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## Synthesis and electrochemical study of iron, chromium and tungsten aminocarbenes: Role of ligand structure and central metal nature

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#### ABSTRACT

Several series of Fischer-type aminocarbene complexes with central Fe, Cr or W atoms and with various carbene substitution were synthesized and electrochemically investigated by dc-polarography and cyclic voltammetry. The shifts and changes of reduction and oxidation potentials were evaluated using the linear free energy relationship (LFER) approach with respect to (a) the type of coordination, (b) the substitution on the carbene ligand and (c) the nature of the central metal atom. The analysis of measured data confirms that the reduction center is localized on the carbene moiety and is strongly influenced by both electronic and sterical properties of its substituents. The oxidation proceeds on the metal and depends mainly on its nature and on the  $\pi$ -acidity of the ligands. Electrochemistry thus represents an important experimental approach to the description and understanding of the molecular electronic structure and redox properties. Experimental results are supported by DFT calculation of HOMO and LUMO orbitals shape and composition.

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#### 1. Introduction

Correlation between composition of metal coordination sphere and redox behaviour of the complex has been studied for a long time. For organometallic compounds, a theory was built [1] in which ligand constants  $P_L$  are used for characterizing influence of certain ligand type on electrochemical properties of the whole molecule. In addition to this, the oxidation and reduction potentials, their sequences and differences can be influenced also by substitution on the organic ligands themselves. Such an influence can be expressed quantitatively and correlated with electrochemical data by means of various  $\sigma$ -constants of Hammett type.

Fischer aminocarbene complexes are widely used in organic synthesis, both as reactants and catalysts, where the substitution on the organic carbene ligand plays an important role. Therefore, various new structural types are being synthesized and tested [2]. Recently, a possibility of using Fischer carbenes as electrochemical probes for biosensors has been shown [3].

Aimed design of new carbene systems requires deeper understanding of their redox abilities and knowledge of the relationship between structure and chemical properties. This investigation is the main goal of the presented contribution.

In our previous paper [4] we reported electrochemical properties of the first series of five chromium non-chelate and four chelate complexes of type I and II, respectively. For comparison, one tungsten non-chelate complex III and one chromium chelate complex VII bearing on the carbene carbon a methyl group instead of the substituted phenyl were synthesized and examined (Fig. 1). Using the linear free energy relationship (LFER) approach [5] we demonstrated experimentally that the reduction takes place on the carbene carbon atom and the reduction potential is sensitive to its substitution. A remarkable influence of sterical hindrance for the type II was observed and explained in agreement with NMR study of the hindered rotation of the aromatic ring attached to the carbene carbon atom [6]. Based on analysis of experimental data it was also concluded that the oxidation center of the molecule should be located prevalently on the central metal atom with strong sensitivity to the nature of the metal and the number of CO ligands bonded to it but with a negligible influence of the carbene substitution.

In the present study, we turned our attention to the Fischer aminocarbenes with iron as a central metal atom and to their comparison with previously studied chromium complexes. Due to its different electron structure and coordination number five, some differences in behaviour of iron compounds can be expected. Two new analogous series of five iron non-chelate ( $\mathbf{V}$ ) and five chelate

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(**VI**) complexes were synthesized and examined in order to (1) characterize electrochemically the new compounds; (2) compare the electronic and redox properties of chromium and iron analogues; (3) compare the electronic and redox properties of chelated and non-chelated compounds; (4) correlate the conclusions derived from the analysis of experimental data with quantum chemical calculations.

In addition to this, in the frame of this contribution several other aminocarbene complexes were synthesized in order to extend and complete the already existing series. They are: tungsten chelate **IV** (analogous to the already synthesized non-chelate **III**), chromium non-chelates **IXa**, **c**, **e** with a methyl in *ortho*-position, two missing compounds in series **II** and **VII** – chromium nonchelates **IIb** and **VIIc** and a chelate analogue to **VIIb** – compound **VIIIb**. Such variety of compounds gives good possibility to refine the previous conclusions and, eventually, formulate more general rules. The overview of investigated aminocarbenes is presented in Table 1.

#### 2. Experimental

#### 2.1. Electrochemistry

All electrochemical measurements were carried out in a 10 ml two-compartment cell of Metrohm type, in non-aqueous dimethylformamide (DMF) purified by azeotropic distillation with 5% water and 5% benzene followed by vacuum fractionation [4]. The solution was deaerated by a stream of argon. Tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>N PF<sub>6</sub>) p.a. Fluka recrystallized from aqueous ethanol was used as supporting electrolyte in concentration 0.1 mol/l. The sample solution was prepared always directly in the cell by dissolving the known amount of solid compound; sample concentration was about  $3 \times 10^{-4}$  mol/l.

For electrochemical experiments a computer-controlled Eco-Tribo polarograph (PC-ETP, ECO-TREND PLUS Prague, Czech Republic) or a PA3 potentiostat (Laboratorní přístroje) was used with a std. Ag/Ag<sup>+</sup> or SCE reference electrode (all data are converted vs. SCE reference electrode) and a platinum sheet as an auxiliary electrode. Reduction was studied by dc-polarography on dropping mercury electrode (DME). For cyclic voltammetry (CV), a freshly polished stationary platinum disk (diameter 0.5 mm) electrode was used for both oxidation and reduction, scan rate ranging from 100 to 800 mV/s. The accuracy of the potential measurement was 0.005 V. Under given condition, it was possible to determine both  $E_{red}$  and  $E_{ox}$  for all the substances:  $E_{red} = E_{1/2}$  from dc-polarography,  $E_{ox(red)} = 1/2(E_{pa} + E_{pc})$  from CV measurement.

#### 2.2. DFT calculations

Ground state electronic structure calculations on carbene Cr and Fe complexes **Ic**, **IIc**, **Vc**, **VIc** and **VIIc** have been done by density functional theory (DFT) methods using Gaussian 03 [7] program package. B3LYP hybrid functional [8–10] was used together with  $6-31G^*$  polarized double- $\zeta$  basis sets [11] for H, C, Fe and Cr atoms. Geometry of all complexes was optimized without any symmetry constrains, vibrational analysis was used for characterization of energy minima. MO analysis was done at optimized structures, MO plots were generated by GaussView software.

#### 2.3. Chemicals for carbene complexes

All experiments were carried out under argon. Tetrahydrofuran was distilled from benzophenone ketyl under argon prior to use. Chromium hexacarbonyl, tungsten hexacarbonyl, iron pentacarbonyl and Me<sub>3</sub>SiCl were purchased from Aldrich and were used without purification. Silica and alumina were obtained from Merck. *N*,*N*-Dimethylbenzamide, *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide were obtained from Aldrich, 4-substituted *N*,*N*-dimethylbenzamides, *N*,*N*-dimethyl-2-methylbenzamide and *N*,*N*-dimethyl-2-methyl-4-methoxybenzamide were obtained by the reaction of the corresponding acylchloride with excess of *N*,*N*-dimethylamine in diethylether. *N*,*N*-Diallylbenzamide [12] and 4-substituted *N*,*N*-diallylbenzamides [6] were prepared according to the reported procedures. Melting points were determined on a Kofler block and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Gemini 300 spectrometer (<sup>1</sup>H at 300 MHz, <sup>13</sup>C at 75.4) in CDCl<sub>3</sub>.

#### 2.3.1. N,N-Dimethyl-2-methyl-4-(trifluoromethyl)benzamide

2-Methyl-4-(trifluoromethyl)benzoic acid was prepared using the methodology for the direct *ortho*-lithiation of unprotected benzoic acids [13]. Reaction started from 4-(trifluoromethyl)benzoic acid (0.32 g, 2 mmol), *sec*-butyllithium (4.4 mmol), TMEDA (0.66 ml, 4.4 mmol) and iodomethane (0.5 ml, 8 mmol) afforded 280 mg (69%) of crude 2-methyl-4-(trifluoromethyl)benzoic acid as a white solid which was recrystallized from heptane.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.71 (s, 3H, CH<sub>3</sub>), 7.55 (br s, 2H, Ar–*H*), 8.14 (d, *J* = 8.79 Hz, 1H, Ar–*H*).

To a solution of 2-methyl-4-(trifluoromethyl)benzoic acid (0.091 g, 0.45 mmol) and DCC (0.103 g, 0.5 mmol) in 5 ml of THF 1 M solution of dimethylamine in Et<sub>2</sub>O (1.4 ml, 1.4 mmol) of was added. Resulting mixture was stirred 17 h at ambient temperature, then acetic acid (2 ml) was added and the mixture was stirred 30 min at ambient temperature. Evaporation of the solvents followed by flash chromatography on silica in hexane–ethyl acetate (1:2) gave 80 mg (81%) of desired *N*,*N*-dimethyl-2-methyl-4-(trifluoromethyl)benzamide as yellow oil.

<sup>1</sup>H NMR: 2.35 (s, 3H, CH<sub>3</sub>), 2.83 (s, 3H, NCH<sub>3</sub>), 3.15 (s, 3H, NCH<sub>3</sub>), 7.30 (d, *J* = 8.79 Hz, 1H, Ar–*H*), 7.48 (br s, 2H, Ar–*H*).

#### 2.4. Preparation of aminocarbene complexes

Chromium, tungsten and iron aminocarbene complexes **Ib,d** [4], **Ic** [14], **IIa,b,d,e** [6], **IIc** [15], **Vc** [16], **VIc** [17], **VIIb,c** [18] and **VIIIb** [19] were prepared according to the reported procedures.

## 2.4.1. General procedure for the preparation of chromium and tungsten aminocarbene complexes **Ia**,*e*, **IIIc**, **IVc** and **IX** [14]

The solution of sodium naphthalenide prepared from sodium (0.43 g, 18.5 mmol), naphthalene (2.37 g, 18.5 mmol) in THF (50 ml) was slowly added under argon atmosphere to the stirred suspension of Cr(CO)<sub>6</sub> (1.54 g, 7 mmol) or W(CO)<sub>6</sub> (2.46 g, 7 mmol) in THF (40 ml) at  $-78 \degree$ C. The mixture was allowed to warm to  $0 \degree$ C and kept at this temperature until all solid carbonyl dissolved (0.5 h). After cooling to  $-78 \,^{\circ}$ C a solution of the corresponding amide (7 mmol) in THF (10 ml) was added through a double-ended needle. The mixture was stirred at -78 °C for 30 min and then 30 min at 0 °C. After cooling to  $-78 \degree$ C, Me<sub>3</sub>SiCl (1.8 ml; 14 mmol) was added via a syringe. The solution was stirred at -78 °C for 30 min, then the cooling bath was removed, the mixture was allowed to warm to  $0 \,^{\circ}$ C and neutral alumina (8 g) was added. The solvent was removed under reduced pressure on a rotatory evaporator (bath temperature <30 °C) and the residue was dried for several hours under high vacuum to remove all the THF. Hexane (50 ml) was then added and the mixture was stirred vigorously for several minutes under argon atmosphere. The formed suspension was then transferred on top of a column filled with 50 g of silica. Naphthalene was eluted with pure hexane and further elution with a hexane-CH<sub>2</sub>Cl<sub>2</sub> mixture (5:1-2:1) gave the product.

#### Table 1

Overview of the studied compounds and Hammett's  $\rho$ -values of individual series.

Structure	R	Number	Synthesis [lit.]	E <sub>red</sub> slope analysis	E <sub>ox</sub> slope analysis
$\begin{array}{c} \begin{array}{c} CO & H_3C \\ CO & \\ R \end{array}$	-0CH <sub>3</sub> -CH <sub>3</sub> -H -Cl -CF <sub>3</sub>	la lb lc ld le	This work [4] [14] [4] This work	ρ = 0.344, R <sup>2</sup> = 0.957	ρ=0.082, R <sup>2</sup> =0.908
	-OCH3 -CH3 -H -Cl -CF3	lla llb llc lld lle	[6] [6] [17] [6] [6]	ρ = 0.224, R <sup>2</sup> = 0.925	ρ = 0.070, R <sup>2</sup> = 0.981
	-H	шс	This work	_	-
	щ	We	This work		
CO CO Fe CO CO R	-0CH <sub>3</sub> -CH <sub>3</sub> -H -Cl -CF <sub>3</sub>	Va Vb Vc Vd Ve	This work This work [16] This work This work	ρ = 0.334, R <sup>2</sup> = 0.976	$\rho = 0.069,$ $R^2 = 0.968$
CO Fe CO CO R	-OCH3 -CH3 -H -Cl -CF3	VIa VIb VIc VId VIe	This work This work [17] This work This work	$\rho = 0.255,$ $R^2 = 0.857$	ho = 0.044, $R^2 = 0.708$
$CO \subset CO H_3C$ $CO \subset CC R$ $CO \subset CO R$	-CH <sub>3</sub> -H -C <sub>6</sub> H <sub>5</sub>	VIIb VIIc VIIf=Ic	[14] This work [14]	$\rho = 1.990,$ $R^2 = 0.882$	ρ = 0.332, R <sup>2</sup> = 0.903
	-CH <sub>3</sub> -C <sub>6</sub> H <sub>5</sub>	VIIIb VIIIf = IIc	[19] [17]	-	-

#### Table 1 (Continued)



Data correlated to  $\sigma_i$  (see the text, Section 3.1).

#### 2.4.2. Pentacarbonyl[(N,N-dimethylamino)

(4-methoxyphenyl)methylene]chromium(0) (Ia)

Elution with hexane–CH<sub>2</sub>Cl<sub>2</sub> mixture (3:1) afforded **Ia** in 81% yield as yellow crystals. M.p. 44–45 °C, Ref. [15]: 47 °C. <sup>1</sup>H NMR:  $\delta$  3.04 (s, 3H; *anti*-NCH<sub>3</sub>), 3.81 (s, 3H; *syn*-NCH<sub>3</sub>), 3.98 (s, 3H; OCH<sub>3</sub>), 6.64 (d, *J* = 8.8 Hz, 2H; Ar–H), 6.91 (d, *J* = 8.5 Hz, 2H; Ar–H).

#### 2.4.3. Pentacarbonyl[(N,N-dimethylamino)

(4-trifluoromethylphenyl)methylene]chromium(0) (Ie)

Mixture of hexane–CH<sub>2</sub>Cl<sub>2</sub> (3:1) was used for the elution. Yellow crystals, yield 66%, M.p. 89–91 °C, Ref. [15]: 90 °C. <sup>1</sup>H NMR: δ 3.02 (s, 3H; *anti*-NCH<sub>3</sub>), 3.98 (s, 3H; *syn*-NCH<sub>3</sub>), 6.78 (d, J=8.0 Hz, 2H; Ar–H), 7.61 (d, J=8.0 Hz, 2H; Ar–H).

#### 2.4.4. Pentacarbonyl[(N,N-dimethylamino)

phenylmethylene]tungsten(0) (**IIIc**)

Elution with hexane–CH<sub>2</sub>Cl<sub>2</sub> mixture (5:1) gave **IIIc** in 62% yield as pale yellow crystals. M.p. 99 °C, Ref. [18]: 93–94 °C. <sup>1</sup>H NMR:  $\delta$  3.05 (s, 3H; NCH<sub>3</sub>), 3.94 (s, 3H; NCH<sub>3</sub>), 6.76 (d, *J* = 8.5 Hz, 2H; Ph–*H*), 7.16 (t, *J* = 15.0 Hz, 1H; Ph–*H*), 7.39 (t, *J* = 15.5 Hz, 2H; Ph–*H*).

## 2.4.5. Tetracarbonyl[( $\eta^2$ -N-allyl-N-allylamino) phenylmethylene]tungsten(0) (**IVc**)

The above method starting from 1.01 g (5 mmol) of *N*,*N*-diallylbenzamide afforded after elution with hexane– $CH_2CI_2$  mixture (5:1) crystalline pentacarbonyl[(*N*,*N*-diallylamino) phenylmethylene]tungsten(0) 0.9 g followed with desired **IVc** (0.081 g). Pentacarbonyl[(*N*,*N*-diallylamino)phenylmethylene] tungsten(0) was dissolved in toluene (10 ml) and the solution was refluxed under argon for 4 h. Chromatography on silica (30 g) in hexane– $CH_2CI_2$  5:1 gave another **IVc** (0.8 g, 33%) as yellow oil.

#### 2.4.5.1. Pentacarbonyl[(N,N-diallylamino)(phenyl)methylene]

*tungsten*(0). Yellow solid; M.p. 49–50 °C; <sup>1</sup>H NMR:  $\delta$  3.97 (d, *J*=5.5 Hz, 2H, NCH<sub>2</sub>), 4.88 (d, *J*=5.5 Hz, 2H, NCH<sub>2</sub>), 5.13 (dd, *J*=1.1, 17.0 Hz, 1H, =CHH), 5.30 (dd, *J*=1.1, 10.4 Hz, 1H, =CHH), 5.41 (dd, *J*=1.1, 17.0 Hz, 1H, =CHH), 5.49 (dd, *J*=1.1, 10.4 Hz, 1H, =CHH), 5.59 (m, 1H, =CH–), 6.02 (m, 1H, =CH–), 6.79 (m, 2H, Ph–H), 7.15 (m, 1H, Ph–H), 7.38 (m, 2H, Ph–H); <sup>13</sup>C NMR:  $\delta$  259.9 (W=C), 204.2 (CO), 198.2 (CO), 153.0 (C–Ph), 131.4 (–CH=), 131.0 (–CH=), 128.2 (CH–Ph), 126.3 (CH–Ph), 120.3 (=CH<sub>2</sub>), 119.8 (=CH<sub>2</sub>), 119.1 (CH–Ph), 64.1 (NCH<sub>2</sub>), 55.2 (NCH<sub>2</sub>); IR (CHCl<sub>3</sub>)  $\nu$  2063 (w), 1980 (w), 1929 (vs) cm<sup>-1</sup>. Anal. Calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>5</sub>W: C, 42.46; H, 2.97; N, 2.75. Found: C, 42.02; H, 2.80; N, 2.69.

2.4.5.2. Tetracarbonyl[( $\eta^2$ -N-allyl-N-allylamino)(phenyl)methylene] tungsten(0) (**IVc**). Yellow oil; <sup>1</sup>H NMR:  $\delta$  3.44 (d, *J*=8.2 Hz, 1H, chelated =CHH), 3.46 (d, *J*=13.2 Hz, 1H, chelated =CHH), 3.90 (m, 1H, chelated NCH<sub>2</sub> and 2H, NCH<sub>2</sub>), 4.56 (m, 1H, chelated =CH–), 4.77 (dd, *J*=4.9, 13.7 Hz, 1H, chelated NCH<sub>2</sub>), 5.20 (dd, *J*=1.1, 17.6 Hz, 1H, =CHH), 5.30 (dd, *J*=1.1, 10.4 Hz, 1H, =CHH), 5.67 (m, 1H, =CH–), 6.81 (brs, 2H, *o*-Ph–*H*), 7.20 (m, 1H, Ph–*H*), 7.37 (m, 2H, Ph–*H*); <sup>13</sup>C NMR:  $\delta$  263.6 (W=C,  $J_{WC}$  = 85 Hz), 210.7 ( $J_{WC}$  = 77 Hz, CO), 210.2 ( $J_{WC}$  = 64 Hz, CO), 203.0 ( $J_{WC}$  = 64 Hz, CO), 202.8 ( $J_{WC}$  = 62 Hz, CO), 149.2 (C–Ph), 131.2 (–CH=), 128.3 (CH–Ph), 126.8 (CH–Ph), 120.3 (CH–Ph), 119.9(=CH<sub>2</sub>), 70.1 (chelated –CH=), 62.8 (chelated NCH<sub>2</sub>), 59.1 (chelated =CH<sub>2</sub>), 56.1 (NCH<sub>2</sub>); IR (CHCl<sub>3</sub>)  $\nu$  2024 (s), 1926 (vs), 1904 (vs), 1516 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>17</sub>H<sub>15</sub>NO<sub>4</sub>W: C, 42.44; H, 3.14; N, 2.91. Found: C, 42.36; H, 3.09; N, 2.78.

#### 2.4.6. Pentacarbonyl[(N,N-dimethylamino)(2-methyl-4methoxyphenyl)methylene]chromium(0)(**IXa**)

General procedure starting from 0.56 g (3 mmol) of 2methyl-4-methoxy-*N*,*N*-dimethylbenzamide afforded elution with hexane–CH<sub>2</sub>Cl<sub>2</sub> mixture (5:1) **IXa** (0.34 g, 31%) in the form of yellow crystals. M.p. 79–82 °C; <sup>1</sup>H NMR:  $\delta$  2.03 (s, 3H; ArCH<sub>3</sub>), 3.02 (s, 3H; *anti*-NCH<sub>3</sub>), 3.80 (s, 3H; *syn*-NCH<sub>3</sub>), 3.99 (s, 3H; OCH<sub>3</sub>), 6.64 (d, *J* = 8.5 Hz, 1H; Ar–*H*), 6.69 (s, 1H; Ar–*H*), 6.78 (d, *J* = 10.9 Hz, 1H; Ar–*H*). <sup>13</sup>C NMR:  $\delta$  277.7 (C=Cr), 223.8 (CO), 217.3 (CO), 157.8 (C–Ar), 145.7 (C–Ar), 127.4 (C–Ar), 121.1 (CH–Ar), 115.9 (CH–Ar), 111.6 (CH–Ar), 55.7 (CH<sub>3</sub>–O), 51.1 (CH<sub>3</sub>–N), 45.1 (CH<sub>3</sub>–N), 19.1 (CH<sub>3</sub>–Ar). IR (KBr):  $\nu$  2052 (m), 1891 (s) cm<sup>-1</sup>.

## 2.4.7. Pentacarbonyl[(N,N-dimethylamino)(2-methylphenyl) methylene]chromium(0) (**IXc**)

The above procedure starting from 2-methyl-*N*,*N*-dimethylbenzamide (0.82 g, 5 mmol) furnished **IXc** (0.93 g, 55%) as yellow crystals.

M.p. >91 °C (decomp.); <sup>1</sup>H NMR:  $\delta$  2.07 (s, 3H, Ph–CH<sub>3</sub>), 3.04 (s, 3H, N–CH<sub>3</sub>), 4.01 (s, 3H, N–CH<sub>3</sub>), 6.71 (d, *J*=7.7 Hz, 1H, Ph–*H*), 7.05–7.17 (m, 2H, Ph–*H*), 7.22 (t, *J*=7.4 Hz, 1H, Ph–*H*). <sup>13</sup>C NMR:  $\delta$  276.5 (C=Cr), 223.2 (CO), 216.8 (CO), 151.6 (C–Ph), 130.6 (CH–Ph), 126.1 (CH–Ph), 126.0 (CH–Ph), 125.4 (C–Ph), 119.5 (CH–Ph), 51.0 (CH<sub>3</sub>–N), 45.2 (CH<sub>3</sub>–N), 18.8 (CH<sub>3</sub>–Ph).

IR (CHCl<sub>3</sub>):  $\nu$  2055, 1972, 1930, 1533, 1400 cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>13</sub>NO<sub>5</sub>Cr: C, 53.10; H, 3.86; N, 4.13. Found: C, 53.37; H, 3.94; N, 4.11.

#### 2.4.8. Pentacarbonyl[(N,N-dimethylamino)(2-methyl-4-

trifluoromethylphenyl)methylene] chromium(0) (IXe)

General procedure starting from 0.206 g (0.89 mmol) of *N*,*N*-dimethyl-2-methyl-4-(trifluoromethyl) benzamide 0.206 g (0.89 mmol) afforded after chromatography in hexane– $CH_2Cl_2$  mixture (5:1) **IXe** (0.07 g, 19%) as yellow solid.

<sup>1</sup>H NMR: 2.13 (s, 3H, CH<sub>3</sub>), 3.06 (s, 3H, NCH<sub>3</sub>), 4.04 (s, 3H, NCH<sub>3</sub>), 6.83 (d, J = 8.2 Hz, 1H, Ar–H), 7.44 (s, 1H, Ar–H), 7.51 (d, J = 8.8 Hz, 1H, Ar–H). <sup>13</sup>C NMR: 18.6 (CH<sub>3</sub>), 45.5 (NCH<sub>3</sub>), 51.08 (NCH<sub>3</sub>)120.1 (CAr), 123.2 (CAr), 123.9 (q, J = 271 Hz, CF<sub>3</sub>), 126.6 (CAr), 127.8 (CAr), 127.9 (q, J = 32 Hz, C–CF<sub>3</sub>), 154.0 (CAr), 216.8 (CO), 223.1 (CO), 275.2 (C=Cr).

For the preparation of iron aminocarbene complexes Va, Vb, Vd, Ve and VIa, the same general procedure described for the preparation of the chromium and tungsten aminocarbene complexes was used. After deposition on alumina and evaporation of the solvents the product was isolated by chromatography on neutral alumina (100 g). Naphthalene was eluted with pure hexane and further elution with a hexane– $CH_2Cl_2$  mixture (5:1–2:1) gave the product.

#### 2.4.9. Tetracarbonyl[(N,N-dimethylamino)(4methoxyphenyl)methyleneliron(0) (**Va**)

General procedure starting from 0.896 g (5 mmol) of 4methoxy-*N*,*N*-dimethylbenzamide gave after elution with hexane-CH<sub>2</sub>Cl<sub>2</sub> mixture (3:1) 0.33 g (20%) of **Va** as bright-yellow crystals.

M.p. 80–85 °C; <sup>1</sup>H NMR:  $\delta$  3.10 (s, 3H; *anti*-NCH<sub>3</sub>), 3.82 (s, 3H; *syn*-NCH<sub>3</sub>), 3.99 (s, 3H; OCH<sub>3</sub>), 6.78 (d, *J*=8.5 Hz, 2H; Ar–*H*), 6.90 (d, *J*=8.8 Hz, 2H; Ar–*H*). <sup>13</sup>C NMR:  $\delta$  260.4 (C=Cr), 215.0 (CO), 158.3 (C–Ar), 146.5 (C–Ar), 122.0 (CH–Ar), 113.9 (CH–Ar), 55.4 (CH<sub>3</sub>–O), 50.5 (CH<sub>3</sub>–N), 45.9 (CH<sub>3</sub>–N). IR (CHCl<sub>3</sub>):  $\nu$  2041 (m), 1966 (w), 1926 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>14</sub>H<sub>13</sub>FeNO<sub>5</sub>: C, 50.78; H, 3.96; N, 4.23. Found: C, 50.69; H, 3.98; N, 4.25.

#### 2.4.10. Tetracarbonyl[(N,N-dimethylamino)

(4-methylphenyl)methylene]iron(0) (**Vb**)

Elution with hexane– $CH_2Cl_2$  mixture (5:1) furnished **Vb** (0.76 g, 48%) as orange-yellow crystals.

M.p. >80 °C (decomp.); <sup>1</sup>H NMR:  $\delta$  2.35 (s, 3H; ArCH<sub>3</sub>), 3.09 (s, 3H; anti-NCH<sub>3</sub>), 3.99 (s, 3H; syn-NCH<sub>3</sub>), 6.73 (d, *J* = 7.9 Hz, 2H; Ar–*H*), 7.18 (d, *J* = 7.9 Hz, 2H; Ar–*H*). IR (CHCl<sub>3</sub>):  $\nu$  2041 (m), 1966 (w), 1925 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>14</sub>H<sub>13</sub>FeNO<sub>4</sub>: C, 53.36; H, 4.16; N, 4.45. Found: C, 53.69; H, 3.99; N, 4.39.

#### 2.4.11. Tetracarbonyl[(N,N-dimethylamino)

(4-chlorophenyl)methylene]iron(0) (**Vd**)

Elution with hexane–CH<sub>2</sub>Cl<sub>2</sub> mixture (4:1) furnished **Vd** (0.60 g, 36%) as yellow crystals. M.p. >110 °C (decomp.); <sup>1</sup>H NMR:  $\delta$  3.11 (s, 3H; *anti*-NCH<sub>3</sub>), 4.00 (s, 3H; *syn*-NCH<sub>3</sub>), 6.79 (d, *J* = 8.2 Hz, 2H; Ar–*H*), 7.36 (d, *J* = 8.5 Hz, 2H; Ar–*H*). <sup>13</sup>C NMR:  $\delta$  259.5 (C=Cr), 214.6 (CO), 151.2 (C–Ar), 132.6 (C–Ar), 129.0 (CH-Ar), 121.8 (CH-Ar), 50.6 (CH<sub>3</sub>-N), 46.2 (CH<sub>3</sub>–N). IR (CHCl<sub>3</sub>):  $\nu$  2044 (m), 1969 (w), 1930 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>13</sub>H<sub>10</sub>CIFeNO<sub>4</sub>: C, 46.54; H, 3.00; N, 4.17. Found: C, 46.32; H, 2.91; N, 4.19.

#### 2.4.12. Tetracarbonyl[(N,N-dimethylamino)

(4-trifluoromethylphenyl)methylene]iron(0) (**Ve**)

Elution with hexane– $CH_2Cl_2$  mixture (3:1) furnished **Ve** (0.76 g, 41%) as bright-yellow crystals.

M.p. 98–100 °C; <sup>1</sup>H NMR:  $\delta$  3.12 (s, 3H; *anti*-NCH<sub>3</sub>), 4.03 (s, 3H; *syn*-NCH<sub>3</sub>), 6.96 (d, *J*=8.2 Hz, 2H; Ar–H), 7.65 (d, *J*=7.9 Hz, 2H; Ar–H). <sup>13</sup>C NMR:  $\delta$  259.1 (C=Cr), 214,4 (CO), 155.4 (C–Ar), 129.4 (C–Ar), 126.0 (CH–Ar), 120.7 (CH–Ar), 50.5 (CH<sub>3</sub>–N), 46.4 (CH<sub>3</sub>–N). IR (CHCl<sub>3</sub>):  $\nu$  2045 (m), 1971 (w), 1932 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>14</sub>H<sub>10</sub>F<sub>3</sub>FeNO<sub>4</sub>: C, 45.56; H, 2.73; N, 3.80. Found: C, 45.58; H, 2.59; N, 3.60.

## 2.4.13. Tricarbonyl[ $(\eta^2$ -N-allyl-N-allylamino) (4-methoxyphenyl)methylene]iron(0) (**VIa**)

General procedure starting from 0.81 g (3.5 mmol) of 4methoxy-*N*,*N*-diallylbenzamide gave after elution with hexane– CH<sub>2</sub>Cl<sub>2</sub> mixture (4:1) 0.33 g (26%) of **VIa** as a brown oil.

<sup>1</sup>H NMR:  $\delta$  1.48 (d, J = 10.4 Hz, 1H, chelated = $CH_2$ ), 2.01 (d, J = 7.7 Hz, 1H, chelated = $CH_2$ ), 3.18 (m, 1H, chelated -CH=), 3.75 (dd, J = 15.1, 6.0 Hz, 1H, NCH<sub>2</sub>), 3.81 (s, 1H, OCH<sub>3</sub>), 3.89 (dd, J = 15.1, 5.8 Hz, 1H, NCH<sub>2</sub>), 4.14 (dd, J = 14.3, 5.2 Hz, 1H, chelated NCH<sub>2</sub>), 4.35 (dd, J = 14.0, 0.8 Hz, 1H, chelated NCH<sub>2</sub>), 5.15 (dd, J = 17.0, 1.0 Hz, 1H, = $CH_2$ ), 5.24 (dd, J = 10.3, 1.0 Hz, 1H, = $CH_2$ ), 5.52–5.66 (m, 1H, -CH=), 5.75–5.95 (m, 4H, H–Ar).

#### 2.4.14. Tricarbonyl[( $\eta^2$ -N-allyl-N-allylamino)

#### (4-methylphenyl)methylene]iron(0) (VIb)

General procedure starting from 0.86 g (4.0 mmol) of 4-methyl-N,N-diallylbenzamide gave after elution with hexane-CH<sub>2</sub>Cl<sub>2</sub> mixture (2:1) 0.44 g (32%) of **VIb** as a yellow oil.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.56 (d, J = 10.5 Hz, 1H, =CH<sub>2</sub>), 2.04 (d, J = 7.8 Hz, 1H, =CH<sub>2</sub>), 2.36 (s, 3H, CH<sub>3</sub>), 3.20 (m, 1H, -CH=), 3.76 (dd, J = 6.0 Hz, J = 15.0 Hz, 1H, NCH<sub>2</sub>), 3.88 (dd, J = 6.0 Hz, J = 15.0 Hz, 1H, NCH<sub>2</sub>), 4.17 (dd, J = 5.1 Hz, J = 14.4 Hz, 1H, NCH<sub>2</sub>), 4.35 (d, J = 14.4 Hz, 1H, NCH<sub>2</sub>), 5.17 (d, J = 17.1 Hz, 1H, =CH<sub>2</sub>), 5.26 (d, J = 10.5 Hz, 1H, =CH<sub>2</sub>), 5.55 (m, 1H, -CH=), 6.78 (brs, 2H, ArH), 7.18 (d, J = 8.1 Hz, 2H, ArH).

## 2.4.15. Tricarbonyl[ $(\eta^2$ -N-allyl-N-allylamino)(4-chlorophenyl) methylene]iron(0) (**VId**)

General procedure starting from 0.95 g (4.0 mmol) of 4-chloro-*N*,*N*-diallylbenzamide gave after elution with hexane-CH<sub>2</sub>Cl<sub>2</sub> mixture (4:1) 0.60 g (42%) of **VIb** as a yellow oil.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.48 (d, J = 10.5 Hz, 1H, =CH<sub>2</sub>), 2.04 (d, J = 9.0 Hz, 1H, CH<sub>2</sub>), 3.20 (m, 1H, -CH=), 3.74 (dd, J = 6.0 Hz, J = 15.0 Hz, 1H, NCH<sub>2</sub>), 3.84 (dd, J = 6.0 Hz, J = 15.0 Hz, 1H, NCH<sub>2</sub>), 4.16 (dd, J = 4.8 Hz, J = 14.4 Hz, 1H, CH<sub>2</sub>), 4.33 (d, J = 14.4 Hz, 1H, CH<sub>2</sub>), 5.15 (d, J = 16.8 Hz, 1H, =CH<sub>2</sub>), 5.26 (d, J = 10.2 Hz, 1H, =CH<sub>2</sub>), 5.55 (m, 1H, -CH=), 6.80 (brs, 2H, ArH), 7.33 (d, J = 8.1 Hz, 2H, ArH).

#### 3. Results and discussion

#### 3.1. General approach

The presented new iron and tungsten complexes together with the previously reported series of aminocarbene complexes of chromium [4] form a "multidimensional" set of analogous compounds (cf. Table 1). This extension enabled more complex evaluation of structural influences in various types of Fischer aminocarbene complexes.

- (1) The series **I** and **II** were correlated with analogous tungsten complexes **III** and **IV** to evaluate parallels within Group 6 metals behaviour.
- (2) The series **I** and **II** were correlated with analogous iron complexes **V** and **VI** to compare complexes with the same ligands but different central atom and different coordination number.
- (3) The effect of the presence/absence of the chelate ring will be followed using comparison between the non-chelates I, V and VIIb on one side and corresponding chelates II, VI and VIIIb on the other side.
- (4) The ρ-value of the small series of the ortho-phenylsubstituted chromium non-chelates IXa, c, e will be compared with those



Fig. 1. Electrochemical reduction of Cr and W complexes.

of the series **I** and **II** to follow the correlation between the ease of phenyl ring rotation and influence of its *p*-substituent on the reduction potential.

(5) The non-chelate compounds VII substituted directly at the carbene carbon represent another small series where the influence of substitution is to be followed.

First, the complete set of electrochemical data was measured using dc-polarography and cyclic voltammetry on Pt and Hg stationary electrodes and fundamental reduction and oxidation properties of all studied compounds were characterized. The reduction proceeds as a two-electron irreversible process around -2 V on both electrode materials, the oxidation is manifested as a one electron, reversible couple at the cyclic voltammogram on platinum electrode [4].

According to the LFER approach [5], the value of the slope  $\rho$  (reaction constant) in the equation:

$$E_{\text{ox(red)}} = \rho \cdot \sigma_{\text{p}}(\sigma_{\text{i}}) + \sigma_{\text{p}$$

reflects the extent of electronic communication between the substituent and the reduction (oxidation) center, whereas the constant  $\sigma_{\rm p}$  characterizes the sum of induction and resonance effects of the substituent in the *p*-position on phenyl ring; eventually, for series **VII** and **VIII** only, the constant  $\sigma_{\rm i}$  characterizes the induction effect of the directly bonded substituent. From the linearity of the correlation  $E_{\rm red}$  (or  $E_{\rm ox}$ ) of all involved derivatives vs. the corresponding  $\sigma_{\rm p}$  ( $\sigma_{\rm i}$ ) values follows, that in the frame of the studied series the same reduction (oxidation) mechanism occurs, the reduction (oxidation) centers remain unchanged and the structure of all starting derivatives as well as intermediates is analogous. Any potential value non-fitting the linear dependence points to a different behaviour of the respective molecule, which means different localization of redox center, or different electron displacement and thus different mechanism.

On the other hand, the  $\rho$ -values reflect the extent of the intramolecular interaction within the molecule, i.e. electronic "conductivity" of the molecular bridge. Every difference in  $\rho$ -values requires explanation on the basis of the structure and electron delocalization.

#### 3.2. Reduction

#### 3.2.1. Reduction of Cr and W complexes

There are five general types of chromium complexes to be discussed: the non-chelates with p-substituted phenyl – type I [(CO)<sub>5</sub>Cr=C{N(CH<sub>3</sub>)<sub>2</sub>}(C<sub>6</sub>H<sub>4</sub>-*p*-R)], the analogous chelates – type II [(CO)<sub>4</sub>Cr=C{N(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>}(C<sub>6</sub>H<sub>4</sub>-*p*-R)], the directly substituted non-chelates – type VII [(CO)<sub>5</sub>Cr=C{N(CH<sub>3</sub>)<sub>2</sub>}R], the analogous chelate VIIIb and the non-chelates with o-Me-p-substituted phenyl – type IX [(CO)<sub>5</sub>Cr=C{N(CH<sub>3</sub>)<sub>2</sub>}(C<sub>6</sub>H<sub>3</sub>-*o*-CH<sub>3</sub>-*p*-R)]. All of them have coordination number six. In molecules of the type II and VIII one of the allylic groups is coordinated to the central metal atom, the chelate ring is formed and, hence, the number of CO ligands is lower by one compared with the types I and VII.

Difference between reduction potentials of series **I** and **II** (chromium non-chelates and chelates, cf. Fig. 1) is very small. On the other hand, there is a remarkable feature concerning their slopes  $\rho$ : the slope of the non-chelated carbenes is higher than that of chelates and both lines cross at the  $\sigma_p$  value equal to zero. This effect was attributed to the lower electronic communication between the para-phenyl substituent and the carbene reduction center in chelates, caused by sterically hindered rotation along the carbene–phenyl C–C bond.

To support this explanation, the series **IX** was synthesized and electrochemically investigated. In this non-chelated series, the

additional methyl group in the *o*-position on the phenyl should also sterically hinder the rotation. In comparison with the analogous series **I**, lower value of the reaction constant was really found. Moreover, it follows from NMR results that for the series **IX** the rotation along the carbene–phenyl C–C bond is blocked and the *ortho*-methylated derivatives are split into two isolable enantiomeres [20] (cf. Table 1; Fig. 1).

According to expectation, the reduction potentials of compounds **IXa,c,e** are in all cases shifted more negatively when comparing with the analogous non-*o*-methylated compounds **Ia,c,e** due to the electron pushing effect of the additional methyl substituent.

Slope  $\rho$  of the Hammett equation gives us a good possibility of experimental observation and evaluation of the electronic communication (depending on the extent of electron delocalization and the distance) between the substituent and the reaction center.

Similarly to the series I and II, in the case of series VII and VIII the difference in potentials between the chelated and analogous nonchelated derivatives is again very small. The dramatic difference, however, was found in the reaction constants  $\rho$ : in the series VII and VIII where the substituent is bonded directly (=closer) to the carbene carbon atom, the Hammett's slope is about 5–6 times higher than in the series I, II or IX. This finding shows that the direct substitution of the reduction center has here an extreme influence on the reduction potential of the whole molecule. This result should be very valuable namely for the design of new generations of carbene complexes and for "tailoring" of their properties.

The investigation of the couple of tungsten complexes – the non-chelate **IIIc** (analogue to **Ic**) and the corresponding chelate **IVc** (analogue to **IIc**) offers a comparison within the Group 6 metals. The tungsten complexes are reduced slightly (about 30-50 mV) less negatively (more easily) than the analogous chromium ones. This fact is in accordance with the higher polarizability of tungsten compared with chromium. When comparing the tungsten chelate and non-chelate compounds, their reduction potentials are also very close to each other like in the case of chromium complexes.

It is possible to conclude (e.g. for the eventual design of new analogues and prediction of their properties) that the reduction potential depends strongly on the substitution of the carbene carbon, in the case of the free rotation along the carbene–phenyl C–C bond, the substitution in the *para*-position on the phenyl ring plays a role, too. On the other hand, the reduction potentials are not substantially affected by the presence of chelating allylic substituent, hence an influence of the nitrogen substitution and the number of CO ligands is negligible. Also the change of the central metal atom (within the Group 6) plays only a minor role.

3.2.1.1. Comparison of aminocarbene and alkoxycarbene complexes. The above measurements permit also a comparison of two types of Fischer carbene complexes with different stabilizing heteroatom: the aminocarbene (data from Fig. 1; Table 1) and alkoxycarbene complexes of Cr and W (data published in [21]), whose reduction potentials were measured by CV under similar conditions (in non-aqueous acetonitrile, vs. SCE).

Replacement of dimethylaminogroup by methoxygroup facilitates reduction of the compounds very strongly – the reduction potentials are shifted positively by about 600 mV as the carbene carbon atom becomes more positively charged when bonded to a more electronegative atom of oxygen. Coming from chromium methoxycarbenes to tungsten ones, reduction becomes easier by several tens of mV, like in the case of aminocarbenes. Some new alkoxycarbenes consisting of four chromium and/or tungsten units attached to macrocyclic ligands were synthesized and their CV was measured [22]. Also here, the reduction potential was found to be some 60–70 mV more positive for tungsten compounds compar-



Fig. 2. Comparison of reduction potentials of the Fe chelates and non-chelates with those of the analogous Cr derivatives.

ing with their chromium analogues in accordance with the higher polarizability of tungsten.

Similarly, the influence of the substituent in para-position of the phenyl ring attached to the carbene carbon on reduction potentials is comparable: For  $[(CO)_5Cr=C(OCH_3)(C_6H_5)]$  complex **I**\*c (analogous to **Ic**),  $E_{1/2} = -1.34$  V was found, for  $[(CO)_5Cr=C(OCH_3)(C_6H_4-p-CH_3)]$  complex **I**\*b (analogous to **Ib**),  $E_{1/2} = -1.37$  V. This difference of 30 mV corresponds well with the 45 mV difference between **Ic** and **Ib** reduction potentials.

#### 3.2.2. Reduction of iron compounds

Two series of new iron aminocarbene complexes were synthesized: the non-chelates with p-substituted phenyl – type **V** [(CO)<sub>4</sub>Fe=C{N(CH<sub>3</sub>)<sub>2</sub>}(C<sub>6</sub>H<sub>4</sub>-*p*-R)], which is similar to the chromium series **I**, and the analogous chelates – type **VI** [(CO)<sub>3</sub>Fe=C{N(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>}(C<sub>6</sub>H<sub>4</sub>-*p*-R)], which corresponds to the chromium series **II**. All iron complexes have the coordination number five. In molecules of the type **VI**, one of the allylic groups is coordinated to the central metal atom, the chelate ring is formed and, hence, the number of CO ligands is lower by one (like in the chromium series **II**).

The iron aminocarbene complexes were investigated electrochemically in order to characterize the new compounds and to compare their redox and other properties with the above investigated chromium and tungsten analogues of the type **I**, **II**, **III** and **IV** (Fig. 2).

From the linearity of the  $E_{1/2}$  vs.  $\sigma_p$  dependence it is evident that the reduction mechanism of all studied iron derivatives is the same, analogously to the chromium compounds. Even in this case, the reduction center is located at the carbene moiety since the reduction potential is substantially affected by the substitution on the phenyl ring according to the LFER and the slopes ( $\rho$ -values) are approximately the same for series **V** and **I**. As in the case of chromium compounds, the slope of chelated iron aminocarbenes **VI** is lower than that for the non-chelated ones (**V**). In contrast to the chromium analogues, however, the reduction of chelated iron aminocarbene complexes (type **VI**) is by 120 mV more difficult than that of non-chelated type **V**. This fact will be discussed later together with the general comparison of iron and chromium analogues.

#### 3.3. Oxidation

#### 3.3.1. Oxidation of Cr and W complexes

According to the Hammett plots shown in Fig. 3, the slopes of the  $E_{\text{ox}} = \rho \cdot \sigma_p$  dependence are very low, hence the oxidation potentials



Fig. 3. Electrochemical oxidation of Cr and W complexes.

of chromium chelates (series I) as well as non-chelates (series II) depend only very slightly on the carbene carbon substitution. In the case of the directly substituted chromium carbenes **VII** and **VIII** the  $\rho$ -value is about 5 times higher, but still by about one order of magnitude lower then the  $\rho$ -value of their reduction plot ( $\rho_{red} = 1.99$ ;  $\rho_{ox} = 0.33$ ).

On the other hand, it is remarkable that the chelates (chromium series **II** and tungsten complex **IVc**) are oxidized 300–400 mV less positively (much more easily) than the corresponding non-chelates (**I** and **III**). The reason is that the oxidation potential depends on the number of carbonyl ligands. Since CO groups have strong  $\pi$ -acceptor properties, they lower the electron density on the metal atom and make its oxidation more difficult. In the chelates, one electron withdrawing carbonyl is replaced by one allyl ligand without pronounced  $\pi$ -acceptor properties; therefore, the oxidation of chelates is significantly easier.

Accordingly, the oxidation of Type I and Type VII complexes, which have the same central atom and the same number of CO ligands, proceeds at mutually close  $E_{ox}$  values. The  $E_{ox}$  values found for both Type II and Type VIII chelated compounds are also close one to another but again, both of them are lower by about 300 mV comparing with I and VII.

Fig. 3 shows another important feature: the oxidation potentials depend strongly on the central metal atom: Tungsten complexes are oxidized about 200 mV more positively (oxidation is more difficult) than their chromium analogues. This fact is in accordance with the easier reduction of the tungsten complexes and is related again to the higher polarizability of tungsten compared with chromium. This is in accordance with the fact that the oxidation center of the whole aminocarbene complex is the metal atom.

The above-described relationships between the structure and redox properties of aminocarbenes seem to be more general. Recently, a work has been published [3] dealing a.o. with electrochemical oxidation of some tungsten and chromium aminocarbene complexes. Even if the structure of compounds, the electrochemical conditions and the aim of the paper were different, their data fit well with our findings mentioned above:

- (1) The compounds  $[(CO)_5Cr=C(H)N(CH_2Ph)_2]$  and  $[(CO)_5Cr=C(CH_3)N(CH_2Ph)_2]$  are analogous to our **VIIc** and **VIIb** and their respective  $E_{ox} + 0.419$  V and + 0.401 V vs. Fc<sup>+</sup>/Fc correspond exactly to  $E_{ox}$  (**VIIc**) = +0.819 V and  $E_{ox}$  (**VIIb**) = +0.800 V vs. SCE.
- (2) For chromium complexes bearing a side chain with chelating group, decrease of the number of CO groups by one leads to lowering of the oxidation potential by 0.33 V (cf. approx. 0.35 V difference between Type I and II.)



Fig. 4. Comparison of the oxidation potentials of the Fe chelates and non-chelates with those of the analogous Cr derivatives.

(3) Two couples of analogous chromium and tungsten complexes were measured. Like in our work, oxidation of tungsten derivatives is always more difficult, ΔE (Cr–W) was 0.11 V and 0.09 V, while we have found ΔE (IC–IIIC) 0.18 V.

#### 3.3.2. Oxidation of iron compounds

The oxidation potentials of iron complexes (series **V** and **VI**) depend only very slightly on the substituent R, the slopes of the  $E_{\text{ox}} = \rho \cdot \sigma_p$  dependence are very low and the  $\rho$ -values are very close to those of analogous chromium complexes **I** and **II** (Fig. 4).

The oxidation potentials of chelated (series **VI**) as well as nonchelated (series **V**) derivatives are less positive than in the case of chromium or tungsten complexes. This finding reflects the fact that iron is more electron-rich metal with higher number of valence electrons and, in addition to this, the number of carbonyl ligands is lower by one.

What is, however, surprising, is the fact that the oxidation of iron chelates and non-chelates proceeds in the same potential region. Moreover, the non-chelates are oxidized even slightly more easily than the chelates, although the chelates bear one CO ligand less (in chromium or tungsten complexes, the difference between the chelate and non-chelate oxidation potentials is very high: about 350 mV, cf. Fig. 4).

These significant differences in redox properties between analogous chromium (or tungsten) and iron aminocarbene complexes will be dicussed in the following section.

#### 3.4. Difference Cr-Fe

Let us summarize the observed differences.

The reduction of chelated iron aminocarbene complexes (type **VI**) is by 120 mV more difficult than that of non-chelated type **V**, whereas the chromium chelates (**II**) and non-chelates (**I**) are reduced in the same potential region (cf. Fig. 2).

The oxidation of iron chelates **VI** and non-chelates **V** proceeds in the same potential region, moreover, the chelates are oxidized even by tens mV more difficultly than the non-chelates, whereas the chromium chelates **II** are oxidized much more easily (by 350 mV) than chromium non-chelates **I** (cf. Fig. 4). The explanation should start with a deeper consideration involving structural aspects and electronic properties of Fischer carbene complexes as well as coordination abilities of ligands. The main feature of Fischer carbene complexes is that the electron withdrawing CO ligands lower the electron density at the central metal atom. The formally double bond between the carbene carbon and metal is polarized towards the metal atom, charging the carbene carbon positively (therefore the Fischer carbenes are called "electron-poor carbene is stabilized by the non-bonding electron pair from the donating heteroatom (nitrogen or oxygen), giving rise to a higher bond order between the carbene carbon and the group **X**, according to the mesomeric expectations (Scheme 1).

Both divergences mentioned above originate in the different properties of the central metal atom. Chromium has coordination number six, iron has coordination number five and two more *d*electrons. Size of the both metals is about the same (single bonded metallic radii of Cr and Fe are 119 pm and 117 pm, respectively).

It follows that in the coordination sphere of chromium some intramolecular repulsion among ligands exists and hence the metal–ligand bond lengths are expected to be longer that in the 5-membered coordination sphere of iron. This premise is supported by the structural data published in [23] for a binuclear aminocarbene complex (CO)<sub>5</sub>Cr=C(NMe<sub>2</sub>)–C<sub>6</sub>H<sub>4</sub>–(NMe<sub>2</sub>)C=Fe(CO)<sub>4</sub>. In this compound, an average distance Cr–CO was 188 pm, Fe–CO 178 pm; length of the metal–carbene carbon bond was 215 pm for Cr=C and 200 pm for Fe=C. This metal–carbene carbon bond variation is supported by DFT calculations. Cr=C and Fe=C bond lengths of 213.4 pm and 198.5 pm were calculated for the non-chelate complexes **Ic** and **Vic** gave Cr=C and Fe=C bond lengths of 208.6 pm and 195.8 pm, respectively.

Thus in chromium complexes the distances Cr-ligand are relatively long, an overlap of  $\pi$ -orbitals is not deep enough and the back donation Cr  $\rightarrow$  C is negligible. Therefore,

- (a) the reduction center (most probably the C=N double bond) is affected neither by the number of CO ligands at the chromium atom nor by the coordinated allyl group. Hence, the reduction of chromium chelates and non-chelates proceeds in the same region of potentials;
- (b) the oxidation center (chromium atom) is isolated, therefore the lower number of CO ligands as well as the replacement of one CO ligand by the allyl influences substantially the oxidation potential. Hence, the oxidation of chromium chelates and non-chelates differ by about 350 mV.

In iron complexes the metal–ligand distances are shorter and the orbital overlap between them is more important. Under these circumstances, importance of the overlap of  $\pi$ -orbitals grows up and increased back donation is observed not only to CO ligands (chromium carbenes I show  $\nu$ (CO) at 2054 cm<sup>-1</sup>, whereas for iron carbenes V the vibration is shifted down to 2041 cm<sup>-1</sup>) but also to carbene carbon and to the  $\pi$ -antibonding orbitals of the allyl group. Simultaneously, better  $\sigma$ -donation from allyl to iron occurs, making thus the electron density at the metal even higher. Therefore

(a) due to the Fe  $\rightarrow$  C back donation, the reduction center (carbene carbon or the C=N bond) is influenced. Hence, the reduction potentials of the iron chelate derivatives (**VI**) are slightly more

 $(CO)_{n} M=C(R)-X: \leftrightarrow (CO)_{n} {}^{(\circ)} M-C {}^{(+)}(R)-X: \leftrightarrow (CO)_{n} {}^{(\circ)} M-C(R)=X {}^{(+)}$ electrophile

Scheme 1. X = NR<sub>2</sub>, O-Alk.



Fig. 5. The visualization of FMOs for chromium and iron complexes:.

#### Table 2

The contributions (%) of individual fragments to FMOs.

		М	CO <sub>total</sub>	C <sub>carb</sub>	Ν	$R_1^{a}$	R <sub>2</sub>	Ph	
lc	LUMO HOMO	5 56	16 36	51 2	17 0	3 0	3 0	6 5	
llc	LUMO HOMO	5 59	9 30	42 2	14 0	4 7 <sup>b</sup>	5 0	20 2	
Vc	LUMO HOMO	9 54	5 40	54 2	18 0	3 2	3 0	8 2	
VIc	LUMO HOMO	8 43	4 17	37 1	13 2	4 35 <sup>b</sup>	5 0	28 2	

 $R_1 = R_2 = CH_3$  for Ic and Vc.  $R_1 = R_2 =$  allyl for IIc and VIc.

<sup>a</sup> The substituent on N closer to the metal atom.

<sup>b</sup> Chelated allyl.

negative (by 120 mV) than the non-chelates (**V**), where the higher number of CO ligands makes the reduction easier.

(b) considering the oxidation center, two contradictional effects can be followed: The presence of the donating allyl in chelates together with the absence of one CO ligand should make the oxidation easier; however, the strong  $Fe \rightarrow C$  back donation (proved by the mentioned reduction behaviour) is able to compensate partially the above effect. Moreover, allylic group itself, situated in very proximity of iron, can act as a  $\pi$ -acidic group and take some electron density off. An additional support for this explanation is given by <sup>1</sup>H NMR spectra of the complexes: chemical shift  $\delta$  of the chelated  $-CH=CH_2$  group is 3.22 for chromium chelates (II), whereas for iron chelates it is only 1.52, due to a partial shielding by increased electron density. As a result, the oxidation potentials of iron chelates and nonchelates are very similar. The attempts of interpretation of experimental data should be, however, supported by quantum chemical calculations.

#### 3.5. DFT calculations

### 3.5.1. Localization of HOMO and LUMO. The role of the allylic chelating ligand

Quantum chemical calculations were performed in order to characterize redox orbitals and to prove and refine the interpretation of experiments. Fig. 5 depicts the displacement of HOMO and LUMO orbitals and Table 2 provides the percentage of composing fragments in these frontier orbitals (FMOs).

From Fig. 5 and Table 2 it is evident that the oxidation center (HOMO orbital) in chromium and iron non-chelate and chelate complexes is preferably localized on the metal center and on carbonyl ligands. On the other hand, in the chelates, the allyl ligand is always involved in the HOMO orbital. Whereas in chromium complexes the participation of allyl is rather small (7%), in iron derivatives allyl participates substantially (35%), with pronounced  $\pi$ -acidic behaviour, as we have discussed based on experimental results. Consequently, the metal contribution (43%) to HOMO is lower than in chromium complexes.

Fig. 5 and Table 2 confirm that the center of reduction (LUMO orbital) in chromium and iron non-chelate complexes (**Ic** and **Vc**, respectively) is localized prevalently on the carbon and nitrogen atoms. This fact demonstrates that among the mesomeric forms of Fischer electrophilic aminocarbene complexes (Scheme 1) the imine form with the formal C=N double bond prevails and is reduced. It is important to note that in non-chelates the phenyl ring attached to the carbene carbon is involved neither in LUMO, nor in HOMO. On the other hand, in the chelates, namely with iron (**VIc**), the LUMO orbital is more spread over the molecule with contributing  $\pi$  orbitals of the phenyl ring.

Calculations also indicate that the reduction of the chelates should be more sensitive to substitution on the phenyl group than in the case of the non-chelates.

#### 4. Conclusions

For purposes of this study, 30 different aminocarbenes were synthesized and their reduction and oxidation potentials were determined in aprotic media. Based on such a large choice of carbene complexes it was possible to correlate the measured electrochemical data with single structural aspects and to compare mutually the results for various homologous series of compounds (Cr–W–Fe as central atoms, chelated or non-chelated complexes, pphenyl ring substitution or direct carbene carbon substitution). We looked for analogies and discrepancies in order to explain the reasons for observed differences, to describe the relationship between the structure and redox properties in the Fischer aminocarbene complexes and to find general rules enabling reliable prediction of behavior of eventual further generations of carbene catalysts.

Experimental data were treated by the LFER approach in order to evaluate extent of the electronic communication in the molecules and to compare relative significance of various effects.

It was found that the reduction potential is very strongly influenced by the direct substituents on the carbene carbon (series **VII**, **VIII**). In the case of the aminocarbenes with aryl substituents (types I, II, II, IV, V, VI and IX), the substitution on this phenyl ring in *para*-position influences reduction potentials significantly.

The values of the oxidation potentials depend on the nature of the central atom and on the number of  $\pi$ -acidic ligands in its coordination sphere and they are nearly insensitive to the carbene carbon substitution. For Cr and W compounds, a straightforward correlation between number of CO ligands and oxidation potential holds: loss of one carbonyl group makes the oxidation by approx. 0.35 V easier – less positive.

The difference between electronic structure of iron and chromium aminocarbenes is reflected namely in the role of chelating allyl and in the extent of the metal-carbene or metal-allyl back donation. The complexes of the Group 6 metals (Cr and W) have their oxidation and reduction centers separated, presence of the allyl plays a negligible role and this back donation is small, too.

In the pentacoordinated iron complexes, however, the bond length metal–ligand is shorter than in the hexacoordinated Cr or W molecules. Hence, better orbital overlap causes increasing of some  $\pi$ -acidic character of the allylic and carbene ligands. Consequently, reduction of iron chelates is more difficult then reduction of non-chelates (carbene moiety becomes more electron rich), and the more easy oxidation of iron chelates shows the ability of the allyl and carbene groups to compensate the missing carbonyl ligand. The existence of Fe  $\rightarrow$  allyl back donation is supported by <sup>1</sup>H NMR data. It is possible to consider the  $\pi$ -acidity of allylic and carbene ligands to be not a constant property of the ligands but rather a property displayed with respect to a given metal.

As a support for the above discussion and for the interpretation of the electrochemical data and their LFER treatment DFT calculations were utilized.

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