

Synthesis, Characterisation of (Arene)tricarbonylchromium Complexes Linked to Cationic Fe and Ru Derivatives and Studies of First Hyperpolarisabilities by Hyper-Rayleigh Scattering

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Keywords: Chromium / Iron / Ruthenium / Non-linear optics / Arene ligands / Carbonyl ligands / Hyperpolarisability

In order to investigate the non-linear optical properties, in particular second-order effects of binuclear organometallic complexes, a series of new cationic binuclear $[\text{MCp}-(\text{DPPE})\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3]^+[\text{PF}_6]^-$ compounds and mononuclear precursors $[\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3]$ have been synthesised [where $\text{M} = \text{Fe}^{\text{II}}$ or Ru^{II} ; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ and spacer = phenyl ring (C_6H_4), thiophene, ($\text{C}_4\text{H}_2\text{S}$), or bithiophene ($\text{C}_4\text{H}_2\text{S}_2$)]. The Fe or Ru organometallic π -donor fragments were linked by an extended π system to the acceptor $\text{Cr}(\text{CO})_3$ fragment. The effect of π back-donation involving the second Fe or Ru metal centre and the π^* orbitals of the $\text{N}\equiv\text{C}$ -coordinated group, was probed by the $\nu_{(\text{N}=\text{C})}$ stretching bands on the IR spectra and also by NMR spectroscopic data. The planarity, largely due

to the π -electron resonance, found on the solid state structure of the mononuclear complex $[\text{N}\equiv\text{C}-\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3]$ (**1Cr**) determined by X-ray diffraction [monoclinic system, $P2_1/c$ space group, with $a = 10.326(2)$ Å, $b = 13.209(5)$ Å, $c = 11.799(2)$ Å and $Z = 4$] emphasises the electronic effect of this building block. The significant values of first hyperpolarisability β determined by hyper-Rayleigh scattering (HRS) indicate that the Fe containing compounds were more efficient on second-order non-linear optical properties than the ruthenium analogues and the parent mononuclear chromium compounds.

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Introduction

Over the past decade a pattern has emerged for the design of organometallic materials with large second-order optical non-linearities, in which the molecules have important changes of dipole moments between ground and excited

states and large transition dipole moments.^[1] Using this molecular criteria, organometallic and coordination chemists have synthesised compounds possessing very intense metal-to-ligand and ligand-to-metal charge transfer bands in the UV/Visible spectrum, which showed very large molecular hyperpolarisabilities.^[2] The use of organometallic polarising groups in dipole structures has been of growing interest in the search for new molecular materials for non-linear optics, and various binuclear compounds have been published in the literature presenting significant values of first hyperpolarisabilities β . Representative examples are the ferrocenyl derivatives where the best reported β values are found for bimetallic compounds possessing an $(\eta^5\text{-thiophene})\text{Mn}(\text{CO})_3$,^[3] a group 6 pentacarbonyl,^[4] or an $\eta^7\text{-cycloheptatrienyltricarbonylchromium}$ ^[5] as the acceptor moieties. Also indenyl or cyclopentadienylruthenium(II) donor moieties and group 6 pentacarbonyl or pentaminceruthenium(III) acceptor partners have been used successfully as building blocks for the synthesis of bimetallic non-linear optical (NLO) active systems.^[6]

Our approach to the synthesis of bimetallic molecules for NLO purposes, was based on the use of the fragment

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$[M(\eta^5\text{-C}_5\text{H}_5)(\text{P-P})]^+$ ($M = \text{Fe}^{\text{II}}$ or Ru^{II} and P-P = diphosphane) as a π -donor building block, bridged through a π -delocalised system to the auxochrome $[\eta^6\text{-(benzene)-Cr(CO)}_3]$. The amphoteric nature has been studied in monometallic compounds.^[7] The π -donor ability of the $\text{Ru}^{\text{II}}/\text{Fe}^{\text{II}}$ fragments and the high values found for the quadratic hyperpolarisabilities of some monometallic molecules based on these moieties, have been explained on the basis of π back-donation towards the π^* empty orbitals of $-\text{N}\equiv\text{C}-$ and $-\text{C}\equiv\text{C}-$ functional groups.^[8,9]

The interest surrounding the use of these $[M(\eta^5\text{-C}_5\text{H}_5)(\text{P-P})]^+$ fragments as building blocks also comes from their cationic nature, where the contribution for the alignment of the chromophores in the solid state can be of potential interest for macroscopic NLO properties, as found for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{(R)\text{-prophos}\}(p\text{-NCC}_6\text{H}_4\text{NO}_2)][\text{PF}_6]$ ($\beta = 545 \cdot 10^{-30}$ esu)^[10].

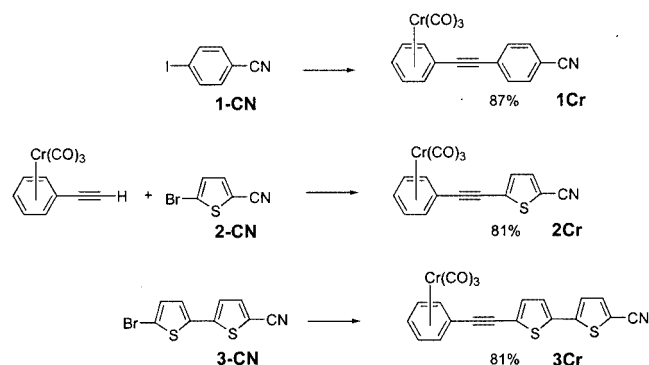
In the present work based on donor-spacer-acceptor structures, besides the exploitation of two donor fragments based on Ru^{II} and Fe^{II} centres, we have studied different spacers, using conjugated π systems containing the benzene ring and alternatively one or two thiophene rings.

Results and Discussion

Preparation of the Mononuclear Chromium

$[\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5]\text{Cr(CO)}_3$ Complexes **1Cr**, **2Cr**, and **3Cr**

Mononuclear chromium complexes of the general formula $[\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5]\text{Cr(CO)}_3$, where the spacer is a phenyl ring $-\text{C}_6\text{H}_4$ (**1Cr**), a thiophene ring $-\text{C}_4\text{H}_2\text{S}$ (**2Cr**) or two thiophene rings $(\text{C}_4\text{H}_2\text{S})_2$ (**3Cr**) were obtained^[11] by a Sonogashira palladium-catalysed cross-coupling reaction^[12] between the (η^6 -phenyl)ethynyltricarboxylchromium complex and various bromo, iodo arenes substituted by a nitrile group, **1-CN**, **2-CN**, and **3-CN** as depicted in Scheme 1. The free ligands **1–3** were synthesised analogously by the palladium copper catalysed coupling of iodonitrile aromatics **1-CN**, **2-CN**, and **3-CN** and phenylacetylene, see Experm. Section.



Scheme 1. Sonogashira-coupling reactions

Preparation of the Bimetallic Iron/Chromium and Ruthenium/Chromium Derivatives

$[\text{FeCp}(\text{DPPE})\{\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5\}\text{Cr(CO)}_3][\text{PF}_6]$ [$\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; spacer = C_6H_4 : **1FeCr**, $\text{C}_4\text{H}_2\text{S}$ (thiophene): **2FeCr**, and $(\text{C}_4\text{H}_2\text{S})_2$ (bithiophene): **3FeCr**] were prepared following the general procedure of iodide abstraction of the parent compound $[\text{FeCp}(\text{DPPE})\text{I}]$ by the use of TIPF_6 , in the presence of a slight excess of the corresponding chromophores,^[13] which in the present case were the mononuclear chromium complexes **1Cr**, **2Cr**, and **3Cr** described above. The reactions were carried out in dichloromethane by stirring at room temperature for several hours, and were followed by thin layer chromatography (TLC). After workup, orange reddish crystalline compounds were obtained in a yield of ca. 90%.

$[\text{RuCp}(\text{DPPE})\{\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5\}\text{Cr(CO)}_3][\text{PF}_6]$ [DPPE = 1,2-diphenylphosphanyl ethane; with the spacer as C_6H_4 : **1RuCr**, $\text{C}_4\text{H}_2\text{S}$ (thiophene): **2RuCr**, and $(\text{C}_4\text{H}_2\text{S})_2$ (bithiophene): **3RuCr**], were prepared following the same general procedure of halide abstraction, by precipitation of TiCl_4 from the parent compound $[\text{RuCp}(\text{DPPE})\text{Cl}]$, with TIPF_6 in the presence of a slight excess of the corresponding chromophores $[\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5]\text{Cr(CO)}_3$ (compounds **1Cr**, **2Cr**, and **3Cr**) in dichloromethane.^[14] Depending on the chromium derivative, the reactions were carried out at room temperature or refluxed for several hours. The evolution of the reactions was followed by TLC, as in the case of the iron analogues. After workup orange crystalline compounds were obtained in a yield of ca. 70%.

Characterisation of the New Mono **1Cr**, **2Cr**, and **3Cr** and Binuclear **1FeCr–3FeCr** and **1RuCr–3RuCr** Compounds

All the new compounds are fairly stable towards oxidation in air and to moisture, but the ruthenium bithiophene derivative $[\text{RuCp}(\text{DPPE})\{\text{N}\equiv\text{C}-2\text{-(5-C}_4\text{H}_2\text{S})_2-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5\}\text{Cr(CO)}_3][\text{PF}_6]$ (**3RuCr**) turned out to be light-sensitive. Analytical data, IR spectroscopy, and ^1H , ^{31}P , and ^{13}C NMR spectroscopy support the formulations. For the cationic binuclear complexes, the molar conductivities of 10^{-3} M solutions in acetone, in the range $101\text{--}115 \text{ }\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, are consistent with values reported for 1:1 electrolytes.^[15]

IR Spectroscopic Studies

Two well resolved CO stretching modes in accordance with the symmetry C_{3v} , are observed from IR measurements on solutions of chromium tricarbonyl arene complexes. The wavenumber of the CO modes is known to reflect the effect of a substituent on the coordinated aromatic ring. For example the complex of anisole presents two bands at 1978.9 and 1908.9 in isoctane whereas the complex of methylbenzoate shows two bands at 1992.5 and 1929.2, which have to be compared with the values of 1984.3 and 1916.5 for $[\text{C}_6\text{H}_6\text{Cr(CO)}_3]$.^[16a] Thus an electron donating group significantly decreases the IR resonance. The two bands relative to the $\nu(\text{C}\equiv\text{O})$ are in the range $1985\text{--}1898 \text{ cm}^{-1}$ for the

mononuclear complexes and in the range 1969–1888 cm^{-1} for the dinuclear complexes. Coordination of **1Cr** with Fe and Ru give the dinuclear complexes **1FeCr** and **1RuCr** which present resonances at lower frequencies: up to -17 cm^{-1} is in good agreement with π back-bonding from the other metal. This effect is also observed for complexes **2FeCr** and **2RuCr**. As for complexes **3FeCr** and **3RuCr**, the spectra exhibit a small decrease of the E mode but an unexpected although small increase of the A1 mode, Table 1.

Table 1. Selected IR data (KBr)

	$\nu \text{ CN } (\text{cm}^{-1})$	$\nu \text{ CO } (\text{cm}^{-1})$
1	2218	—
1Cr	2222	1985–1902
1FeCr	2216	1969–1900
1RuCr	2227	1968–1890
2	2220	—
2Cr	2214	1972–1915
2FeCr	2197	1969–1890
2RuCr	2216	1969–1892
3	2220	—
3Cr	2212	1957–1898
3FeCr	2197	1965–1888
3RuCr	2212	1966–1889

The $\nu(\text{N}\equiv\text{C})$ IR analysis of mononuclear complexes **1Cr**, **2Cr**, **3Cr** shows the presence of the characteristic nitrile band in the range 2212 to 2222 cm^{-1} . For the binuclear derivatives, typical IR bands confirm the presence of the cyclopentadienyl ligand ($\approx 3060 \text{ cm}^{-1}$), the $[\text{PF}_6]^-$ anion (840 and 545 cm^{-1}), the characteristic band of the coordinated nitrile $\nu(\text{N}\equiv\text{C})$ in the range 2197 to 2227 cm^{-1} . Comparison of $\nu(\text{N}\equiv\text{C})$ upon coordination of the chromium mononuclear complexes to iron or ruthenium centres, reveals a negative shift -6 to -17 cm^{-1} for the iron binuclear compounds indicating the existence of π back-bonding from the metal to the $\text{N}\equiv\text{C}$ group, Table 1. The unexpected slight positive shifts, $+5 \text{ cm}^{-1}$ for **1RuCr**, $+2 \text{ cm}^{-1}$ for **2RuCr**, and no shift for **3RuCr**, observed for the corresponding ruthenium atom which are less effective π donors than the iron derivatives, can also be correlated with a weaker π back-donation effect, since normal σ coordination leads to significant positive shifts on $\nu(\text{N}\equiv\text{C})$ (up to $+80 \text{ cm}^{-1}$). The present results for terminal nitrile coordination are in good agreement with our earlier reports dealing with iron and ruthenium related monometallic compounds.^[13,14]

NMR Spectroscopic Studies

^1H NMR spectroscopic data of arenetricarbonylchromium complexes **1Cr**, **2Cr**, **3Cr** are presented together with the corresponding data for the free aromatic ligands and the binuclear iron **1FeCr–3FeCr** and ruthenium

Table 2. ^1H NMR spectroscopic data of ligand **1** derivatives

	$\text{H}^{2,6}$	$\text{H}^{3,5}$	H^4	$\text{H}^{10,14}$	$\text{H}^{11,13}$	C_5H_5	$\delta(\text{H}_3) - \delta(\text{H}_2)$	$x \%$
1	7.45	7.28	7.28	7.52	7.49	—	-0.17	—
1Cr	5.55	5.34	5.34	7.57	7.63	—	-0.21	38
1FeCr	5.49	5.34	5.34	7.62	6.45 ^[a]	4.48	-0.15	41
1RuCr	5.49	5.33	5.33	7.53	6.52 ^[b]	4.83	-0.16	41

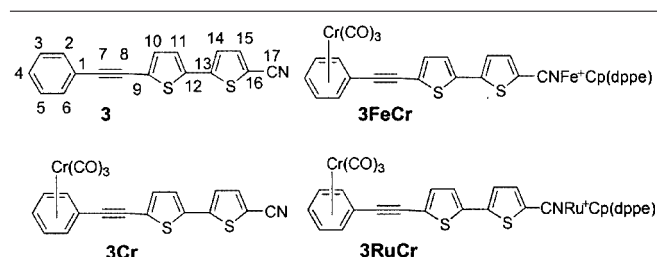
^[a] $\delta_{1\text{Cr}} - \delta_{1\text{FeCr}} = 1.18 \text{ ppm}$. ^[b] $\delta_{1\text{Cr}} - \delta_{1\text{RuCr}} = 1.11 \text{ ppm}$.

Table 3. ^1H NMR spectroscopic data of ligand **2** derivatives

	$\text{H}^{2,6}$	$\text{H}^{3,5}$	H^4	H^{10}	H^{11}	C_5H_5	$\delta(\text{H}_3) - \delta(\text{H}_2)$	$x \%$
2	7.44	7.30	7.30	7.10	7.40	—	-0.14	—
2Cr	5.52	5.34	5.34	7.23	7.51	—	-0.18	40
2FeCr	5.48	5.32	5.32	6.94 ^[a]	6.65 ^[b]	4.46	-0.16	41
2RuCr	5.51	5.35	5.35	7.00 ^[c]	6.79 ^[d]	4.84	-0.16	41

^[a] $\delta_{2\text{Cr}} - \delta_{2\text{FeCr}} = 0.29 \text{ ppm}$. ^[b] $\delta_{2\text{Cr}} - \delta_{2\text{FeCr}} = 0.86 \text{ ppm}$. ^[c] $\delta_{2\text{Cr}} - \delta_{2\text{RuCr}} = 0.23 \text{ ppm}$. ^[d] $\delta_{2\text{Cr}} - \delta_{2\text{RuCr}} = 0.72 \text{ ppm}$.

1RuCr–3RuCr complexes in Tables 2, 3, and 4. The complexation of the benzene ring to the chromiumtricarbonyl moiety in complexes **1Cr**, **2Cr**, **3Cr** was easily identified due to the characteristic upfield shift to the region 5.3–5.6 ppm.^[16b] The protons of the free arene give rise to different sets of signals and multiplicity in the region 7.2–7.5 ppm. We took into account that in the case of diphenyl acetylene, the protons H^2 and H^6 resonated at the highest frequency and the protons H^3 , H^5 , and H^4 resonated almost at the same frequency (increment $\text{H}_{ortho} = +0.19$, increment $\text{H}_{meta} = +0.02$ and increment $\text{H}_{para} = +0.00$). It is worth noting that in the case of tricarbonylchromiumarene complexes, the differences in the chemical shifts between the *meta* and the *ortho* protons: $\delta(\text{H}^3) - \delta(\text{H}^2)$ can give an idea as to the effect of the substituent and about the conformation of the tripod in solution with respect to the arene ring.^[17a–17g] By using the classical equation $\delta(\text{H}^3) - \delta(\text{H}^2) = (2x - 1) \cdot \Delta\delta_{\text{max}}$ ^[17g] we calculated the percentage of the conformation eclipsing the substituted

Table 4. ^1H NMR spectroscopic data of ligand **3** derivatives


	H ^{2,6}	H ^{3,5}	H ⁴	H ¹⁰	H ¹¹	H ¹⁴	H ¹⁵	C ₅ H ₅	$\delta(\text{H}_3) - \delta(\text{H}_2)$	x %
3	7.40	7.28	7.28	7.08	7.11	7.05	7.43	—	−0.12	—
3Cr	5.53	5.28	5.28	7.16	7.16	7.22	7.52	—	−0.25	36
3FeCr	5.50	5.31	5.31	7.15	7.01	6.87 ^[a]	6.65 ^[b]	4.45	−0.19	39
3RuCr	5.51	5.32	5.32	7.20	7.03	6.90 ^[c]	6.75 ^[d]	4.80	−0.19	39

[a] $\delta_{3\text{Cr}} - \delta_{3\text{FeCr}} = 0.35$ ppm. [b] $\delta_{3\text{Cr}} - \delta_{3\text{FeCr}} = 0.87$ ppm. [c] $\delta_{3\text{Cr}} - \delta_{3\text{RuCr}} = 0.32$ ppm. [d] $\delta_{3\text{Cr}} - \delta_{3\text{RuCr}} = 0.77$ ppm.

aromatic carbons. Thus we obtained populations x of 38, 40, and 36% for complexes **1Cr**, **2Cr**, and **3Cr** respectively, Tables 2–4, in good agreement with the almost staggered conformation found in the solid state, Figure 1.

Analysis of the ^1H NMR spectroscopic data of the iron binuclear complex $[\text{FeCp}(\text{DPPE})(\text{N}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\eta^6-\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3][\text{PF}_6]$ (**1FeCr**), and its ruthenium analogue $[\text{RuCp}(\text{DPPE})(\text{N}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\eta^6-\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3][\text{PF}_6]$ (**1RuCr**), Table 2, shows a shielding $\delta_{1\text{Cr}} - \delta_{1\text{FeCr}} = 1.18$ and $\delta_{1\text{Cr}} - \delta_{1\text{RuCr}} = 1.11$ ppm, respectively, for protons H_{11,13}, placed at the *ortho* position relative to the $\text{N}\equiv\text{C}$ functional group with respect to the mononuclear complex **1Cr**. Such shielding could be in good agreement with the π back-donation from the other metal already suggested by the $\Delta\nu(\text{N}\equiv\text{C})$ found for both compounds, and also with the results earlier reported for other monocyclopentadienylruthenium/iron mononuclear compounds containing benzonitrile ligands as chromophores.^[13,14] This is better proved by the fact that the H_{2,6} protons even farther from the Fe and the Ru residues resonate at slightly lower frequencies for **1FeCr**–**3FeCr** and **1RuCr**–**3RuCr** with respect to the mononuclear complex

1Cr–**3Cr**, the anisotropy of the Cp and the phenyl groups of the phosphane ligand being unable to interfere at this distance. This indicated a weak electron donating ability of the $-\text{CC}-\text{C}_6\text{H}_4-\text{CNFeCp}(\text{DPPE})$ residue; indeed, it is well reported that the protons of $\text{C}_6\text{H}_5\text{R}-\text{Cr}(\text{CO})_3$ (R = electron donating group) resonate at lower frequencies than the protons of $\text{C}_6\text{H}_6-\text{Cr}(\text{CO})_3$.^[16b]

In a similar manner the analysis of Tables 3 and 4, for compounds containing one and two thiophene units, reveals a shielding of 0.86 ppm ($\delta_{2\text{Cr}} - \delta_{2\text{FeCr}}$) and 0.72 ppm ($\delta_{2\text{Cr}} - \delta_{2\text{RuCr}}$) for protons H¹¹ (*ortho* to the NC group) with respect to the mononuclear complex **2Cr** and smaller shieldings for the adjacent H¹⁰ protons. Similar shielding values were also found for the equivalent protons H¹⁴ and H¹⁵ of the bithiophene containing compounds. Nevertheless this shift effect is barely felt on the H¹¹ proton of the second thiophene ring where only the small shielding values of ca. 0.15 ppm were observed for H¹¹. The chemical shifts of the H^{2,6} protons of complexes **2FeCr**, **3FeCr** and **2RuCr**, **3RuCr** resonate at lower frequencies with respect to the mononuclear complexes **2Cr**, **3Cr** but the shielding is small.

Selected ^{13}C NMR spectroscopic data of mononuclear complexes are reported in Table 5. The carbon resonances of the C¹ to C⁴ atoms (complexed phenyl rings of **1Cr**, **2Cr**,

Table 5. Selected ^{13}C NMR spectroscopic data of complexes 1, 2, 3-Cr: and complexing chemical shifts (CCS)

	C ¹ [a]	C ²	C ³	C ⁴	C ⁷	C ⁸
1	121.1	130.7	127.5	128.1	92.7	86.7
1Cr	88.3	95.0	91.3	91.3	89.6	87.6
CCS ^[b]	32.9	35.7	36.2	36.8	3.1	−0.9
2	120.5	130.6	127.5	128.4	95.7	79.5
2Cr	87.3	95.1	91.1	91.6	91.9	80.5
CCS ^[b]	33.2	35.5	36.4	36.8	3.8	−1.0
3	121.3	130.4	127.5	127.9	94.5	81.1
3Cr	88.8	94.7	91.0	91.2	90.5	82.0
CCS ^[b]	32.5	35.7	36.5	36.7	.0	−0.9

[a] CDCl_3 . [b] CCS = Complexing Chemical Shift.

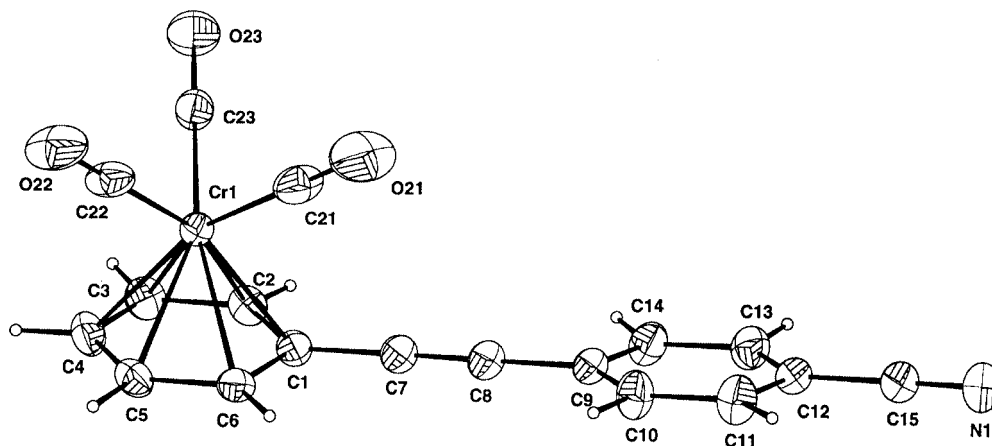


Figure 1. ORTEP diagram and atomic numbering scheme of the molecular structure of complex **1Cr** including a view along the Cr–ring axis. Thermal ellipsoids are presented at the 30% probability level

3Cr) are assigned by CH correlation spectroscopy. They are shifted to lower frequency in the region 88–96 ppm. It is worth calculating the complexing chemical shifts (CCS)^[18,19] of these carbons. Indeed the shifts due to the complexation are characteristic of each carbon, this is also true for the resonances of the alkyne carbon atoms C⁷ and C⁸. Thus the quaternary carbon C¹ is shifted by 32.8±0.4 ppm, the carbons C², C³, and C⁴ are shielded by 35.6±0.1, 36.3±0.3, and 36.7±0.1 ppm, respectively. The carbon C⁷ is shielded by 3.5±0.5 ppm whereas the carbon C⁸ is deshielded by 1.0±0.1 ppm. The carbonyl carbon resonances of complexes **1Cr**, **2Cr**, and **3Cr** appeared almost at the same frequency δ = 231.8 ppm for **1Cr** and **2Cr**, δ = 231.9 ppm for **3Cr**.

The ¹³C NMR spectra of the binuclear compounds reveal a deshielding of up to ca. 7.5 ppm of the carbon atom of the NC group, as expected. The ³¹P NMR spectra of the Fe/Cr and Ru/Cr binuclear compounds display one singlet relative to the dppe coligand at δ ≈ 97 ppm for the Fe derivatives and at δ ≈ 79 ppm for the Ru analogues, at about the same chemical shifts found for other related compounds.^[14] The signal relative to the PF₆[−] counterion is placed for all the compounds at δ ≈ −143 ppm as a septet.

X-ray Structural Determination of

[N≡C–C₆H₄–C≡C–η⁶-C₆H₅)Cr(CO)₃]

Information on [N≡C–C₆H₄–C≡C–η⁶-C₆H₅)Cr(CO)₃] (**1Cr**) and conformation of the solid state could be obtained from the X-ray crystal analysis, Table 6. Suitable crystals were obtained by crystallisation of complex **1Cr** in a mixture of diethyl ether and petroleum ether. The structure represented in Figure 1 shows an almost staggered conformation of the Cr(CO)₃ tripod with respect to the carbon atoms of the aromatic ring, with the Cr–C²¹ bond rotating 23° away from the alkynyl substituent.

The C⁷≡C⁸ triple bond: 1.196(3) Å is slightly longer than those observed in two relevant examples in the literature

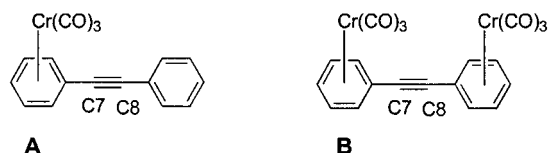


Figure 2. Complexes **A**^[18] and **B**^[19]

shown in Figure 2. 1.167 Å for C⁷≡C⁸ in complex **A**,^[18] 1.188(5) Å for complex **B**.^[19] The slight elongation observed for the C⁷≡C⁸ triple bond in our compound [N≡C–C₆H₄–C≡C–η⁶-C₆H₅)Cr(CO)₃] when compared with complex **B** [with two Cr(CO)₃ tripods attached to the phenyl rings] shows that the effect of the N≡C group can be compared with the effect of the Cr(CO)₃ acceptor group.

The C¹⁵–N bond length of 1.113 Å in **1Cr** should be compared with a similar value of 1.114 Å described in the case of a nitrile coordinated to a cationic Ru(Cp)(PPh₃)₂ fragment: [CpFeC₅H₄–CH=CH–*p*-C₆H₄–CN–Ru(Cp)(PPh₃)₂].^[2c] These values seem similar but with the nature of the phosphanes being different it is hard to compare the back-donation of the metal in these mono and dinuclear complexes.

The deviation from co-planarity of the complexed and uncomplexed phenyl rings in **1Cr** is small (10°) whereas the corresponding dihedral angle in complex **A** is 50.9° (in complex **B** this deviation is small: 3°). It would be interesting to evaluate the preservation of the planarity in the spacer in the binuclear compounds. Nevertheless, attempts of growing suitable single crystals for this purpose have been unsuccessful so far.

UV/Visible Studies

The UV/Vis electronic spectra of the aromatic free ligands **1–3**, the new monometallic **1Cr–3Cr** and the bimetallic **1FeCr–3FeCr** and **1RuCr–3RuCr** compounds were studied in acetone and chloroform solutions, in order to characterise the absorption bands and to obtain some idea of their hyperpolarisabilities, Table 7.

The spectra of the aromatic free ligands **1–3** displayed one intense π–π* intraligand absorption band (ILCT) in the region 317 to 370 nm.

The spectra of the monometallic complexes **1Cr–3Cr** in chloroform solutions, were characterised by two bands, one at ca. 425 nm and the other one in the region 300–360 nm. The first band was assigned to a metal-to-ligand charge transfer (MLCT) transition originating due to the charge transition from the chromium centre to the π- and σ-bound ligands. Although spectroscopic and theoretical studies^[20,21] predict the existence of two bands for the dominant excitations d_π-to-2π*(CO) and d_π-to-π*(arene) in [(η⁶-C₆H₆)Cr(CO)₃] related compounds, only one band was clearly observed in the present studies. A similar situation was also reported by other authors for related complexes, namely alkynyl and the alkenyltricarbonylchromium derivative.^[7c] The second and more intense absorption band, predicted for the π–π* intraligand transitions (ILCT),^[20] was

Table 6. Selected interatomic distances (Å) for **1Cr**

1Cr	
C1–C2	1.398(4)
C2–C3	1.406(3)
C3–C4	1.391(4)
C4–C5	1.407(4)
C5–C6	1.397(3)
C6–C1	1.427(3)
C7–C8	1.196(3)
C1–C7	1.431(3)
C8–C9	1.430(3)
C15–N	1.133(4)
C12–C15	1.447(4)
Cr–C1	2.216(2)
Cr–C2	2.220(2)
Cr–C3	2.211(2)
Cr–C4	2.215(2)
Cr–C5	2.220(2)
Cr–C6	2.216(2)

Table 7. UV/Vis spectroscopic data for compounds [MCp-(DPPE)N≡C(arene)C≡CC₆H₄Cr(CO)₃][PF₆] measured in solutions $\approx 10^{-4}$ M of acetone and chloroform (M = Fe^{II} and Ru^{II}).

Compound ^[a]	Acetone		Chloroform	
	λ_{max} (nm)	ϵ_{max} (mol ⁻¹ ·L·cm ⁻¹)	λ_{max} (nm)	ϵ_{max} (mol ⁻¹ ·L·cm ⁻¹)
1FeCr	— ^[b]	—	317	19500
	366	13500	348	14750
	430	13850	429	12000
2FeCr	— ^[b]	—	307	30120
	385 ^[c]	—	374	12820
	443	15920	444	12690
3FeCr	365	29760	398 ^[d]	26840
	392	27920	—	—
1RuCr	— ^[b]	—	317	30690
	338(sh)	≈ 26540	—	—
	376(sh)	≈ 12530	—	—
2RuCr	352	20990	330	38070
	414	11150	414	16420
3RuCr	362	31980	364	32130
	426	16650	426	17110
1Cr	— ^[b]	—	325	13090
	416	4550	422	4720
2Cr	— ^[b]	—	305	27110
	424	5290	430	5490
3Cr	351	28860	355	29640
	424	8070	424	9010
1	—	—	317	17680
2	—	—	349	7170
3	—	—	370	10010

^[a] [Fe] = FeCp(DPPE)–, [Ru] = RuCp(DPPE)–, [Cr] = Cr(η^6 -C₆H₅)(CO)₃. ^[b] Obscured by the solvent signal. ^[c] Broad band. ^[d] Very broad and intense band.

found in the range 300–360 nm, in agreement with the electronic spectra of the aromatic free ligands **1–3**.

The spectra of the bimetallic compounds (chloroform solution) showed the expected MLCT (at ca. 430 nm) and ILCT (in the range 320–400 nm) bands attributed to the monometallic parent [$\{\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5\}-\text{Cr}(\text{CO})_3$] complexes. The MLCT band was found to be insensitive to the polarity of the solvent, when chloroform was replaced by acetone, suggesting that there is no significant variation of polarity between the fundamental and the excited states, while the ILCT band showed some solvochromicity. In addition to these bands, a third band emerged in the electronic spectra of some of the binuclear complexes, namely **1FeCr** (348 nm) and **2FeCr** (374 nm), and it was attributed to a new metal-to-ligand charge transfer band involving the iron centre. The characterisation of this new band as a MLCT transition centred at the iron fragment, was supported by our previous studies in other related mononuclear iron compounds and explained by π back-donation involving $d_{\pi}-\pi^*(\text{N}\equiv\text{C})$ orbitals.^[8,22]

In Figure 3, the electronic spectrum of the binuclear compound **2FeCr** is compared with the spectrum of the parent mononuclear compound **2Cr** in chloroform. The arrow in the figure points indicates this new Fe centred MLCT band, clearly absent in the spectrum of the mononuclear parent compound.

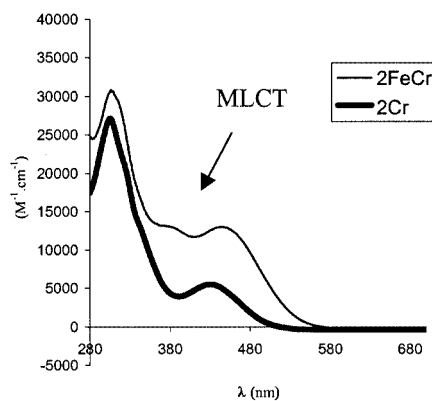


Figure 3. UV/Vis. Electronic spectra of **2FeCr**, showing a weak MLCT band, and **2Cr**

Interestingly, the **3FeCr** showed only one very broad and intense band (chloroform solution), centred at 398 nm, with the shape suggesting the overlap of the observed bands for **1FeCr** and **2FeCr**. The complexity of this band was corroborated by the optical spectrum of this compound in acetone, where two peaks seem to emerge clearly from that broad band.

The general characteristic of the electronic spectra of the studied set of binuclear complexes was a comparative increase of the intensity of the MLCT (Cr centred) and ILCT absorption to the corresponding mononuclear chromium derivatives. This effect was more pronounced on the ILCT band and particularly for ruthenium derivatives. In addition, the existence of a new MLCT, centred on the second metal, clearly observed in the binuclear iron derivatives and located in the same direction of the strengthened ILCT transition, might be the origin of the higher hyperpolarisabilities found for the binuclear derivatives, discussed below.

Nonlinear Optical Studies

The dynamic first hyperpolarisabilities β of the new complexes were measured in chloroform using the HRS technique^[23–25] with a 1064 nm Nd:YAG laser fundamental. Results are presented in Table 8. The applicability of the two-level model to these types of chromium tricarbonyl arene derivatives has been questioned.^[20] For the push-pull extended organic π -system chromophores func-

Table 8. Experimental first hyperpolarisability β determined by hyper-Rayleigh scattering of mono Cr complexes and the corresponding Fe and Ru binuclear derivatives

Compound	$\beta(10^{-30}\text{esu})$
1FeCr	94
2FeCr	170
3FeCr	197
1RuCr	42
2RuCr	83
3RuCr	143
1Cr	28
2Cr	59
3Cr	88

tionalised with the $\text{Cr}(\text{CO})_3$ group, this model has been applied based on the assumption that the major contribution to the hyperpolarisabilities arises from the ILCT transition occurring along the chromophore molecular axis.^[7c] The additional MLCT band centred at the second metal (Fe^{II} or Ru^{II}) fragment due to an enhanced back-donation to the π^* nitrile group, found clearly for the iron binuclear derivatives, and the evidence found in the IR and ^1H NMR spectroscopic data, for its existence in the ruthenium analogues, strongly suggests that the two-level approximation should not be applied in this case and therefore the corresponding static hyperpolarisabilities β_0 were not calculated. Moreover, the similarity in the positions of the charge-transfer bands would result in approximately identical resonance enhancement for all the complexes.

The β values found for compounds $[\{\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$ ($28\text{--}88 \times 10^{-30}$ esu), where $\text{N}\equiv\text{C}-$ is an acceptor group, are similar to those reported in the literature for compounds of the same general formula, namely $[\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{CO})_3]$ with $\text{R} = -\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{R}'$ or $-\text{C}(\text{H})=\text{C}(\text{H})-\text{C}_6\text{H}_4\text{R}'$ ($\text{R}' = \text{NMe}_2, \text{NO}_2$), corroborating that the chromium tricarbonyl arene fragment is amphoteric with respect to its electronic behaviour.^[7] Indeed, electron donating or electron withdrawing behaviour in NLO chromophores depends on the electronic nature of the far end group of the chromophore.^[7c] In addition, the substitution of the phenyl spacer **1Cr** by a thiophene spacer **2Cr** causes a twofold increase in the β value, probably due to the reduced aromaticity of the thiophene. The introduction of the second thiophene unity **3Cr** also enhances the hyperpolarisability, as expected due to the increase of the conjugation length.

The experimental β values measured for all the binuclear compounds studied (Table 8) showed that the best values of β were obtained for the Fe binuclear derivatives **2FeCr** and **3FeCr**, 170 and 197×10^{-30} esu, respectively. These values are relatively higher than those of the precursor mononuclear compounds **2Cr** (59×10^{-30} esu) and **3Cr** (88×10^{-30} esu). The ruthenium series **1RuCr**, **2RuCr**, and **3RuCr** showed lower β values relative to the iron series, as would be expected from our previous studies on similar systems^[8] and in accordance with the better donor role of the iron fragment. Comparison of the different spacers follow the same trend observed for the corresponding mononuclear chromium complexes. The β values obtained can be compared with other β values of organometallic congeners described in the literature^[1b,2i,5,7c] and with the 31×10^{-30} esu β value in the case of the prototypical “push-pull” chromophore (Z)-1-ferrocenyl-2-(4-nitrophenyl)ethylene complex^[2m] which has an SHG efficiency 62 times that of urea.

The comparison of the β values of mono and binuclear compounds studied in the present work show relatively higher values for the binuclear derivatives. These results might be expected by the higher intensity of the ILCT transitions observed in the optical spectra of the binuclear compounds and the existence of a second MLCT band (iron/ruthenium centred) in the axis of the chromophore, due to $d_{\pi}-\pi^*(\text{N}\equiv\text{C})$ π back-donation. It is important to note that

the direction of the ILCT transition is reversed when the binuclear compounds are formed. In fact, the $\text{N}\equiv\text{C}$ ending group, in the chromium mononuclear compounds $[\{\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$, plays the role of acceptor while the chromiumtricarbonylarene fragment acts as the donor group (see Figure 4, a). However, the coordination of this $\text{N}\equiv\text{C}$ group to a second metal (Fe/Ru) makes it behave as a π^* acceptor relatively to this new metal centre. Thus, in the binuclear complexes, the new ending group $[\text{MCp}(\text{DPPE})(\text{N}\equiv\text{C})-]^+$ acts as a π donor while the chromiumtricarbonyl fragment now behaves as an acceptor (see Figure 4, b). These results are in good agreement with the electronically amphoteric character reported for the chromium tricarbonyl arene fragment in analogous compounds of general structure $[\{\text{R}-(\text{spacer})-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$ where R is the donor NMe_2 or the acceptor NO_2 .^[7c]

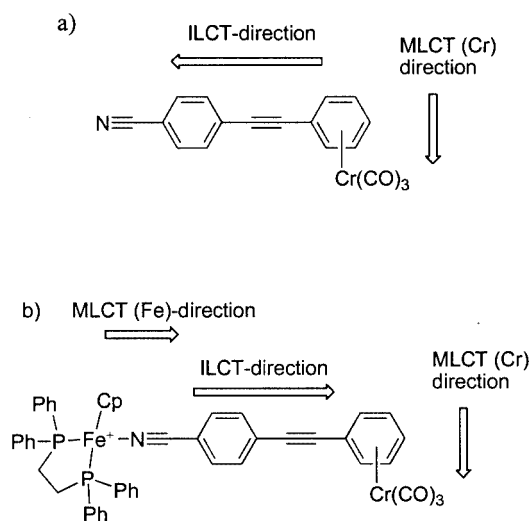


Figure 4. Ground state dipole vectors of chromium mononuclear complexes compared with the corresponding binuclear complexes. The direction of the ILCT contribution in the binuclear complexes is reversed, due to the role of the new ending group $[\text{MCp}(\text{DPPE})(\text{N}\equiv\text{C})-]^+$

Conclusion

The synthesis of nitrile ligands linked to tricarbonyl (η^6 -arene)chromium complexes $[\{\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$ by conjugated spacers is performed by reacting aromatic bromo or iodo nitrile derivatives with tricarbonyl chromium complexed phenylacetylene using the Sonogashira-coupling reaction. Characterisation of these mononuclear complexes obtained and the corresponding dinuclear $[\text{M}\{\text{N}\equiv\text{C}-(\text{spacer})-\text{C}\equiv\text{C}-\eta^6\text{-C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$ complexes $\text{M} = \text{Fe}(\text{dppe})\text{Cp}$, $\text{Ru}(\text{dppe})\text{Cp}$ has been studied using ^1H , ^{13}C , IR, and UV/Vis spectroscopy and in the case of one of them by X-ray crystallography. Measurements of the dynamic first hyperpolarisabilities (β) by HRS, showed significant higher values for the binuclear derivatives when

compared with the corresponding monometallic parent compounds. This enhancement of β observed upon coordination of the $[\{N\equiv C-(\text{spacer})-C\equiv C-\eta^6\text{-C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$ ligand complex to a second iron(II) or ruthenium(II) metal centre can be explained by the significant enhancement observed for the molar absorptivity of the ILCT band relative to the nitrile chromophore and the synergic effect of a new MLCT band originating due to π back-bonding from the second metal towards the nitrile functional group.

Experimental Section

General Procedures: All the experiments were carried out under vacuum or nitrogen atmosphere using standard Schlenk techniques, and solvents were dried following published methods.^[26] $[\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{-C}\equiv\text{CH})(\text{CO})_3]$ was easily prepared as reported recently.^[18] Chlorobenzene tricarbonylchromium complex was prepared according to literature procedures.^[27] The halo nitrile aromatics **1-CN**–**3-CN** are commercially available or prepared using standard literature procedures.^[28] The synthesis of some new chromium derivatives was recently published in a preliminary communication.^[11] $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})(\text{I})$ ^[22] and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})(\text{Cl})]$ ^[29,30] were prepared according to the procedures described in the literature. IR spectra were recorded in KBr pellets on a Perkin–Elmer 683 spectrophotometer; only significant bands are cited. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded in CDCl_3 on a Varian Unity 300 spectrometer at probe temperature. The UV/Vis spectra were taken on a Perkin–Elmer $\lambda 9$ UV/Vis/Nir spectrophotometer. Elemental analysis of mononuclear compounds were performed by “le service de Microanalyses” (Université Pierre et Marie Curie). Binuclear compounds were analysed at Laboratório de Análises, Instituto Superior Técnico, using a Fisons Instruments EA1108 system. Data acquisition, integration, and handling were performed using a PC with the software package Eager-200 (Carlo Erba Instruments). Melting points were obtained on a Reichert Thermovar. The molar conductivities of 10^{-3} mol·L $^{-1}$ solutions of the complexes in acetone were recorded with a Schott CGB55 Konduktometer. The ^1H ($[\text{D}]\text{chloroform}$) and ^{13}C ($[\text{D}]\text{chloroform}$) chemical shifts are reported in parts per million downfield from internal Me_4Si and the ^{31}P NMR spectra are reported downfield from external 85% H_3PO_4 ($[\text{D}]\text{chloroform}$). Spectral assignments follow the numbering scheme shown in Tables 2–4.

Synthesis of the Free Ligands 1, 2, and 3: The free ligands were synthesised in a similar manner to the chromium complexes (see below) by the palladium copper catalysed coupling of the aromatic iodonitriles **1-CN**, **2-CN**, and **3-CN** and phenylacetylene.

$N\equiv C-(\text{C}_6\text{H}_4)-C\equiv C-\text{C}_6\text{H}_5$ (**1**): 54% yield. IR: see Table 1. ^1H NMR: see Table 2. ^{13}C NMR: see Table 5 and 127.2 (C^9), 131.0 ($\text{C}^{10}, \text{C}^{14}$), 131.0 ($\text{C}^{11}, \text{C}^{13}$), 110.4 (C^{12}), 117.5 (C^{15}), (UV/Vis, see Table 7).

$N\equiv C-2-(5\text{-C}_4\text{H}_2\text{S})-C\equiv C-\text{C}_6\text{H}_5$ (**2**): 49% yield. IR: see Table 1. ^1H NMR: see Table 3. ^{13}C NMR: see Table 5 and 129.7 (C^9), 130.4 (C^{10}), 136.2 (C^{11}), 108.8 (C^{12}), 112.6 (C^{13}).

$N\equiv C-2-(5\text{-C}_4\text{H}_2\text{S})_2-C\equiv C-\text{C}_6\text{H}_5$ (**3**): 33% yield. IR: see Table 1. ^1H NMR: see Table 4. ^{13}C NMR: see Table 5 and 134.7 (C^9), 124.8 (C^{10}), 131.8 (C^{11}), 149.7 (C^{12}), 123.8 (C^{13}), 123.8 (C^{14}), 137.3 (C^{15}), 109.7 (C^{16}), 113.0 (C^{17}).

General Procedure for the Synthesis of Chromium Mononuclear Complexes

$[\{N\equiv C-(\text{C}_6\text{H}_4)-C\equiv C-\eta^6\text{-C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$ (**1Cr**): (η^6 -Phenyl)ethynyltricarbonylchromium complex (171 mg, 0.71 mmol), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (25 mg, 0.035 mmol), CuI (7 mg, 0.035 mmol), and *p*-iodobenzonitrile (158 mg, 0.69 mmol) were placed in a bicol under unit atmosphere and dried in vacuo for 30 min. NEt_3 (5 mL) and anhydrous THF (10 mL) were then added and the mixture was immediately heated to reflux for 3 h. After cooling at room temperature, the suspension was filtered, washed with Et_2O (3×20 mL) and the solvents were removed under reduced pressure. The residue was chromatographed on silica gel (diethyl ether/ petroleum ether 96:4 to 80:20) to afford **1Cr** (210 mg) in 87% yield as an orange solid. m.p. 168 °C (dec). IR: see Table 1. ^1H NMR: see Table 2. ^{13}C NMR: see Table 5 and 126.8 (C^9), 132.2 ($\text{C}^{10}, \text{C}^{14}$), 132.5 ($\text{C}^{11}, \text{C}^{13}$), 112.4 (C^{12}), 118.4 (C^{15}), 231.6 (CO) ppm. $\text{C}_{18}\text{H}_9\text{CrNO}_3$ (339.3): calcd. C 63.72, H 2.65, N 4.13; found C 63.13, H 2.84, N 3.96.

$[\{N\equiv C-2-(5\text{-C}_4\text{H}_2\text{S})-C\equiv C-\eta^6\text{-C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$ (**2Cr**): (η^6 -Phenyl)ethynyltricarbonylchromium complex (119 mg, 5 mmol), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (175 mg, 0.25 mmol), 2-bromocyanothiophene (6.05 g, 25 mmol), and NEt_3 (30 mL) were added together in a bicol under N_2 . The mixture was heated for 3 h. By using the same procedures complex **2Cr** was obtained in 81% (1.38 g) as an orange solid. m.p. 140 °C (dec). IR (KBr): see Table 1. ^1H NMR: see Table 3. ^{13}C NMR: see Table 5 and 129.2 (C^9), 132.9 (C^{10}), 137.4 (C^{11}), 111.1 (C^{12}), 113.6 (C^{13}), 231.8 (CO) ppm. $\text{C}_{16}\text{H}_7\text{CrNO}_3\text{S}$: calcd. C 55.65, H 2.02, N 4.05; found C 55.43, H 2.21, N 3.92.

$[\{N\equiv C-2-(5\text{-C}_4\text{H}_2\text{S})_2-C\equiv C-\eta^6\text{-C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$ (**3Cr**):^[11] 81% yield; m.p. 141 °C (dec). IR: see Table 1. ^1H NMR: see Table 4. ^{13}C NMR: see Table 5, and 134.2 (C^9), 125.9 (C^{10}), 132.7 (C^{11}), 143.4 (C^{12}), 123.1 (C^{13}), 124.2 (C^{14}), 138.4 (C^{15}), 112.2 (C^{16}), 114.2 (C^{17}), 231.9 (CO) ppm.

General Procedure for the Synthesis of the Bimetallic Iron/Chromium Derivatives

$[\text{FeCp}(\text{dppe})\{N\equiv C-(\text{spacer})-C\equiv C-\text{C}_6\text{H}_5\}\text{Cr}(\text{CO})_3][\text{PF}_6]$: A slight excess of the adequate amount of chromium chromophore $[\{N\equiv C-(\text{arene})-C\equiv C-\text{C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$ (1.1 mmol) and TiPF_6 (1.1 mmol) was added to a solution of the $[\text{CpFe}(\text{dppe})(\text{I})]$ (1 mmol) in dichloromethane (25 mL) followed by stirring, at room temperature, for 3 h in the case of $[\{N\equiv C-(\text{C}_6\text{H}_4)-C\equiv C-\eta^6\text{-C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$ and 18 h for the thiophene derivatives. The evolution of these reactions was followed by TLC (thin layer chromatography). A colour change was observed from brown to red with simultaneous precipitation of thallium iodide.

After filtration, the solution was evaporated under vacuum to dryness and washed several times with diethyl ether to remove the excess of chromium $[\{N\equiv C-(\text{arene})-C\equiv C-\text{C}_6\text{H}_5\}\text{Cr}(\text{CO})_3]$ starting material. The residue was recrystallised from dichloromethane/ diethyl ether.

$[\text{FeCp}(\text{dppe})(N\equiv C-\text{C}_6\text{H}_4-C\equiv C-\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3][\text{PF}_6]$ (**1FeCr**): 90% yield, red-orange, m.p. 128–130 °C. IR: see Table 1. ^1H NMR: see Table 2. ^{13}C NMR: δ = 79.8 ($\eta^5\text{-C}_5\text{H}_5$), 88.3 (C^1), 95.1 (C^2, C^6), 91.3 ($\text{C}^3, \text{C}^4, \text{C}^5$), 90.1 (C^7), 87.6 (C^8), 126.5 (C^9), 132.7 ($\text{C}^{10}, \text{C}^{14}$), 131.6 ($\text{C}^{11}, \text{C}^{13}$), 112.0 (C^{12}), 110.9 (C^{15}), 231.9 (CO) ppm. ^{31}P NMR: δ = 97.59 (s, dppe), –143.69 (hept, PF_6) ppm. $\text{C}_{49}\text{H}_{38}\text{CrF}_6\text{FeNO}_3\text{P}_3 \cdot 1/2(\text{C}_2\text{H}_5)_2\text{O}$: calcd. C 58.64, H 3.80, N 1.39; found C 59.8, H 3.70, N 1.47. Molar conductance: 113.7 $\text{cm}^{-1}\cdot\text{mol}^{-1}\cdot\Omega^{-1}$.

$[\text{FeCp}(\text{dppe})\{N\equiv C-2-(5\text{-C}_4\text{H}_2\text{S})-C\equiv C-\text{C}_6\text{H}_5\}\text{Cr}(\text{CO})_3][\text{PF}_6]$ (**2FeCr**): 86% yield, red, m.p. 130–132 °C. IR: see Table 1. ^1H

NMR: see Table 3. ^{13}C NMR: $\delta = 80.2$ ($\eta^5\text{-C}_5\text{H}_5$), 87.0 (C^1), 95.0 (C^2, C^6), 91.0 ($\text{C}^3, \text{C}^4, \text{C}^5$), 91.4 (C^7), 80.8 (C^8), 129.3 (C^9), 132.6 (C^{10}), 138.6 (C^{11}), 110.4 (C^{12}), 108.8 (C^{13}), 231.6 (CO) ppm. ^{31}P NMR: $\delta = 97.43$ (s, dppe), -143.53 (hept, PF_6) ppm. $\text{C}_{47}\text{H}_{36}\text{CrF}_6\text{FeNO}_3\text{P}_3\text{S}$: calcd. C 55.90, H 3.57, N 1.38, S 3.18; found C 55.8, H 3.52, N 1.31, S 3.0. Molar conductance: $109.4\text{ cm}^{-1}\cdot\text{mol}^{-1}\cdot\Omega^{-1}$.

[CpFe(dppe){N≡C-2-(5-C₄H₂S)₂-C≡C-C₆H₅}Cr(CO)₃][PF₆]

(3FeCr): 91% yield, orange reddish, m.p. 127–129 °C. IR: see Table 1. ^1H NMR: see Table 4. ^{13}C NMR: $\delta = 80.0$ ($\eta^5\text{-C}_5\text{H}_5$), 88.9 (C^1), 94.8 (C^2, C^6), 91.3 ($\text{C}^3, \text{C}^4, \text{C}^5$), 91.1 (C^7), 82.0 (C^8), 134.3 (C^9), 132.6 (C^{10}), 131.1 (C^{11}), 143.2 (C^{12}), 122.9 (C^{13}), 130.7 (C^{14}), 139.6 (C^{15}), 124.2 (C^{16}), 106.9 (C^{17}); 231.9 (CO) ppm. ^{31}P NMR: $\delta = 97.48$ (s, dppe), -143.63 (hept, PF_6) ppm. $\text{C}_{51}\text{H}_{38}\text{CrF}_6\text{FeNO}_3\text{P}_3\text{S}_2\cdot 2(\text{CH}_3\text{CH}_2)_2\text{O}$: calcd. C 57.14, H 4.70, N 1.10, S 5.17; found C 57.13, H 4.73, N 0.90, S 5.14. Molar conductance: $101.2\text{ cm}^{-1}\cdot\text{mol}^{-1}\cdot\Omega^{-1}$.

General Procedure for the Synthesis of the Bimetallic Ruthenium/Chromium Derivatives

[RuCr(DPPE){N≡C-(spacer)-C≡C-C₆H₅}Cr(CO)₃][PF₆]

(1RuCr-3RuCr): The corresponding chromium complex [$\text{N}\equiv\text{C}-(\text{arene})-\text{C}\equiv\text{CC}_6\text{H}_5\text{Cr(CO)}_3$] (1.1 mmol) was added to a solution of the $[\text{RuCr}(\text{dppe})\text{Cl}]$ (1 mmol) in dichloromethane (25 mL) followed by addition of TiPF_6 (1.1 mmol) at room temperature. The mixture was refluxed for 12 h in the case of [$\text{NC}-\text{C}_6\text{H}_4-\text{CC}-\text{C}_6\text{H}_5\text{Cr(CO)}_3$] and 48 h for [$\{\text{N}\equiv\text{C}-2-(5-\text{C}_4\text{H}_2\text{S})-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5\text{Cr(CO)}_3\}$]. In the case of the bithiophene derivative the reaction was carried out at room temperature for 14 h. The evolution of these reactions was followed by TLC. A colour change was observed from red to orange with the simultaneous precipitation of thallium chloride. After filtration, the solution was evaporated under vacuum to dryness and washed several times with diethyl ether to remove the excess of the chromium chromophores [$\{\text{N}\equiv\text{C}-(\text{arene})-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5\text{Cr(CO)}_3\}$]. The residue was recrystallised from dichloromethane/diethyl ether.

[CpRu(dppe)(N≡C-C₆H₄-C≡C-C₆H₅)Cr(CO)₃][PF₆] (1RuCr):

70% yield, red-orange, m.p. 125–128 °C. IR: see Table 1. ^1H NMR: see Table 2. ^{13}C NMR: $\delta = 82.2$ ($\eta^5\text{-C}_5\text{H}_5$), 88.3 (C^1), 95.1 (C^2, C^6), 91.3 ($\text{C}^3, \text{C}^4, \text{C}^5$), 90.1 (C^7), 87.7 (C^8), 126.7 (C^9), 133.0 ($\text{C}^{10}, \text{C}^{14}$), 131.7 ($\text{C}^{11}, \text{C}^{13}$), 112.0 (C^{12}), 110.4 (C^{15}), 231.8 (CO) ppm. ^{31}P NMR: $\delta = 79.85$ (s, dppe), -143.73 (hept, PF_6) ppm. $\text{C}_{49}\text{H}_{38}\text{CrF}_6\text{NO}_3\text{P}_3\text{Ru}\cdot 2(\text{CH}_3\text{CH}_2)_2\text{O}$: calcd. C 57.19, H 4.88, N 1.20; found: C 57.10, H 4.10, N 1.29. Molar conductance: $114.8\text{ cm}^{-1}\cdot\text{mol}^{-1}\cdot\Omega^{-1}$.

[RuCr(dppe)(N≡C-2-(5-C₄H₂S)-C≡C-C₆H₅)Cr(CO)₃][PF₆]

(2RuCr): 71% yield, orange, m.p. 133–135 °C. IR: see Table 1. ^1H NMR: see Table 3. ^{13}C NMR: $\delta = 82.5$ ($\eta^5\text{-C}_5\text{H}_5$), 87.0 (C^1), 95.0 (C^2, C^6), 91.1 ($\text{C}^3, \text{C}^4, \text{C}^5$), 91.6 (C^7), 80.2 (C^8), 129.3 (C^9), 132.9 (C^{10}), 138.9 (C^{11}), 109.0 (C^{12}), 108.0 (C^{13}), 231.7 (CO) ppm. ^{31}P NMR: $\delta = 79.59$ (s, dppe), -143.71 (hept, PF_6) ppm. $\text{C}_{47}\text{H}_{36}\text{CrF}_6\text{NO}_3\text{P}_3\text{RuS}$: calcd. C 53.51, H 3.42, N 1.32, S 3.04; found: C 53.50, H 3.41, N 1.33, S 2.90. Molar conductance: $115.2\text{ cm}^{-1}\cdot\text{mol}^{-1}\cdot\Omega^{-1}$.

[RuCr(dppe){N≡C-2-(5-C₄H₂S)₂-C≡C-C₆H₅}Cr(CO)₃][PF₆]

(3RuCr): Light-sensitivity prevented complete characterisation by elemental analysis. NMR samples were prepared in the dark. 70% yield; orange-brownish; m.p. 94–97 °C. IR: see Table 1. ^1H NMR: see Table 4. ^{13}C NMR: $\delta = 82.5$ ($\eta^5\text{-C}_5\text{H}_5$), 89.2 (C^1), 94.7 (C^2, C^6), 91.1 ($\text{C}^3, \text{C}^4, \text{C}^5$), 82.0 (C^8), 134.8 (C^9), 133.1 (C^{10}), 131.5 (C^{11}), 130.7 (C^{14}), 138.3 (C^{15}), 124.1 (C^{16}), 106.7 (C^{17}); 231.8 (CO) ppm.

^{31}P NMR: $\delta = 79.66$ (s, dppe), -143.61 (hept, PF_6) ppm. * Located under a broad signal.

Crystal Structure of 1Cr: [(CO)₃Cr(C₁₅H₉N)], $M = 339.27$, $\mu = 0.735\text{ mm}^{-1}$, $\rho = 1.46\text{ g}\cdot\text{cm}^{-3}$, monoclinic, $P2_1/c$, $Z = 4$, $a = 10.326(2)$, $b = 13.209(5)$, $c = 11.799(2)\text{ Å}$, $\beta = 106.61(2)^\circ$, $V = 1542.3(7)\text{ Å}^3$, from 25 reflections ($27.6^\circ < 2\theta < 28.4^\circ$). Cell dimensions and intensities were measured at 295 K on a Nonius CAD4 diffractometer with graphite-monochromated Mo- K_α radiation ($\lambda = 0.71069\text{ Å}$). $\omega/2\theta$ scans, two standard reflections measured every hour showed no significant variation. $1^\circ < \theta < 28^\circ$ ($0 < h < 13$, $0 < k < 17$, $-15 < l < 14$), 4085 measured reflections, 3715 unique reflections of which 2590 were observed [$F_o^2 > 3\sigma(F_o^2)$]; $R_{\text{int}} = 0.03$ for equivalent reflections. Data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods using SHELXS,^[31] all other calculations used CRYSTALS.^[32] Atomic scattering factors and anomalous dispersion terms were taken from the literature.^[33] Full-matrix least-squares refinement based on F and a Chebychev weighting scheme gave final values $R = 0.0399$, $wR = 0.0508$, and $s = 1.05$ for 209 variables and 2590 contributing reflections. The maximum shift/esd on the last cycle was 1.75. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located on a difference Fourier map; they were allocated an overall isotropic thermal parameter. The final difference electron density map showed a maximum of 0.42 and a minimum of $-0.30\text{ e}\cdot\text{Å}^{-3}$.

Hyper-Rayleigh Scattering: Details of the HRS experiment have been discussed previously.^[20] A Q-switched Nd:YAG laser emitting at 1064 nm was used to obtain the incident light. A reference value of $23\cdot 10^{-30}\text{ esu}^{[23]}$ for 4-nitroaniline in chloroform was used to calculate the hyperpolarisability of the compounds by the external reference method. Solutions for measurements until 10^{-4} M depending on the nature of the complex under study, the low concentration being necessary to minimise absorptive losses. One-dimensional hyperpolarisability is assumed, i.e. $\beta_{1064} = \beta_{333}$, and a relative error of $\pm 10\%$ is estimated.

Supplementary Material: Crystallographic data for the structural analysis of compound $[\text{Cr}(\eta^6\text{-C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{C}\equiv\text{N})(\text{CO})_3]$ (excluding structure factors) have been deposited in the Cambridge data base. CCDC-147256 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/contents/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Financial support for this work was provided by the TMR “Organometallic dipoles with NLO properties” contract ERBFMRXCTCT980166, by COST D14 and partly by Fundação para a Ciência e Tecnologia PRAXIS PCEX/C/QUI/96/96 and CNRS.

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Received April 3, 2003