

The electrochemical activity of heteroatom-stabilized Fischer-type carbene complexes

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Abstract

A cyclic voltammetry study of some alkoxy, amino and hydrazino carbene complexes of chromium and tungsten has been performed, affording for the first time a detailed overview on the electrochemical activity of this useful and versatile compound class, focusing on the modulating effects of both the carbene metal and substituents.

The interest for the above results is also related to the possibility of using Fischer carbenes as new electrochemical active probes for labeling 'peptide nucleic acids', which are DNA analogues, for diagnostic purposes.

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1. Introduction

Fischer carbene complexes (FCCs) of group 6 (Fig. 1) are, without any doubt, one of the most versatile, useful, eclectic and unforeseeable class of organometallics so far known. Since their discovery by Fischer and Maasböl in 1964 [1], they have been widely studied as a powerful tool by synthetic organic chemists all over the world. They also have been the object of very interesting physical organic studies, which clarified the mechanisms involved in their reactions with nucleophiles [2]. Photochemical [3] and thermal [4] transformations, as well as

the reactivity of anions, in the α -position with respect to the carbene carbon, with electrophiles have shown the great utility of FCC as stoichiometric reagents for preparative and stereoselective organic chemistry. This chemistry led to the obtainment of even very sophisticated structures, interesting from the biological or pharmacological point of view. Very interesting and recent reviews [5] witness that, forty years after their introduction, the popularity and general interest for these metal carbenes are still high.

On the other hand, the creativity of chemists in using FCC has always been rewarded with unconventional and often unexpected performance emerged from their use. The versatility of FCC is also related to the influence of the nature of the heteroatom present on the carbene carbon, on their stability and, more interestingly, on their reactivity. Recently, a new class of stable and

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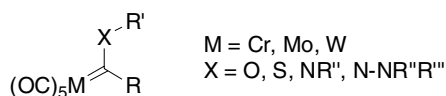


Fig. 1. General structure of heteroatom-stabilized Fischer-type carbene complexes.

easy-to-handle nitrogen-stabilized Fischer-type carbenes, namely alkyl(hydrazino)carbene complexes (Fig. 1, $X = N-NR''R'''$), have been synthesized in our laboratory and their reactivity has been explored showing that they have high synthetic potentialities in carbon–carbon bond forming reactions, even in a stereoselective way [6].

Among the various synthetic transformations, the use of Fischer carbenes as substrates in metathesis reactions using Grubbs catalysts [7,8] emerged as a very useful way for the obtainment of seven-, eight- and nine-membered heterocyclic rings, particularly in the case of hydrazino carbene complexes. The exploitation of this reactivity allowed us to label a monomer of a peptide nucleic acid (PNA, an interesting analogue of natural nucleic acids) [9] thus opening the way to new transition metal carbene conjugates of PNAs. The rationale behind this research, in progress in our laboratory, is to provide biomolecules with metal residues, useful both to modify their physicochemical characteristics (e.g., lipophilicity) and to endow them with suitable analytical probes useful for diagnostic purposes. In this light, Fischer-type carbenes appear particularly convenient, since they show peculiar and strong IR absorption, due to the stretching of the CO groups, in the region between 2070 and 1820 cm^{-1} , where no absorption of organic molecules are usually present, thus providing a potentially useful tool for the potential analytical detection of a metal-modified biomolecule. The above-mentioned studies also showed the compatibility of carbene complexes with biomolecules, and, in some cases, the possibility of employing them in aqueous or physiological conditions [10,11].

A further new and promising application of FCC is their use as electrochemical probes for the detection of the PNA–DNA binding event in the DNA recognition. Electrochemistry has been widely applied to DNA–DNA recognition, and so far it appears the most promising method in terms of sensitivity, response time, and low costs [12]. This analytical technique is based on the formation of α duplex between a single-stranded target DNA and a suitable DNA probe molecule, labeled with an appropriate fragment affording easy detection. In this light, efficient DNA sensors based on the electrochemically active ferrocene DNA probe, have recently been developed [12]. However, there is still a great need to improve the analytical methods that use PNAs as probes for DNA and RNA recognition [13].

Only few report have so far been reported in the literature concerning the redox properties of carbene com-

plexes of chromium and tungsten [14–16]. In the present paper, we present the first detailed overview on the electrochemical activity of heteroatom-stabilized chromium and tungsten carbenes, enlightening the role of both the carbene metal and substituents. It emerges that chromium and tungsten FCC exhibit a significant electrochemical activity, featuring normalized currents comparable to the reference ferrocene redox couple. In particular, despite the fact that Fischer carbenes are known to be quite sensitive to oxidation, a reaction which transforms the double metal carbon bond into an oxygen carbon one thus destroying the complex, both compound series exhibit a neat first oxidation peak, being monoelectronic and chemically and electrochemically reversible in the chromium case. The first FCC-conjugated PNA monomers have also been characterized, resulting in a quite satisfactory electrochemical activity, notwithstanding their bulky structures.

2. Results and discussion

Within a wide research programme concerning the synthesis of metal-labeled PNAs [17] as probes for DNA and RNA recognition, we were interested in designing new metal-conjugated PNAs by exploiting our expertise in carbene complexes of chromium and tungsten. As already mentioned above, Fischer-type carbene complexes show peculiar IR absorptions that could provide a way to detect the nucleic acids recognition event through this spectroscopic technique.

However, owing to the fact that Fischer carbenes could also exhibit unexpected and interesting electrochemical behavior [14–16], and on the basis of our interest in labeling PNAs with FCC for diagnostic purposes, we selected a series of amino and hydrazino carbenes for submission to a cyclic voltammetry study in order to verify their stability under redox conditions, as well as the chemical and electrochemical reversibility and current intensity.

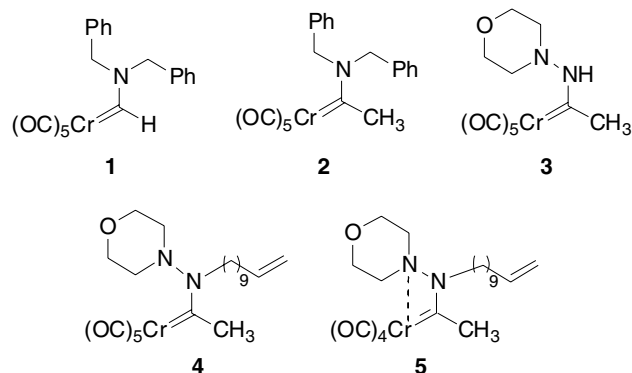


Fig. 2. Amino and hydrazino carbene complexes of chromium.

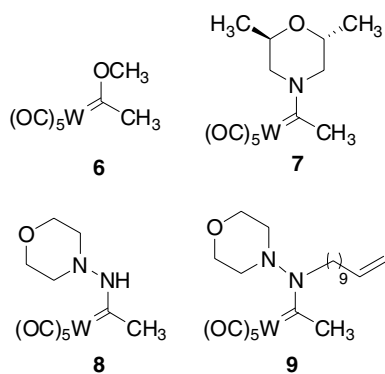
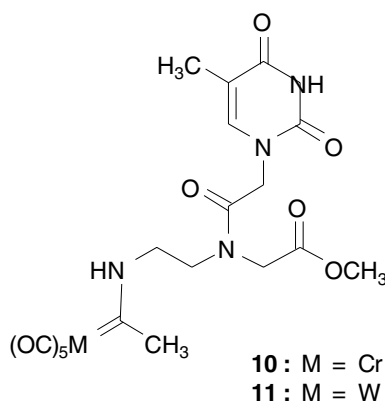


Fig. 3. Alkoxy, amino and hydrazino carbene complexes of tungsten.

Fig. 4. Peptide nucleic acid monomers **10** and **11** labeled with chromium and tungsten carbenes.

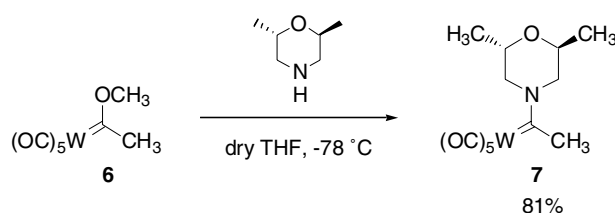
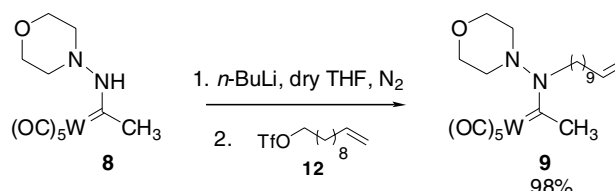
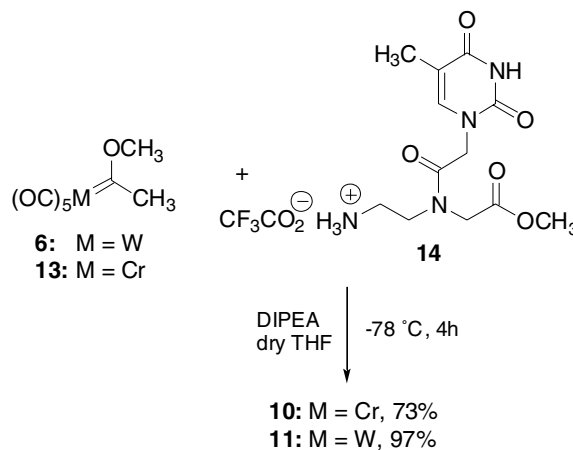
Here, we report a cyclic voltammetry performed on carbenes **1–9** (Figs. 2 and 3) and on the new PNA monomers **10** and **11**, labeled with chromium and tungsten aminocarbenes (Fig. 4).

We have chosen a set of chromium **1–5** (Fig. 2) and a set of tungsten complexes **6–9** (Fig. 3), in order to verify if the different nature of the two metals, chromium and tungsten, could influence the electrochemical behavior.

2.1. Synthesis of the chromium and tungsten carbene complexes

Carbenes **1** and **2** have already been described in the literature [18,19], although we have modified the synthetic procedure for obtaining complex **2** (see Section 4).

Complexes **3–5**, **8** and **9** are methyl(hydrazino)metal complexes and they all have been designed and synthesized in our laboratory. In particular, complexes **3** and **5** have already been mentioned in the literature [8,9] but the experimental details for their preparation are reported in this paper (see Section 4). Tungsten complex **7** has been reported in the literature (without experimental details), obtained as by-product in hydrazinolysis of alkoxy carbene complex **6** [6d]. For the electrochemical study reported in this paper, we have synthesized it

Scheme 1. Synthesis of complex **7**.Scheme 2. Synthesis of complex **9**.Scheme 3. Synthesis of PNA monomers **10** and **11** labeled with chromium and tungsten carbenes.

through the aminolysis reaction of complex **6** with the (\pm)-*trans*-2,6-dimethylmorpholine, in the classical conditions generally used for this reaction (Scheme 1).

The hydrazino carbene of tungsten **9** was obtained, in high yield, through the *N*-alkylation of complex **8** with the triflate of 10-undecene-1-ol (**12**) (Scheme 2).

Complexes **10** and **11** (Scheme 3) are the first examples of PNA monomers labeled with an amino Fischer carbene and they have been obtained through the aminolysis reaction of the corresponding pentacarbonyl(methoxy)-methyl carbenes of chromium and tungsten **6** and **13**, respectively, with the PNA monomer **14**.

2.2. Cyclic voltammetry studies

The electrochemical activity of the FCC synthesized as described above has been investigated by cyclic voltammetry on stationary glassy carbon GC electrode

Table 1
Selected features of the first oxidation peaks of different chromium and tungsten FCCs at concentration c in CH_2Cl_2 with 0.1 M TBAP as the supporting electrolyte

Substrate	I oxidation peak									
	CV								Convolution	
	$c/(\text{mol dm}^{-3})$	$E_{p,a1}/V$ (Fc ⁺ /Fc)	$(E_p - E_{p/2})/V$	$\Delta E_{p(a-c)}/V$	$E_{1/2}/V$	Fc ⁺ /Fc	$d(i_{p,a}/c)/dv^{0.5}/(\text{A cm}^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ V}^{-0.5} \text{ s}^{0.5})$	$dE_p/d\log v/V$	$E_{1/2}/V$ (Fc ⁺ /Fc)	α_{app}
Fc	0.000645	0.032	0.059	0.064	0		$(1.36 \pm 0.02)^{20}$	$0.00^{0.02-2}$	-0.001	0.97
M = Cr										
1	0.000685	0.458	0.062	0.079	0.419		$(0.68 \pm 0.01)^2$	$0.00^{0.02-0.2}$ $0.05^{0.5-5}$	0.424	0.94
2	0.000837	0.442	0.061	0.083	0.401		$(0.70 \pm 0.02)^2$	$0.00^{0.02-2}$ 0.06^{2-10}	0.404	0.97
3	0.000687	0.323	0.063	0.084	0.281		$(0.769 \pm 0.004)^5$	$0.00^{0.05-0.2}$ $0.04^{0.5-5}$	0.279	0.89
4	0.000641	0.315	0.063	0.093	0.269		$(0.614 \pm 0.008)^2$	$0.00^{0.02-2}$ 0.05^{2-10}	0.271	1.05
5	0.000638	-0.023	0.067	0.073	-0.060		$(0.43 \pm 0.02)^2$	$0.00^{0.02-0.5}$ $0.04^{0.5-10}$	-0.067	0.94
10	0.000721	0.308	0.054	0.053	0.282		$(0.88 \pm 0.01)^5$	$0.008^{0.05-2}$	0.279	0.93
M = W										
6	0.000288	0.732	0.073	–	–		$(3.63 \pm 0.45)^1$	$0.06^{0.02-5}$	0.681	0.77
7	0.000656	0.556	0.047	–	–		$(1.26 \pm 0.04)^2$	$0.00^{0.02-0.1}$ $0.05^{0.2-5}$	0.527	1.29
8	0.000741	0.427	0.052	–	–		$(1.76 \pm 0.03)^2$	$0.00^{0.02-0.5}$ $0.06^{0.5-5}$	0.393	1.03
9	0.000464	0.389	0.049	–	–		$(1.33 \pm 0.09)^{0.5}$	$0.03^{0.1-2}$	0.358	1.08
11	0.000667	0.520	0.076*	–	–		$(0.717 \pm 0.004)^{10}$	$0.03^{0.02-10}$	0.482	0.71

Data from the CV characteristics at 0.2 V s^{-1} : first oxidation peak potentials, E_p , referred to the ferricinium/ferrocene redox couple in the working medium; half-peak widths, $(E_p - E_{p/2})$; distances between anodic and cathodic peaks, $\Delta E_{p(a-c)}$; “half-wave” potentials, $E_{1/2} = (E_{p,a} + E_{p,c})/2$. Data from CV characteristics at scan rates v in the $0.02\text{--}20 \text{ V s}^{-1}$ range: slopes of the normalized peak current densities i_p/c vs. $v^{0.5}$, in the linearity range (its upper limit being represented by the superscript); slopes of E_p vs. $\log v$, in the linearity range (its lower and upper limits being specified in the superscript). Convulsive analysis results for the CV peak at 0.2 V s^{-1} : half-wave potential, $E'_{1/2}$, and α_{app} .

* Two merging peaks.

Table 2

Selected features of the second oxidation peaks of different chromium and tungsten FCCs at concentration c in CH_2Cl_2 with 0.1 M TBAP as the supporting electrolyte

Substrate	II oxidation peak		
	$E_{p,aII}/V (\text{Fc}^+/\text{Fc})$	$(E_p - E_{p/2})/V$	$(E_{p,aI} - E_{p,aII})/V$
Fc	–	–	–
M = Cr			
1	0.932	0.081	0.474
2	0.887	0.060	0.445
3	0.872	0.089	0.549
4	0.857	0.063	0.542
5	0.714	0.132	0.727
10	0.772	0.066	0.464
M = W			
6	–	–	–
7	0.872	0.078	0.316
8	0.786	0.071	0.359
9	0.838	0.152	0.449
11	1.055	0.143	0.535

Data from the CV characteristics at 0.2 V s^{-1} : second oxidation peak potentials, E_{pII} referred to the ferricinium/ferrocene redox couple in the working medium; half-peak widths, $(E_p - E_{p/2})$; distances between second and first oxidation peaks, $(E_{pII} - E_{pI})$.

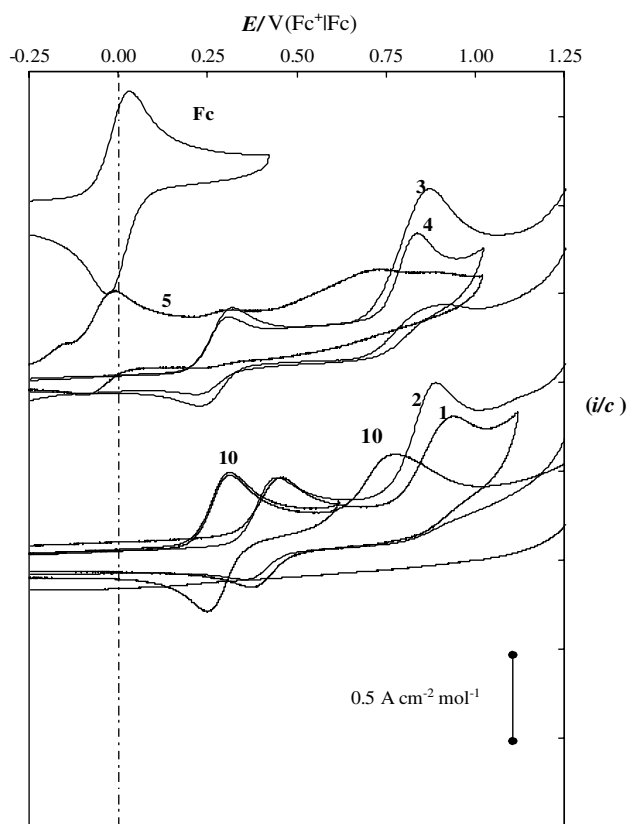


Fig. 5. A synopsis of the CV characteristics of chromium FCCs 1–5 and 10 at 0.2 V s^{-1} in CH_2Cl_2 + 0.1 M TBAP.

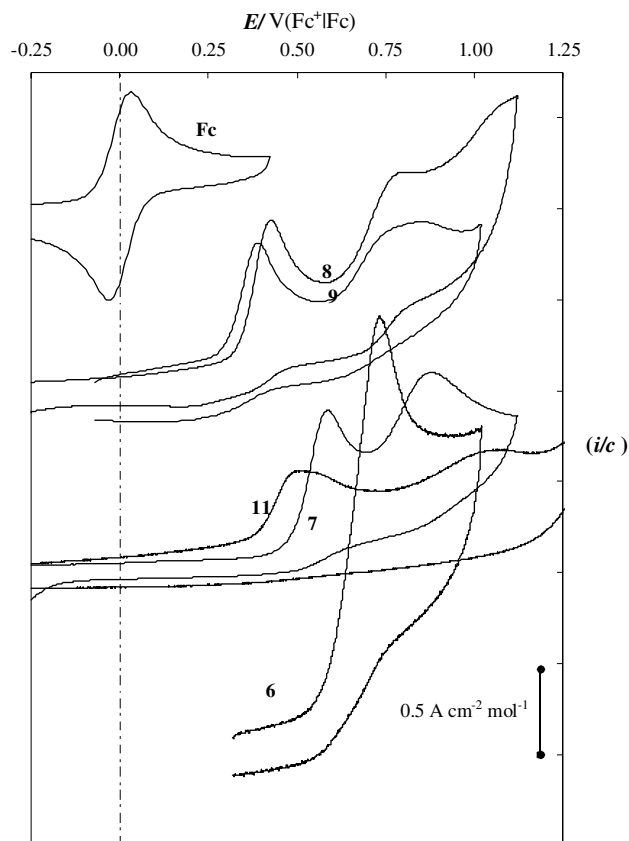


Fig. 6. A synopsis of the CV characteristics of tungsten FCCs 6–9 and 11 at 0.2 V s^{-1} in CH_2Cl_2 + 0.1 M TBAP.

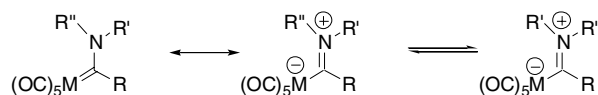


Fig. 7. Rotamers in Fischer-type carbene complexes.

(a usual choice as working electrode for mechanistic studies on non-electrocatalytic electron transfer reactions), in CH_2Cl_2 + 0.1 M tetrabutylammonium perchlorate, TBAP, medium. The most significant cyclovoltammetric (CV) features obtained for each compound are summarized in Tables 1 and 2 and synopsised in Fig. 5 for chromium carbene complexes and Fig. 6 for tungsten carbene complexes with ferrocene (Fc) as a reference substrate, being currently the most popular organometallic labeling group in probe molecules for biosensor applications.

2.2.1. The effect of the nature of the carbene metal

Our wide range of FCC includes four parallel cases of chromium and tungsten carbenes with the same (or similar) substituents on the carbene carbon, i.e. the hydrazino carbene complexes 3 versus 8 and 4 versus 9, and the amino carbene complexes 2 versus 7 and 10 versus 11. Comparing the relevant CV characteristics it is evident that:

- The first oxidation step of each chromium compound is significantly easier than that of its tungsten counterpart ($\Delta E_{p,a}(Cr-W) = -0.10, -0.07, -0.11,$ and -0.21 V, respectively, for the above mentioned four couples). This can be correlated to the difference in the first ionization potentials of the two metals in gas phase ($652.9 \text{ kJ mol}^{-1}$ for chromium and 770 kJ mol^{-1} for tungsten [20]). Similar differences in first oxidation peak potentials have been found in other parallel literature cases of chromium and tungsten compounds [14–16,21]; therefore the first oxidation step should be centered on the carbene metal. On the contrary, the second oxidation peak is located almost at the same potentials for both the chromium and the tungsten compound series, looking quite unaffected by the metal nature.
- All of the tungsten carbene complexes feature a chemically irreversible first oxidation peak (in association with significant electrode filming effects) while all of the chromium carbene complexes feature a chemically reversible and monoelectronic first oxidation peak; in other words, the product of the first oxidation step appears chemically stable in the chromium case but not in the tungsten one.
- The peak current densities i_p , normalized versus the substrate concentrations, are regularly double for the tungsten compounds with respect to the chromium ones (as it is evident from the slopes of the normalized peak current density versus $v^{0.5}$ linear characteristics, reported for each compound in Table 1). On the other hand, the molecular structures (and therefore the bulkiness and the diffusion coefficients) are the same or nearly the same within each couple. This features, together with the half-peak widths being significantly lower than 0.057 V in most tungsten cases, point to the first oxidation peaks being bielectronic in the tungsten cases. In other words, it appears that in the tungsten case the first electron abstraction immediately leads to the loss of a second electron, which could justify the chemical irreversibility of the oxidation peak (i.e., only the monovalent cation could be enough stable to be reconverted into the initial substrate in the return scan). This feature might be connected to the different electronic structure of the two metals (Cr = [Ar] $3d^5 4s^1$ and W = [Xe] $4f^{14} 5d^4 6s^2$); on the other hand, however, also the second ionization potential is higher for tungsten than for chromium. The different stability of the cations formed by the first electron loss could be also related to the different potentials at which they are formed.
- Examination of the first oxidation peaks in terms of half-peak width ($E_p - E_{p/2}$), potential shift at increasing scan rates, E_p versus $\log v$, and convolutive analysis [22,23], points: (a) in the chromium case, to electrochemical reversibility (i.e., to no or very low

activation barrier for the first electron abstraction) although such electrochemical reversibility declines at high scan rates, unlike the ferrocene case; (b) in the tungsten case, to electrochemical quasi-reversibility, if the above assumption of a bielectronic first oxidation peak holds.

- Comparing the CV characteristics of FCC-conjugate PNAs **10** versus **11**, in the tungsten case the first oxidation peak appears the result of two merging peaks. Such two peaks could be justified either in terms of a slight differentiation of the two subsequent electron losses (if the above assumption of a bielectronic first oxidation peak holds), or with the typical isomerism of the Fischer-type carbenes shown in Fig. 7, resulting in the existence of two rotamers.

2.2.2. The effects of the XR' and R substituents

Our systematic substrate series also affords a rationalization of the effects of the XR' and R substituents on the electrochemical activity of the FCC. In particular:

- *Hydrazino versus amino carbenes (3 versus 2, 8 versus 7)*: at constant R = CH₃, hydrazino carbenes are easier to oxidize than the corresponding amino ones ($\Delta E_{p,a}(3-2) = -0.12$ V, $\Delta E_{p,a}(8-7) = -0.13$ V), i.e., the organometallic site is more electron rich with a hydrazino substituent than with a (tertiary) amino one. This can be justified in terms of the so-called “hydrazine α effect”, resulting in higher availability of the lone pairs of the nitrogen atom adjacent to the carbene carbon as a consequence of the repulsion between the two nitrogen doublets.
- *Alkoxy versus amino carbenes (6 versus 7)*: at constant R = CH₃, alkoxy carbenes are more difficult to oxidize than the corresponding amino ones ($\Delta E_{p,a}(6-7) = 0.18$ V). This is consistent with the higher electronegativity of the oxygen atom with respect to the nitrogen one.
- *Alkylation of the R position (2 versus 1)*: substitution of an hydrogen atom with a methyl group as the R substituent results in a slightly electron richer organometallic site ($\Delta E_{p,a}(2-1) = -0.02$ V), consistently with the electron donating character of the methyl group.
- *Alkylation of the R' position (4 versus 3), (9 versus 8)*: the electron donating effect of the alkyl groups is still detectable also in the R' position (i.e., in β position with respect to the organometallic group) in the tungsten case ($\Delta E_{p,a}(9-8) = -0.04$ V), while it appears not significant in the chromium case ($\Delta E_{p,a}(4-3) = -0.01$ V).
- *Substitution of a CO group with the morpholine nitrogen atom in metal coordination*: only in the chromium case it is possible to convert hydrazino carbene **4** into the “cyclic” hydrazino carbene **5** in which one of the five metal-coordinated CO groups is replaced by the

nitrogen atom of the morpholine ring. This results in a remarkable anticipation of the first oxidation peak potential $\Delta E_{p,a(5-4)} = -0.33$ V, which is fully consistent with the substitution of a strong electron attracting group with a strong electron donating group in metal coordination. It is also worthwhile noticing that the CV characteristics of carbene **5** clearly points to the co-presence of a slight amount of its parent carbene **4**, a feature typical of this compound and confirmed by NMR.

2.2.3. Comparison with ferrocene

Since our aim is to test the new molecules as labeling groups in probe molecules for nucleic acid biosensors, it is worthwhile comparing the electrochemical activity of our FCCs with the electrochemical activity of ferrocene. Looking at Figs. 5 and 6, it is evident that each chromium and tungsten FCC exhibits a significant electrochemical activity, featuring normalized peak current densities comparable to the ferrocene one, notwithstanding their bulky structures. Also conjugation to a PNA monomer (compounds **10** and **11**) only slightly affects the peak currents. In particular:

- The performance of the chromium carbenes appears very similar to the ferrocene one since they also exhibit a monoelectronic, chemically and electrochemically reversible (although to a lesser extent than ferrocene) oxidation peak; the currents are somehow smaller than in the ferrocene case, consistently with their bulkier structure implying lower diffusion coefficients; the potentials are widely modulable by changing the XR' and R substituents (as when adding substituents on the cyclopentadienyl rings in the ferrocene case).
- Tungsten carbenes, although giving chemically irreversible oxidation peaks, a drawback in view of their use as labeling redox groups, result in higher currents than ferrocene, notwithstanding their bulkier structures, since their first oxidation peak is very probably a bielectronic one. Also in this case the potentials are widely modulable by changing the XR' and R substituents.

3. Conclusions

In this paper, Fischer-type carbene complexes emerge as a class of compounds of significant electrochemical activity, widely modulable in terms of both redox potential and reaction mechanism by changing the carbene metal and/or the carbene substituents. In particular, chromium carbenes exhibit a monoelectronic, chemically and electrochemically reversible first oxidation

peak thus resembling the case of ferrocene, a popular organometallic group for the labeling of nucleic acid probe molecules. Changing from chromium to tungsten results in more positive first oxidation peaks, being chemically irreversible but neat and reproducible, and with higher peak currents on account of the different reaction mechanism. Also conjugation of our FCCs to bulky PNA monomers only moderately affects the electrochemical activity of the organometallic center.

Therefore, the results of the present study could be usefully exploited in bio-organometallic chemistry. In fact, the carbene residue could be used, as new electrochemical active probe, in labeling biomolecules for diagnostic purposes for the detection of affinity and specificity of the binding between a peptide nucleic acid oligomer and the complementary DNA single strand. Work is already in progress in our laboratory, aimed at the obtainment of PNA oligomers labeled with chromium and tungsten carbene residues and the study of their properties included the electrochemical behavior.

4. Experimental details

4.1. General experimental considerations

All of the reactions were carried out under an atmosphere of dry argon or nitrogen; the glassware was flame-dried before use. THF was dried by means of distillation over sodium wires/benzophenone before use; the butyllithium solutions were titrated before use. Flash and vacuum chromatography were performed using Merck silica gel 60, 230–400 mesh. The melting points were determined using a Büchi 510 apparatus and are uncorrected. The ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectra were recorded using a Bruker AC 300 and Bruker AMX 300. The IR spectra were recorded using a Perkin–Elmer FT-IR 1725X. The mass spectra (EI, FAB) were recorded using a Vg Analytical 7070 EQ and a Thermo Finnigan LCQ Advantage.

4.2. Synthesis of complex **2**

Cs_2CO_3 (1.494 g, 4.58 mmol, 2.1 equiv) and benzyl bromide (0.51 mL, 4.29 mmol, 2 equiv) were added to a solution of pentacarbonyl(methyl)benzylamino carbene chromium [**19a**] (0.698 g, 2.15 mmol, 1 equiv) in 30 mL of acetone degassed by means of ultrasound. The mixture was left to react under magnetic stirring overnight and then the solvent was evaporated at reduced pressure. The residue was taken-up with CH_2Cl_2 , filtered on celite pad and the solvent was removed at reduced pressure. The crude product was purified by vacuum chromatography over silica gel (eluent: CH_2Cl_2 /light petroleum 1:1) to give 0.889 g of complex **2** as

yellow oil. Yield: 98%. The complex resulted to be the same reported in the literature [19b].

4.3. Synthesis of (*Z*)-pentacarbonyl[1-(4-morpholinyl-amino)ethylidene]-chromium(0) (**3**)

N-Amino morpholine (0.11 mL, 1.14 mmol, 1.1 equiv) was added to a solution of LiCl (0.095 g, 2.24 mmol, 2.15 equiv) in 3 mL of dry THF at room temperature, and a white slurry was formed. After cooling to $-78\text{ }^{\circ}\text{C}$, a solution of pentacarbonyl(methoxy)methyl carbene chromium(0) (0.261 g, 1.04 mmol, 1 equiv) in 2 mL of dry THF was added dropwise over 10 min. After 2 h and 30 min, the organic solvent was evaporated at reduced pressure, the residue taken up with CH_2Cl_2 and filtered on a celite pad to remove the LiCl. After evaporation of the solvent, the residue was purified by vacuum chromatography over silica gel (eluent: light petroleum/*ter*-butyl methyl ether 6:4) to give 0.293 g of complex **3**. Yield: 88%. Yellow solid; m.p. $110\text{ }^{\circ}\text{C}$ (CH_2Cl_2 -pentane). Anal. Found: C, 41.15; H, 3.17; N, 8.11%. Calc. for $\text{C}_{11}\text{H}_{12}\text{O}_6\text{N}_2\text{Cr}$: C, 41.26; H, 3.78; N, 8.75. ^1H NMR (CDCl_3 , 300 MHz) δ (ppm) 8.70 (1H, broad s, NH), 3.90 (4H, broad s, H_2COCH_2), 3.2–2.7 (4H, m, H_2CNCH_2), 2.70 (3H, s, CH_3); ^{13}C NMR DEPT (CDCl_3 , 75 MHz) δ (ppm) 275.3 ($\text{C}_{\text{carbene}}$), 234.4 (*trans* CO), 218.1 (*cis* CO), 65.4 (CH_2O), 55.7 (CH_2N), 40.5 (CH_3); IR/FT (nujol) ν (cm^{-1}) 3161 (NH), 2052 (*trans* CO), 1913 (*cis* CO).

4.4. Synthesis of complex **4**

Trifluoromethanesulfonic anhydride (0.73 mL, 4.60 mmol, 1.5 equiv) was added to a solution of 10-undecen-1-ol (0.58 mL, 2.9 mmol, 1 equiv) and triethylamine (0.40 mL, 2.90 mmol, 1 equiv) in 40 mL of dry CH_2Cl_2 , under nitrogen atmosphere and at $0\text{ }^{\circ}\text{C}$. The reaction was checked by TLC (eluent: CH_2Cl_2 /*n*-hexane 2:8). After 20 min, the organic solvent was evaporated at reduced pressure giving a crude product that was purified by vacuum chromatography over silica gel (eluent: CH_2Cl_2 /light petroleum 1:9) to give 0.886 g of triflate **12** as colorless oil. Yield: 98%. ^1H NMR (CDCl_3 , 300 MHz) δ (ppm) 5.9–5.7 (1H, m, $\text{CH}=\text{CH}_2$), 5.1–4.9 (2H, m, $\text{CH}=\text{CH}_2$), 4.52 (2H, t, $J = 6.5\text{ Hz}$, SOCH_2), 2.1–2.0 (2H, m, $\text{H}_2\text{C}=\text{CHCH}_2$), 1.9–1.5 (2H, m, $\text{H}_2\text{CCH}_2\text{O}$), 1.4–0.8 (12H, m, $(\text{CH}_2)_6$). A solution 1.52 M in hexane of *n*-BuLi (1.61 mL, 2.44 mmol, 1 equiv) was added to a solution of hydrazino carbene complex **3** (0.781 g, 2.44 mmol, 1 equiv) in 15 mL of dry THF, under nitrogen atmosphere and at $-78\text{ }^{\circ}\text{C}$. After 30 min, triflate **12** (0.814 g, 2.69 mmol, 1.1 equiv) was added. The mixture was let to react at $-78\text{ }^{\circ}\text{C}$ for 5 h and at $-20\text{ }^{\circ}\text{C}$ for a night. The reaction was quenched with 0.25 mL of water and then the solvent was evaporated at reduced pressure. Crude product was purified

by vacuum chromatography over silica gel (eluent: CH_2Cl_2 /light petroleum 1:1) to give 1.038 g of complex **4** as yellow-orange oil. Yield: 90%. ^1H NMR (CDCl_3 , 300 MHz) δ (ppm) 5.9–5.7 (1H, m, $\text{CH}=\text{CH}_2$), 5.1–4.9 (2H, m, $\text{CH}=\text{CH}_2$), 4.0–3.9 (4H, m, H_2COCH_2), 3.7–3.5 (2H, m, NNCH_2), 3.1–2.9 (4H, m, H_2CNCH_2), 2.81 (3H, s, CH_3), 2.02 (2H, q, $J = 6.9\text{ Hz}$, $\text{H}_2\text{C}=\text{CHCH}_2$), 1.7–1.2 (14H, m, $(\text{CH}_2)_7$). ^{13}C NMR DEPT (CDCl_3 , 75 MHz) δ (ppm) 277.0 ($\text{C}_{\text{carbene}}$), 224.0 (*trans* CO), 228.0 (*cis* CO), 138.9 ($\text{CH}=\text{CH}_2$), 114.0 ($\text{CH}=\text{CH}_2$), 65.6 (CH_2O), 54.3 (CH_2N), 46.4 (NNCH_2), 38.5 (CH_3), 33.6 ($\text{CH}_2\text{CH}=\text{CH}_2$), 30.6 ($\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$), 30.3, 29.2, 28.9, 27.0 (CH_2); IR/FT (neat) ν (cm^{-1}) 2058 (*trans* CO), 1967, 1930, 1887 (*cis* CO); MS (FAB⁺), m/z 472 (M^+), 444 ($\text{M}^+ - 1\text{CO}$), 416 ($\text{M}^+ - 2\text{CO}$), 360 ($\text{M}^+ - 3\text{CO}$), 332 ($\text{M}^+ - 5\text{CO}$), 281 ($\text{M}^+ + 1 - \text{Cr}(\text{CO})_5$).

4.5. Synthesis of complex **5**

Complex **4** (0.604 g, 1.28 mmol) was dissolved in 200 mL of dichloromethane and the solution degassed by ultrasound for 30 min. The mixture was then heated at reflux for 8 h. After cooling to r.t., the solvent was removed under reduced pressure. The crude product was purified by vacuum column chromatography over silica gel. With CH_2Cl_2 /light petroleum 4:6 as eluent, the starting complex **4** was recovered (0.242 g) while, with CH_2Cl_2 as eluent, complex **5** was obtained (0.341 g) as red oil. Yield: 60%. ^1H NMR (CDCl_3 , 300 MHz) δ (ppm) 5.9–5.7 (1H, m, $\text{CH}=\text{CH}_2$), 5.1–4.9 (2H, m, $\text{CH}=\text{CH}_2$), 4.1–3.8 (4H, m, H_2COCH_2), 3.6–3.5 (2H, m, NNCH_2), 3.2–2.8 (4H, m, H_2CNCH_2), 2.77 (3H, s, CH_3), 2.03 (2H, q, $J = 6.9\text{ Hz}$, $\text{H}_2\text{C}=\text{CHCH}_2$), 1.7–1.2 (14H, m, $(\text{CH}_2)_7$). ^{13}C NMR DEPT (CDCl_3 , 75 MHz) δ (ppm) 287.8 ($\text{C}_{\text{carbene}}$), 231.8, 228.5, 217.4 (CO), 138.9 ($\text{CH}=\text{CH}_2$), 114.2 ($\text{CH}=\text{CH}_2$), 64.4 (CH_2O), 57.6 (CH_2N), 52.6 (NNCH_2), 44.2 (CH_3), 39.7 ($\text{CH}_2\text{CH}=\text{CH}_2$), 33.6 ($\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$), 30.5, 29.6, 28.7, 26.9 (CH_2); IR/FT (neat) ν (cm^{-1}) 2000 (*trans* CO), 1922, 1876, 1838 (*cis* CO); MS (FAB⁺), m/z 444 (M^+), 360 ($\text{M}^+ - 3\text{CO}$), 332 ($\text{M}^+ - 5\text{CO}$), 281 ($\text{M}^+ + 1 - \text{Cr}(\text{CO})_5$).

4.6. Synthesis of complex **7**

(\pm)-*trans*-2,6-Dimethyl-morpholine (0.820 g, 6.5 mmol) was added to a solution of carbene complex **6** (2.480 g, 6.5 mmol) in 13 mL of dry THF at $-78\text{ }^{\circ}\text{C}$, under nitrogen atmosphere and magnetic stirring. The reaction was checked by TLC (eluent: CH_2Cl_2 /light petroleum 4:6) and after 6 h the organic solvent was evaporated at reduced pressure. The residue was purified by vacuum chromatography over silica gel (eluent: CH_2Cl_2 /light petroleum 3:7) to give 2.430 g of complex **7** as yellow solid. Yield: 80.4%; m.p. $98\text{--}99\text{ }^{\circ}\text{C}$

(CH₂Cl₂–pentane). ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 4.6–4.5 (1H, m, NH_{eq} on metal side), 4.3–4.1 (2H, m, CHO), 3.85 (1H, ddd, *J*_{vic}=4.3 Hz, *J*_{gem}=13.2 Hz, *J*_w=1.2 Hz, NH_{eq} on methyl side), 3.8–3.6 (2H, m, NH_{ax}), 2.79 (3H, s, WCCH₃), 1.28 (3H, d, *J* = 6 Hz, CH_{3eq}), 1.20 (3H, d, *J*=6 Hz, CH_{3ax}); IR/FT (nujol) ν (cm⁻¹) 2061 (*trans* CO), 1894 (*cis* CO); MS (APCI), *m/z* 46391 (M – 1), 436.0 (M – 1 – CO).

4.7. Synthesis of complex 9

A solution 1.56 M in hexane of *n*-BuLi (0.67 mL, 1.05 mmol, 1 equiv) was added to a solution of hydrazino carbene complex **8** (0.476 g, 1.05 mmol, 1 equiv) in 9 mL of dry THF, under nitrogen atmosphere and at –78 °C. After 30 min, triflate **12** (0.351 g, 1.16 mmol, 1.1 equiv) was added. The mixture was let to react at –78 °C for 5 h and at –20 °C for a night. The reaction was quenched with 0.2 mL of water and then the solvent was evaporated at reduced pressure. Crude product was purified by vacuum chromatography over silica gel (eluent: CH₂Cl₂/light petroleum 1:1) to give 0.640 g of complex **9** as yellow oil. Yield: 98%. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 5.9–5.7 (1H, m, CH=CH₂), 5.1–4.9 (2H, m, CH=CH₂), 4.0–3.9 (4H, m, H₂COCH₂), 3.7–3.5 (2H, m, NNCH₂), 3.1–2.9 (4H, m, H₂CNCH₂), 2.90 (3H, s, CH₃), 2.03 (2H, q, *J* = 7.0 Hz, H₂C=CHCH₂), 1.7–1.2 (14H, m, (CH₂)₇). ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 256.0 (C_{carbene}), 204.5 (*trans* CO), 199.3 (*cis* CO), 138.9 (CH=CH₂), 114.0 (CH=CH₂), 65.4 (CH₂O), 52.2 (CH₂N), 45.5 (NNCH₂), 39.8 (CH₃), 33.6 (CH₂CH=CH₂), 30.2 (CH₂CH₂CH=CH₂), 28.8–26.6 (CH₂); IR/FT (neat) ν (cm⁻¹) 2058 (*trans* CO), 1967, 1930, 1898 (*cis* CO); MS (APCI), *m/z* 605.2 (M + H⁺).

4.8. Synthesis of complex 10

DIPEA (0.08 mL, 0.49 mmol, 1.2 equiv) and thymine-PNA monomer **14** (0.200 g, 0.49 mmol, 1.2 equiv) was added to a solution of pentacarbonyl(methoxy)methyl carbene of chromium (0.099 g, 0.40 mmol, 1 equiv) in 1 mL of dry THF at –78 °C. The reaction was checked by TLC (eluent CH₂Cl₂/light petroleum 2:8) and finished after 4 h. The organic solvent was evaporated at reduced pressure, and the residue taken-up with 30 mL of CH₂Cl₂ and 20 mL of water. The organic layer was separated, filtered on celite, dried over Na₂SO₄. After evaporation of the solvent, the residue, was purified by vacuum chromatography over silica gel (eluent: AcOEt) to give 0.147 g of complex **10** as yellow solid. Yield: 72.2%; m.p. 124–126 °C (MeOH-*ter*-butyl methyl ether). ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 9.90 (1H, broad s, NH thymine), 8.45 (1H, broad s, NH), 7.02 (1H, s, CH thymine), 4.38 (2H, s, majority rotamer COCH₂NCO), 4.32 (2H, s, minority rotamer

COCH₂NCO), 3.9–3.5 (6H, m, CH₂NH, CH₂CH₂NCO, CH₂COO), 3.87 (3H, s, OCH₃), 2.77 (3H, s, minority rotamer CrCCH₃), 2.63 (3H, s, majority rotamer CrCCH₃), 1.93 (3H, s, CH₃ thymine). ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 280.9 (C=Cr), 224.5 (*trans* CO), 219.3 (*cis* CO), 117.5 (COO), 169.8 (NCOCH₂), 167.0 (NHCOCCH₃), 153.0 (NCON), 143.6 (HC=CCH₃), 111.1 (HC=CCH₃), 53.4 (OCH₃), 50.8 (NHCH₂), 50.2 (NCOCH₂), 46.8 (CH₂COO), 46.7 (NHCH₂CH₂), 35.7 (CrCCH₃), 12.2 (CH₃ thymine); IR/FT (nujol) ν (cm⁻¹) 3269 (NH), 2053 (*trans* CO), 1920 (*cis* CO), 1753 (COOCH₃); MS (electrospray ionization⁺), *m/z* 539.0 (M + Na)⁺, 511.1 (M – CO + Na)⁺, 482.6 (M – 2CO + Na)⁺, 454.4 (M – 3CO + Na)⁺, 416.9 (M – 4CO + Na)⁺, 325.3 (M – Cr(CO)₅)⁺; MS (electrospray ionization⁻), *m/z* 514.9 (M – 1)⁻, 458.7 (M – 2CO – 1)⁻.

4.9. Synthesis of complex 11

DIPEA (0.08 mL, 0.49 mmol, 1.2 equiv) and thymine-PNA monomer **14** (0.210 g, 0.51 mmol, 1.2 equiv) was added to a solution of complex **6** (0.157 g, 0.40 mmol, 1 equiv) in 1 mL of dry THF at –78 °C. The reaction, checked by TLC (eluent CH₂Cl₂/light petroleum 2:8), was finished after 4 h. The organic solvent was evaporated at reduced pressure, and the residue taken-up with 30 mL of CH₂Cl₂ and 20 mL of water. The organic layer was separated, filtered on celite, dried over Na₂SO₄. After evaporation of the solvent, 0.258 g of complex **11** was obtained as yellow solid. Yield: 97%; m.p. 126–128 °C (MeOH-*ter*-butyl methyl ether). ¹H NMR (CDCl₃, 200 MHz) δ (ppm) 9.87 (1H, broad s, NH thymine), 8.41 (1H, broad s, NH), 7.03 (1H, s, CH thymine), 4.38 (2H, s, majority rotamer COCH₂NCO), 4.33 (2H, s, minority rotamer COCH₂NCO), 3.9–3.5 (6H, m, CH₂NH, CH₂CH₂NCO, CH₂COO), 3.87 (3H, s, OCH₃), 2.76 (3H, s, minority rotamer WCCH₃), 2.67 (3H, s, majority rotamer WCCH₃), 1.94 (3H, s, CH₃ thymine). IR/FT (nujol) ν (cm⁻¹) 2061 (*trans* CO), 1916 (*cis* CO), 1742 (COOCH₃); MS (electrospray ionization⁺), *m/z* 671.0 (M + Na)⁺, 615.1 (M – 2CO + Na)⁺, 587.1 (M – 3CO + Na)⁺, 531.2 (M – 5CO + Na)⁺; MS (electrospray ionization⁻), *m/z* 647.3 (M – 1)⁻, 591.3 (M – 2CO – 1)⁻.

4.10. Electrochemical studies

The CV investigations were carried out in methylene chloride (Merck, HPLC grade >99.5%) with 0.1 M tetrabutylammonium perchlorate, TBAP (Fluka, electrochemical grade) as the supporting electrolyte, in a cell thermostated at 298 K, in solutions carefully deaerated by nitrogen bubbling, their concentrations ranging 2.88 10⁻⁴–8.37 10⁻⁴ mol dm⁻³, by means of an Autolab PGSTAT 30 potentiostat/galvanostat (EcoChemie, The

Netherlands) run by a PC with GPES software, correcting the ohmic drop by the positive feedback technique [24], with a glassy carbon GC (Amel, surface 0.071 cm^2) as the working electrode, a platinum counter electrode, and an aqueous saturated calomel electrode (SCE) as the operating reference electrode (the half-wave potential of the ferricinium/ferrocene redox couple, recommended by IUPAC for intersolvental comparison of potential scales [25], being 0.481 V when measured in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M TBAP}$ against our aqueous SCE). The optimized polishing procedure for the working GC electrode consisted in surface treatment with diamond powder (Aldrich, diameter $1 \mu\text{m}$) on a wet cloth (DP-Nap, Struers). The chemical and electrochemical reversibility of each well defined CV peak were checked by classical tests [22] including analysis of (a) the half-peak width ($E_p - E_{p/2}$), (b) the E_p versus $\log v$ characteristics, (c) the distance between anodic and cathodic peak potential ($E_{p,a} - E_{p,c}$), (d) the i_p versus $v^{1/2}$ characteristics, and (e) the “stationary”, step-like waves obtained by convolutive analysis of the original CV characteristics [23].

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