.; Schmalle, H.; Berke, H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2270−2273.

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organometallic architectures in nonlinear optics (NLO)[13] suggest promising perspectives as well.[2,14]

Our work deals more specifically with polynuclear organoiron derivatives bearing several "[Fe]−C≡C−" fragments, where [Fe] represents the electron-rich and redox-active "$(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}$" endgroup (dppe = 1,2-bis(diphenylphosphinoethane).[6−8] Thus, with a central phenylene linker, polynuclear compounds that present interesting second-order NLO activities in all redox states have been obtained.[2] To gain additional basic knowledge about the electronic contribution of an isolated "[Fe]−C≡C−" unit on the electronic properties of these compounds, we have synthesized several classes of mononuclear $[([\text{Fe}]-\text{C}\equiv\text{C}-\text{Ar})]^{n+}$, $n(\text{PF}_6)^-$ iron acetylides ($n = 0$, 1) containing the prototypical piano-stool "$(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}$" endgroup.[1,2,15] The spectroscopic investigations of Fe(II) and Fe(III) iron acetylides bearing a pyridyl group (**1a**−**c**),[15a] a pyridinium group ($\mathbf{2}^+\text{PF}_6^-$),[15b] or functional "$\text{C}_6\text{H}_4\text{X}$" aryl groups (**3a**−**f**)[1a] indicate a strong dependence of the structure of the alkynyl spacer upon the electronic nature of the aryl group, as well as on the redox state of the metal center.[1,2]

We investigate here the second-order NLO properties (i.e., the second-order molecular polarizability β) of these complexes by means of electric field induced second harmonic (EFISH). The second-order (or quadratic) polarizability of most donor−bridge−acceptor compounds is related to the magnitude of the through-bridge electronic delocalization between donor and acceptor groups induced by an external electric field. Thus, in a series of structurally related complexes such as **3a**−**f**/**3a**−$\mathbf{f}^+\text{PF}_6^-$, the second-order polarizability (β) can provide information on the way aryl-based structural changes or metal-centered redox processes influence the donor or acceptor character of the endgroups. For comparison purposes, we also report the EFISH measurements on two Ru(II) analogues. In addition, comparison with existing data for related acetylides should give a first evaluation of the potential of $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}]^{n+}$ centers to be used as donor ($n = 0$) or acceptor ($n = 1$) groups in organometallic molecules designed for exhibiting second-order NLO properties.

Results

EFISH allows the measurement of the "$\mu\cdot\beta$" product in solution.[16−18] This product is derived according to eq 1, considering that $\gamma_0(-2\omega;\ \omega, \omega, 0)$, the third-order term at frequency ω of the incident light, is negligible for the compounds under study. The $\mu\cdot\beta$ term provides direct information on the intrinsic molecular NLO properties.[16b] The second-order molecular polarizability derived by EFISH represents in fact the vectorial projection of the β polarizability tensor along the molecular dipole moment μ.

$$\gamma_{\mathrm{EFISH}} = (\mu\cdot\beta/5kT) + \gamma_0(-2\omega;\ \omega, \omega, 0) \qquad (1)$$

For all Fe(II) complexes but $\mathbf{2a}$,$\mathbf{b}^+$, $\mu\cdot\beta$ measurements were carried out in dichloromethane at 25 °C, with incident light at 1907 nm. With our EFISH equipment, measurements can also be performed on ionic species in favorable cases (i.e., low dielectric constant of the solvent) by application of a short duration (1 μs) static electric field synchronized with the laser pulses.[19] In these instances, a solvent with a lower dielectric constant than dichloromethane has to be used. Typically, with the cationic complex **2**, the measurements were performed in chloroform.

Next, nonresonant (static) $\mu\cdot\beta_0$ values were calculated from $\mu\cdot\beta$ values and corresponding UV data using the two-level model for Fe(II) complexes (eq 2),[16] assuming that only the lowest energy excited state (MLCT) made a significant contribution to β (Table 1).[1,15,20]

$$\beta = \beta_{\mathrm{o}}\{1/[1 - (2\lambda_{\mathrm{ge}}/\lambda_0)^2][1 - (\lambda_{\mathrm{ge}}/\lambda_0)^2]\} \qquad (2)$$

Among complexes **1a**−**c** and $\mathbf{2a}$,$\mathbf{b}^+$, the pyridinium-substituted complex $\mathbf{2a}^+\text{BPh}_4^-$, bearing the most electron-poor heterocycle, exhibits the largest value. For **1a**−**c**, regardless of the substitution pattern, overall weaker and negative values were found. Similarly, among the complexes **3a**−**f** featuring a substituted aryl group (Table 1), the nitro- or cyano-substituted compounds **3a** and **3b** are also the most active. The quadratic polarizability obviously decreases with the electron-withdrawing character of the substituent/aryl group. It is noteworthy that the $\mu\cdot\beta$ and $\mu\cdot\beta_0$ products derived for ruthenium analogues **4a** and **4b** are significantly lower than those obtained for **3a** and **3b**, respectively.

For the cationic Fe(III) congeners, $\mu\cdot\beta$ products were measured in chloroform. Smaller and overall negative values were found for **1a**−$\mathbf{e}^+\text{PF}_6^-$ relative to their corresponding Fe(II) parents (Table 1). Given the weakness of the contribution derived in several instances by EFISH for ionic Fe(III) compounds in comparison to the contribution of the pure solvent, these values are possibly subject to larger uncertainties than in the corresponding Fe(II) series. From the available UV data, static $\mu\cdot\beta_0$ values were derived as well in most cases using the two-level model (eq 2).

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[12] Colbert, M. C. C.; Lewis, J.; Long, N. J.; Raithby, P. R.; Younus, M.; White, A. J. P.; Williams, D. J.; Payne, N. J.; Yellowlees, L.; Beljonne, D.; Chawdhury, N.; Friend, R. H. *Organometallics* **1998**, *17*, 3034−3043.

[13] (a) di Bella, S. *Chem. Soc. Rev.* **2001**, *30*, 355−366. (b) Coe, B. J. *Chem. Eur. J.* **1999**, *5*, 2464−2471. (c) Whittall, I. R.; MacDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *42*, 291−362. (d) Whittall, I. R.; MacDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *43*, 349−322. (e) Hendrickx, E.; Clays, K.; Persoons, A. *Acc. Chem. Res.* **1998**, *31*, 675−683. (f) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21−38. (g) Zyss, J. *Molecular Nonlinear Optics*; Academic Press: New York, 1994. (h) Marder, S. R. In *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; Wiley & Sons: New York, 1992; pp 115−164.

[14] (a) Hurst, S. K.; Cifuentes, M. P.; Morrall, J. P. L.; Lucas, N. T.; Whittal, I. R.; Humphrey, M. G.; Aselberghs, I.; Persoons, A.; Samoc, M.; Luther-Davies, B.; Willis, A. C. *Organometallics* **2001**, *20*, 4664−4675. (b) MacDonagh, A. R.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B. *Organometallics* **1999**, *18*, 5195−5197. (c) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Asselberghs, I.; Houbrechts, S.; Clays, K.; Persoons, A.; Borge, J.; Garcia-Granda, S. *Organometallics* **1999**, *18*, 582−597. (d) MacDonagh, A. R.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Houbrechts, S.; Wada, T.; Sasabe, H.; Persoons, A. *J. Am. Chem. Soc.* **1999**, *121*, 1405−1406. (e) Hendrickx, E.; Persoons, A.; Samson, S.; Stephenson, G. R. *J. Organomet. Chem.* **1997**, *542*, 295−297.

[15] (a) Le Stang, S.; Paul, F.; Lapinte, C. *Inorg. Chim. Acta* **1999**, *291*, 403−425. (b) Le Stang, S.; Lenz, D.; Paul, F.; Lapinte, C. *J. Organomet. Chem.* **1998**, *572*, 189−192.

[16] (a) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446−457. (b) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664−2668.

[17] Ledoux, I.; Zyss, J. *Chem. Phys.* **1982**, *73*, 203-213.

[18] Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690−703.

[19] Alain, V.; Blanchard-Desce, M.; Ledoux-Rak, I.; Zyss, J. *Chem. Commun.* **2000**, 353−354.

[20] In eq 2, λ_{ge} is the wavelength of the lowest energy excited state (in nm), and λ_0 is the wavelength of the incident light (1907 nm).

Table 1. Data for the Lowest Electronic Transition and EFISH Data for Selected Fe(II), Ru(II), and Fe(III) Acetylide Complexes

			M(II)				M(III)		
[M]−C≡C−Ar Ar (compd)	M	$\mu\cdot\beta$ (esu/10^{-48})[a,b]	λ_{max} (nm)[a]	ϵ_{max} (M^{-1} cm^{-1})[a]	$\mu\cdot\beta_0$ (esu/10^{-48})[c]	$\mu\cdot\beta$ (esu/10^{-48})[b,d]	λ_{max} (nm)[a]	ϵ_{max} (M^{-1} cm^{-1})[a]	$\mu\cdot\beta_0$ (esu/10^{-48})[c]
p-(C_5H_4N) (**1a**/**1a**$^+$PF$_6^-$)	Fe	−139	403	7900	−110	−9	521	1600	−6
m-(C_5H_4N) (**1b**)	Fe	−169	401	8300	−133	n.d.[e]	634	1900	n.d.[e]
o-(C_5H_4N) (**1c**)	Fe	−137	391	8900	−109	n.d.[e]	632	1500	n.d.[e]
p-[$C_5H_4N(CH_3)^+$] (**2a**$^+$BPh$_4^-$)	Fe	948[d]	580	20474	552				
o-[$C_5H_4N(CH_3)^+$] (**2b**$^+$PF$_6^-$)	Fe	662	538	9670	415				
p-(C_6H_4)NO$_2$ (**3a**/**3a**$^+$PF$_6^-$)	Fe	2100	595	13000	1155	1	650	1200	1
p-(C_6H_4)CN (**3b**/**3b**$^+$PF$_6^-$)	Fe	789	445	16400	583	−56	652	900	−26
p-(C_6H_4)CF$_3$ (**3c**)	Fe	265	387	13200	212	n.d.[e]	635	1500	n.d.[e]
(C_6H_5) (**3d**/**3d**$^+$PF$_6^-$)	Fe	269	350	13600	225	−12	662	3100	−5
p-(C_6H_4)OMe (**3**^{e}/**3**$^{e+}$PF$_6^-$)	Fe	44	333	13200	37	−145	718	6100	−53
p-(C_6H_4)NH$_2$ (**3f**/**3f**$^+$PF$_6^-$)	Fe	54	322	17600	47	−334	789	9700	−87
p-(C_6H_4)NO$_2$ (**4a**)	Ru	690	500	14600	465				
p-(C_6H_4)CN (**4b**)	Ru	155	384	19300	124				

[a] Solution in CH_2Cl_2. [b] The precision of the measurements is about 10%. Correlation between SI units: $\beta(SI) = 4.172 \times 10^{-10}\beta(esu)$. [c] Calculated from UV data using eq 2 with $\lambda_0 = 1.9$ μm. [d] Solution in $CHCl_3$. [e] Not determined.

Table 2. DFT-Computed Molecular Dipole Moments (*D*) for Model Compounds and Resulting Second-Order Polarizabilities (esu/10^{-30}) Derived from EFISH Data for Selected Fe(II), Ru(II), and Fe(III) Acetylide Complexes

	Fe(II)						Fe(III)					
compd	μ_x	μ_y	μ_z	μ (D)	β	β_0[a]	μ_x	μ_y	μ_z	μ (D)	β	β_0[a]
p-(C_6H_4)NO$_2$ (**3a**)	0.00	−2.93	12.07	12.42	168.9	93.0	0.00	−3.82	32.13	32.36	0.04	>0.02
p-(C_6H_4)CN (**3b**)	0.00	−2.88	10.92	11.30	69.8	51.0	−0.17	−3.75	30.41	30.64	−1.8	−0.8
(C_6H_5) (**3d**)	0.00	−2.76	4.11	4.96	54.2	45.3	0.27	−2.67	23.96	24.24	−0.5	−0.2
p-(C_6H_4)OMe (**3e**)	−0.49	−1.84	3.54	4.02	10.9	9.2	−0.61	−5.50	5.36	7.71	−18.8	−6.9
p-(C_6H_4)NH$_2$ (**3f**)	−0.01	−2.81	1.19	3.05	17.8	15.3	−0.01	−3.35	14.84	15.21	−22.0	−5.7
p-(C_6H_4)NO$_2$ (**4a**)	−0.13	−2.03	11.74	11.92	57.9	39.0						
p-(C_6H_4)CN (**4b**)	0.00	−2.62	10.99	11.30	33.9	11.0						

[a] Calculated from UV data[1a] using eq 2 with $\lambda_0 = 1.9$ μm.

The theoretical dipole moments have been computed by means of density functional theory (DFT) for several Fe(II) and Fe(III) model complexes (see Experimental Section).[21] This dipole moment is very close to that of the actual molecules and can therefore be used to derive the dynamic second-order polarizability β_{EFISH} (noted β here) by simply dividing the experimental $\mu\cdot\beta$ product by the DFT-calculated μ. The corresponding static second-order polarizability β_0 can similarly be obtained from the $\mu\cdot\beta_0$ (Table 2).

For Fe(II) complexes **3a**−**f**, a similar ordering is found regarding the β values (respectively β_0 values) with respect to the experimental $\mu\cdot\beta$ products (respectively $\mu\cdot\beta_0$ products). Notably, significantly higher β_0 values are also found for **3a** and **3b** in comparison to the ruthenium analogues **4a** and **4b**. In contrast, for Fe(III) derivatives, the β values (respectively β_0 values) derived are less correlated with the $\mu\cdot\beta$ products (respectively $\mu\cdot\beta_0$ products). Moreover, these values are also much weaker in magnitude than the ones obtained for the corresponding Fe(II) parents and are often negative.

Correlations with electronic substituent parameter sets (ESPs) constitute usually a good means to point out the decisive influence of a given substituent like X here.[1b] While no linear relationship is found when the $\mu\cdot\beta_0$ products of the entire data set are plotted against several electronic substituent parameter sets (ESPs) (see Supporting Information),[22,25−26] a trend is however apparent between the β_0 values determined for **3a**−**f** or **3a**−**f**$^+$PF$_6^-$ and the classic Hammett σ set (Figure 1).[27] A good linear correlation can hardly be expected given the various factors influencing β_0 (eq 2) and the experimental/theoretical uncertainties associated with the derivation of the present β_0 values by means of EFISH;[28,29] nevertheless, this trend evidences the determining electronic influence of the *para*-substituent on β_0 for Fe(II) acetylides.

Discussion

In comparison to published data for transition metal complexes,[30] significant EFISH figures were obtained for Fe(II) complexes with electron-withdrawing aryl groups, especially with **2a**$^+$BPh$_4^-$, **3a**, and **3b**. The

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(21) Costuas, K.; Paul, F.; Halet, J.-F.; Lapinte, C. Work in progress.

(22) Concerning complexes **1a**−**c**, electronic substituent parameter σ values for *ortho*-, *meta*-, and *para*-pyridines are available in the literature, assimilating the heteroatom of the aryl group as a substituent.[23] However these values are subject to a large variation which induces a large uncertainty in the corresponding points.[24] Concerning complexes **2a**,**b**$^+$, to the best of our knowledge, no σ_p was ever determined for the *ortho*- or *para*-*N*-methylpyridinium heterocycles, and the value determined for *para*-pyridinium substituents was used for **2a**$^+$.

(23) Blanch, J. H. *J. Chem. Soc. B* **1966**, 937−938.

(24) Jaffé, H. H.; Jones, H. L. *Adv. Heterocycl. Chem.* **1964**, *3*, 209−261.

(25) March, J. *Advanced Organic Chemistry. Reactions, Mechanisms and Structures*, 4th ed.; J. Wiley & Sons: New York, 1992.

(26) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

(27) It is noteworthy that slightly better correlations are actually obtained with the σ^- set for the neutral complexes ($R = 0.89$ vs 0.88) and with the σ^+ set with the cationic parents ($R = 0.88$ vs 0.80).[1b]

(28) Ulman, A. *J. Chem. Phys.* **1988**, *92*, 2385−2390.

(29) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631−10643.

Table 3. β and β_0 Values Determined by HLS or EFISH for Related D−Bridge−A Compounds

donor (D)	bridge	acceptor (A)	β (esu/10^{-30})	β_0 (esu/10^{-30})	method	E_0(M/M$^+$)[a]	refs
4-$(C_6H_4)NH_2$	C≡C	*p*-$(C_6H_4)NO_2$	24	19[b]	EFISH[c]		42
4-$(C_6H_4)NH_2$	C≡C	*p*-$(C_6H_4)CN$	20	18[b]	EFISH[c]		42
(dppe)(Cp*)Fe−	C≡C	C_6H_5	52	24	HLS[d]		2
$(Ph_3P)_2$(Ind)Ru−	C≡C	*p*-$(C_6H_4)NO_2$	746	119[f]	HLS[d]		14c, 40b
(dppe)(Ind)Ru−	C≡C	*p*-$(C_6H_4)NO_2$	516	107[f]	HLS[d]		14c
(dppm)(Ind)Ru−	C≡C	*p*-$(C_6H_4)NO_2$	540	117[f]	HLS[d]		14c
$(Ph_3P)_2$(Cp)Ru−	C≡C	*p*-$(C_6H_4)NO_2$	468	96	HLS[e]	0.73	46, 48, 61
$(Ph_3P)_2$(Cp)Ru−	C≡C	C_6H_5	16	10	HLS[e]	0.55	46, 61, 62
$(Me_3P)_2$(Cp)Ru−	C≡C	*p*-$(C_6H_4)NO_2$	248	39	HLS[e]	0.42	46, 48, 61
$Cl(dppm)_2Ru$−	C≡C	*p*-$(C_6H_4)NO_2$	767	129	HLS[e]	0.72	14a
$Cl(dppm)_2Ru$−	C≡C	C_6H_5	20	12	HLS[e]	0.55	14a
$Cl(dppe)_2Ru$−	C≡C	*p*-$(C_6H_4)NO_2$	351	55	HLS[e]	0.74	14a
$Cl(dppe)_2Ru$−	C≡C	C_6H_5	6	3	HLS[e]	0.55	14a, 14b
(Ph_3P)CpNi−	C≡C	*p*-$(C_6H_4)NO_2$	221	59	HLS[e]	0.81	46, 62
(Ph_3P)CpNi−	C≡C	C_6H_5	24	15	HLS[e]	0.90	46, 62
(Ph_3P)Au−	C≡C	*p*-$(C_6H_4)NO_2$	22	12	HLS[e]		62, 63
(Ph_3P)Au−	C≡C	C_6H_5	6	4	HLS[e]		62, 63
(dppe)(Cp)Fe−	N≡C	*p*-$(C_6H_4)NO_2$	375	80[b]	HLS[d]		44
(dppe)(Cp)Ru−	N≡C	*p*-$(C_6H_4)NO_2$	126	34[b]	HLS[d]		44

[a] E_0 values in V vs Ag/AgCl reference electrode, CH_2Cl_2, −50/25 °C, 100 mV s^{-1} (Fc/Fc$^+$ couple located at 0.56 V).[14a] [b] Computed using eq 2 from UV data and corresponding λ_0 values reported. [c] In $CHCl_3$ solvent. [d] In CH_2Cl_2 solvent. [e] In THF solvent. [f] Evaluated following a different correction than eq 2 [4ob].

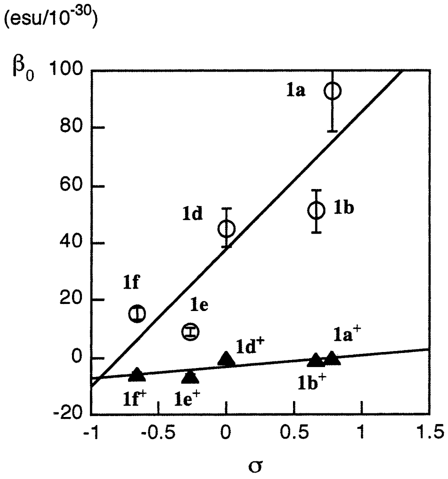

Figure 1. Static second-order molecular polarizabilities β_0 derived for $[(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)Fe{-}C{\equiv}C{-}(C_6H_4)X]^{n+}$, $n(PF_6)^-$ complexes vs Hammett electronic substituent parameter (σ) for $n = 0$ (empty circles) and $n = 1$ (filled triangles). The error on β_0 values corresponds to the experimental uncertainty during determination (ca. 10%).

negative values found for **1a**−**c** indicate that the β tensor and the molecular dipole moment (μ) have opposite directions. According to the definition of the static (i.e., at zero frequency) second-order polarizability (β_o) in the two-level approximation (eq 3),[31] a negative value found for β_o or $\mu{\cdot}\beta_o$ means that the "$\Delta\mu$" term is negative. In other words, the dipole moment of the excited state is decreased or reversed relative to that of the ground state.[16a,32−33] Moreover, the comparison between $\mu{\cdot}\beta$ and $\mu{\cdot}\beta_0$ clearly evidences that **3a** like **2a**$^+$BPh$_4^-$ benefits from resonant enhancement and that their strong values relative to **3b** result in part from the red-shift of the MLCT transition, from 445 nm for **3b** to 595 nm for **3a** and to 580 nm for **2a**$^+$ (Table 1).

$$\beta_o = (3/2)(\Delta\mu)(\mu_{ge})^2/(E_{ge})^2 \qquad (3)$$

The β_0 values presently derived for the Fe(II) and Ru(II) acetylide complexes **3a**−**f** and **4a**,**b** are typically in the range of values reported for other group VIII mononuclear alkynyl complexes (Table 3).[13c] For **3a** and **3b**, β_0 values compare also with the values previously found by HLS for the closely related polynuclear $\{[(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)Fe(C{\equiv}C)]_m(C_6H_{6-m})\}^{n+}$, $n(PF_6)^-$ ($m = 1$, 2; $n = 1{-}3$) complexes (around 200 × 10^{-30} esu).[2] More generally, a qualitatively similar (hetero)aryl substituent-dependence of the quadratic polarizabilities was often reported for organometallic complexes in which the metal center acts as a donor group.[30b,34−35] Thus, the 4-nitrophenyl group appears usually as one of the better acceptor groups among simple aryls,[36,37] whereas the pyridyl rings are often less efficient.[38,40,41]

The β values found for **3a** and **3b** or for **4a** and **4b** are significantly larger than those obtained by EFISH for the 4,4′-nitroamino tolane and 4,4′-cyanoamino

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(30) (a) Sharma, H. K.; Pannell, K. H.; Ledoux, I.; Zyss, J.; Ceccanti, A.; Zannello, P. *Organometallics* **2000**, *19*, 770−774. (b) Roberto, D.; Ugo, R.; Bruni, S.; Cariati, E.; Cariati, F.; Fantucci, P. C.; Invernizzi, I.; Quici, S.; Ledoux, I.; Zyss, J. *Organometallics* **2000**, *19*, 1775−1788. (c) Hilton, A.; Renouard, T.; Maury, O.; Le Bozec, H.; Ledoux, I.; Zyss, J. *Chem. Commun.* **1999**, 2521−2522.

(31) In eq 3, $\Delta\mu = \mu_{ee} - \mu_{gg}$ is the difference between the ground state dipole moment and the excited state dipole moment, μ_{ge} is the electronic transition moment, and E_{ge} is the energy difference between the ground and excited state.

(32) Marder, S. R.; Beratan, D.-N.; Cheng, L.-T. *Science* **1991**, *252*, 103−106.

(33) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195−242.

(34) Lee, I. S.; Seo, H.; Chung, Y. K. *Organometallics* **1999**, *18*, 1091−1096.

(35) Dias, R.; Garcia, M. H.; Robalo, M. P.; Green, M. L. H.; Lai, K. K.; Pulham, A. J.; Kuebler, S. M. *J. Organomet. Chem.* **1993**, *453*, 241−247.

(36) Müller, T. J. J.; Netz, A.; Ansorge, M.; Schmälzlin, E.; Bräuchle, C.; Meerholz, K. *Organometallics* **1999**, *18*, 5066−5074.

(37) Barlow, S.; Bunting, H. E.; Ringham, C.; Green, J. C.; Bublitz, G. U.; Boxer, S. G.; Perry, J. W.; Marder, S. R. *J. Am. Chem. Soc.* **1999**, *121*, 3715−3723.

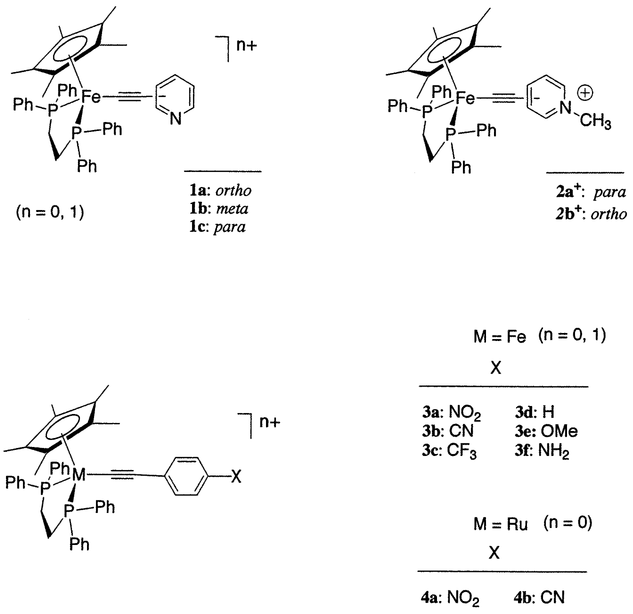
(38) Coordination to a Lewis acidic complex like $W(CO)_5$ for instance may enhance the pyridyl ring accepting properties. However, for a caveat about the beneficial effect of pyridine complexation, see refs 13, 30a, and 39.

(39) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8203−8204.

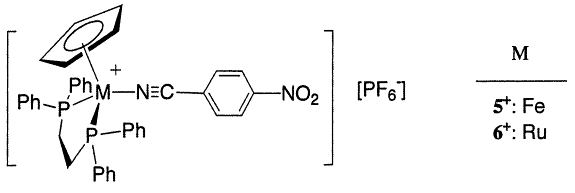
(40) (a) Mata, J.; Uriel, S.; Peris, E.; Llusar, R.; Houbrechts, S.; Persoons, A. *J. Organomet. Chem.* **1998**, *562*, 197−202. (b) Houbrechts, S.; Clays, K.; Persoons, A.; Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Organometallics* **1996**, *15*, 5266−5268.

(41) Wu, I.-Y.; Lin, J. T.; Luo, J.; Li, C.-S.; Tsai, C.; Wen, Y. S.; Hsu, C.-C.; Yeh, F.-F.; Liou, S. *Organometallics* **1998**, *17*, 2188−2198.

Scheme 1



Scheme 2



tolane (see Table 3). This indicates that the organometallic (η^2-dppe)(η^5-C_5Me_5)M fragments (M = Ru(II) or Fe(II)) exhibit a stronger donor character than the purely organic *para*-aminophenyl group.[42] In addition, our data indicate that the Fe(II) center constitutes a stronger donor endgroup than the corresponding Ru(II) center. This is somewhat in contrast with DFT computations, which predicted similar donor properties for these two nuclei in related acetylide complexes.[43] Together with the HLS data recently reported by Dias and co-workers for the 4-nitrobenzonitrile complexes $\mathbf{5}^+PF_6^-$ and $\mathbf{6}^+PF_6^-$, closely related to **3a** and **4a** (Scheme 2 and Table 3),[44] our work constitutes one of the first experimental evidence of the larger quadratic polarizabilities of Fe(II) acetylide complexes relative to Ru(II) analogues.[45] As suggested by Humphrey and co-workers,[46] the present trend seems to parallel the ease of the oxidation of the different metal centers in the corresponding acetylides (see Supporting Information). The overall lower values found for $\mathbf{5}^+$ (80×10^{-30} esu) and $\mathbf{6}^+$ (34×10^{-30} esu) can be traced back to the different nature of the unsaturated bridge, as well as to the positive charge of the metal center in these complexes, which certainly restricts their electron-donating capability with respect to **3a** and **4a**.

DFT computations indicate that the molecular dipole moments for most Fe(II) and for the Ru(II) complexes are roughly aligned with the C≡C bond in the ground state (Table 2).[21] This direction also constitutes the main charge transfer axis corresponding to the lowest energy MLCT electronic excitation.[1,21] Thus, the β or β_0 values presently derived for **3a**,**b** and also for the Ru(II) analogues **4a**,**b** possibly correspond to the main component of these tensors. However, going from **3d** to **3f**, the dipole moment deviates more and more from this axis (Table 2). In this connection, the slight discrepancy found between the β_0 value presently derived for **3d** (45×10^{-30} esu) and that previously determined by HLS (24×10^{-30} esu) is not surprising. Indeed, harmonic light scattering (HLS) usually measures a different combination of the β tensor components than EFISH.[13e,47] Very similar results between EFISH and HLS are expected only for compounds where the β tensor and the dipole moment are strictly collinear with the donor–acceptor axis.[48] Actually, the present EFISH measurement confirms the magnitude of the quadratic polarizability previously found for **3d**.[2]

Regarding the cationic Fe(III) complexes, overall much weaker second-order polarizabilities have been obtained for Fe(III) usually with a negative sign for β or β_0 relative to Fe(II) parents (Table 1). As mentioned above, this is diagnostic of a decrease or reversal of the dipole moment in the excited state. Comparison between static and dynamic quadratic polarizabilities suggests also the contribution of resonant enhancement for electron-releasing substituents. However, the β_0 values determined during this work for Fe(III) complexes should be considered with care, since several low-energy (forbidden) transitions with weak extinction coefficients are present in the visible range for these compounds.[21] As underlined by Marks, Ratner, and co-workers, the two-level model is often inappropriate for compounds with open-shell electronic configurations.[49] In this connection, the charge transfer direction corresponding to the low-energy excitations contributing to β could deviate significantly from the alkynyl axis where the dipole moment also lies (Table 2). This could explain why the β value presently determined by EFISH for $\mathbf{3d}^+$ differs in sign and magnitude from that determined by HLS ($(80 \pm 8) \times 10^{-30}$ esu).[2]

Analyzed in the framework of the two-level model, the EFISH data for the **3a**–**f**/$\mathbf{3a}$–$\mathbf{f}^+$ series can be sketched by oppositely polarized valence bond (VB) structures for the excited state of each parent (Scheme 3). Indeed, DFT computations reveal a similar orientation of the molecular dipole moment along the alkynyl axis in the ground state, regardless of the X substituent and of the oxidation state of the metal center. Considering that the Fe(II) center acts exclusively as a donor, the high quadratic polarizabilities found for several Fe(II) representatives

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[42] Stiegman, A. E.; Graham, E. M.; Perry, K. J.; Kundkar, L. R.; Cheng, L.-T.; Perry, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 7658–7666.

[43] Delfs, C. D.; Stranger, R.; Humphrey, M. G.; MacDonagh, A. M. *J. Organomet. Chem.* **2000**, *607*, 208–212.

[44] Wenseleers, W.; Gerbrandij, A. W.; Goovaerts, E.; Garcia, M. H.; Robalo, M. P.; Mendes, P. J.; Rodrigues, J. C.; Dias, R. *J. Mater. Chem.* **1998**, *8*, 925–930.

[45] Another article making this point was published during the reviewing process of the present contribution. See: Garcia, M. H.; Robalo, M, P.; Dias, A. R.; Duarte, M. T.; Wenseleers W.; Aerts, G.; Govaerts, E.; Cifuentes, M. P.; Hurst, S.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B. *Organometallics* **2002**, *21*, 2107–2118.

[46] Whittall, I. R.; Cifuentes, M. P.; Humphrey, M. G.; Luther-Davies, B.; Samoc, M.; Houbrechts, S.; Persoons, A.; Heat, G. A.; Bogsanyi, D. *Organometallics* **1997**, *16*, 2631–2637.

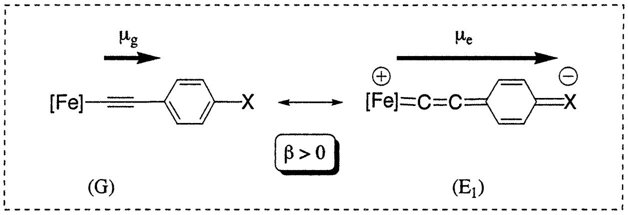
[47] Terhune, R. W.; Maker, P. D.; Savage, C. M. *Phys. Rev. Lett.* **1965**, *14*, 681–682.

[48] Whittall, I. R.; Humphrey, M. G.; Persoons, A.; Houbrechts, S. *Organometallics* **1996**, *15*, 1935–1941.

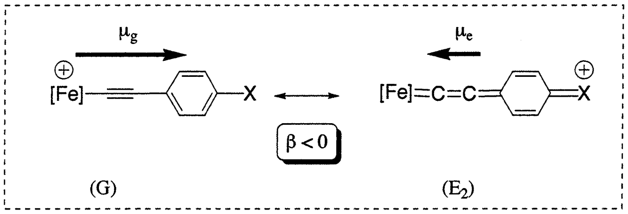
[49] di Bella, S.; Fragala, I.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 12747–12751.

Scheme 3

Fe(II) complexes / X acceptor



Fe(III) complexes / X donor



might be related to the dominant participation of a (d→π*) MLCT state like E_1.[44] Such a state does indeed correspond to the lowest energy excitation for most Fe(II) complexes.[1,21] In contrast, when opposed to electron-releasing substituents X, the cationic Fe(III) center appears to behave as a weak acceptor, as suggested by the negative β_0 values found for **3b**$^+$−**3f**$^+$, and (π→d) LMCT states such as E_2 might mostly contribute to the quadratic polarizability. Notably, the data reported for **5**$^+$ and **6**$^+$ suggest however that the cationic Fe(III) center can also behave as a donor when opposed to strong acceptors.[44] As mentioned above, though the strict application of the two-level model might be questionable for several of the acetylides investigated here, such a simple picture still rationalizes our data and is consistent with independent investigations carried out on related complexes.[1,2,15,21,37]

Finally, the rough linear relationship with Hammett substituent parameters found for **3a**−**f** and **3a**−**f**$^+PF_6^-$ (Figure 1) shows that the molecular quadratic polarizability is sensitive to the electronic nature of the X substituent on the aryl group in a given redox state. This indicates that the triple bond mediates efficiently the iron(II/III)−aryl electronic interactions. A corollary of this statement is that the second-order polarizability can be fine-tuned by a judicious choice of the substituent in these Fe(II/III) acetylide compounds. Moreover, as shown in Figure 1, oxidation constitutes a convenient means to switch off the second-order polarizability of Fe(II) acetylide complexes such as **3a** or **3b**. The second-order NLO activity for the Fe(II) and Fe(III) redox states appears however much more contrasted than for the redox isomers of polynuclear complexes $\{[(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)Fe(C{\equiv}C)]_m(C_6H_{6-m})\}^{n+}$, $n(PF_6)^-$ ($m = 1, 2$; $n = 1-3$).[2] As recently illustrated by Persoons and coworkers for mononuclear pentaamine ruthenium(II) 4,4′-bipyridinium complexes,[50] oxidation, when occurring in a reversible fashion, constitutes a very attractive feature for the elaboration of redox-switchable NLO-active molecules.[13b,14a,51] Within such a perspective, the complexes that we have studied here are also of interest since the reversible oxidation takes place in a quite accessible redox potential range.[1]

Conclusion

We have shown in this contribution that mononuclear electron-rich organoiron(II) [M]−C≡C−Ar compounds can show significant quadratic polarizabilities. Thus, with electron-deficient aryl or heteroaryl groups, β_0 values comparable to those reported for related NLO-active acetylides of group VIII metals were measured by EFISH. We also evidence that the Fe(II) center in $[(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)Fe]$ behaves as a more effective electron-donor group than Ru(II). The corresponding cationic Fe(III) parents are also stable and isolable, but show a strongly depressed second-order polarizability relative to that of the Fe(II) congeners. Given that oxidation occurs reversibly in an accessible redox potential range, the $[(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)Fe{-}C{\equiv}C{-}]^{n+}$ ($n = 0, 1$) fragment appears to be a promising building block for the realization of other NLO-active organometallic molecular architectures, allowing facile redox switching of β.

Experimental Section

General Data. All manipulations were carried out under inert atmospheres. Solvents or reagents were purified as follows and purged with argon: CH_2Cl_2 was distilled from CaH, and $CHCl_3$ was dried on molecular sieves. The synthesis of **1a**−**c**/**1a**−**c**$^+$ and **3a**−**f**/**3a**−**f**$^+PF_6^-$ was previously reported.[1,15a] Complexes **2a**$^+BPh_4^-$ and **2b**$^+PF_6^-$ were synthesized analogously to published procedures,[15b] while the synthesis and characterization of **4a**,**b** will be reported shortly.[52]

EFISH Measurements. Measurements were carried out in dichloromethane for neutral Fe(II) complexes and in chloroform for cationic Fe(III) parents at a fundamental wavelength of $\lambda_0 = 1.907$ μm, using a Q-switched mode-locked Nd^{3+}:YAG laser with pulse durations of 15 ns at 10 Hz repetition rate synchronized with a pulsed static electric field applied during 1 μs. Measurements were conducted on 10^{-2}−10^{-3} M solutions of the complexes. Further details regarding the EFISH experiment have been described previously.[16,17] All the EFISH β_λ values measured are defined according to the "phenomenologic convention".[53]

Computational Details. DFT calculations[54,55] were carried out using the Amsterdam Density Functional (ADF) program.[56] The model compounds $(\eta^5\text{-}C_5H_5)(PH_3)_2M(C{\equiv}C\text{-}p\text{-}C_6H_4X)^{n+}$ (M = Fe, Ru; X = NO_2, CN, H, OMe, NH_2; $n = 0, 1$) were used for complexes **3a**−**f**/**3a**−**f**$^+$ and **4a**,**b** in order to reduce computational effort. Electron correlation was treated within the local density approximation (LDA) in the Vosko−Wilk−Nusair parametrization.[57] The nonlocal corrections of Becke[58] and Perdew[59] were added to the exchange and cor-

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(50) Coe, B. J.; Houbrechts, S.; Asselberghs, I.; Persoons, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 366−368.

(51) Malaun, M.; Reeves, Z. R.; Paul, R. L.; Jeffery, J. C.; MacCleverty, J. A.; Ward, M. D.; Asselberghs, I.; Clays, K.; Persoons, A. *Chem. Commun.* **2001**, 49−50.

(52) Ellis, B. G.; Paul, F.; Lapinte, C.; Bruce, M. I. Work in progress.

(53) Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.* **1992**, *97*, 7590−7599.

(54) (a) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84−98. (b) Boerrigter, P. M.; te Velde, G.; Baerends, E. J. *J. Quantum Chem.* **1988**, *33*, 87−113.

(55) (a) Baerends, E. J.; Ros, P. *J. Quantum Chem.* **1978**, *S12*, 169−190. (b) Baerends, E. J.; Ellis, D. E.; Ros, P. *J. Chem. Phys.* **1973**, *2*, 41−51.

(56) *Amsterdam Density Functional (ADF) program; version 2.3*; Vrije Universiteit: Amsterdam, The Netherlands, 1996.

(57) Vosko, S. D.; Wilk, L.; Nusair, M. *Can. J. Chem.* **1990**, *58*, 1200−1211.

(58) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (b) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524−4529.

(59) (a) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824.

relation energies, respectively. The numerical integration procedure applied for the calculations was developed by te Velde et al.[54] The basis set used for the metal atoms was a triple-ζ Slater-type orbital (STO) basis for Fe 3d and 4s and Ru 4d and 5s, and a single-ζ function for 4p and 5p of Fe and Ru, respectively. A triple-ζ STO basis set was employed for H 1s and for 2s and 2p of C, N, and O, extended with a single-ζ polarization function (2p for H; 3d for C, N, and O) for X groups. The valence orbitals of the atoms of the other groups (C_5H_5, PH_3) were described by a double-ζ STO basis set. Full geometry optimizations (assuming C_1 symmetry) were carried out on each complex, using the analytical gradient method implemented by Verluis and Ziegler.[60] Spin-unrestricted calculations were performed for all the considered open-shell systems.

Acknowledgment. We thank S. Le Stang and B. G. Ellis for assistance in the synthesis of several Fe(II) and Ru(II) complexes tested. The Centre National de la Recherche Scientifique (CNRS) is acknowledged for financial support.

Supporting Information Available: Table of electrochemical data (E_0) and plot of $\mu\cdot\beta_0$ vs σ for the Fe(II) and Fe(III) complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(60) Verluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322−328.

(61) Whittall, I. R.; Cifuentes, M. P.; Humphrey, M. G.; Luther-Davies, B.; Samoc, M.; Houbrechts, S.; Persoons, A.; Heat, G. A.; Hockless, D. C. R. *J. Organomet. Chem.* **1997**, *549*, 127−137.

(62) Naulty, R. H.; Cifuentes, M. P.; Humphrey, M. G.; Houbrechts, S.; Boutton, C.; Persoons, A.; Heath, G. A.; Hockless, D. C. R.; Luther-Davies, B.; Samoc, M. *J. Chem. Soc., Dalton Trans.* **1997**, 4167−4174.

(63) Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Persoons, A.; Hockless, D. C. R. *Organometallics* **1996**, *15*, 5738−5745.