Substituent effect in *para* substituted Cr(CO)₅–pyridine complexes

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This work is dedicated to Professor Sławomir J. Grabowski on the occasion of his 50th birthday.

Abstract

Systematic studies on the substituent effect in *para* substituted Cr(CO)₅–pyridine complexes have been carried out on the basis of DFT quantum-chemical calculations. Ten simple and mostly common substituents were chosen in order to analyze possibly the largest spectrum of substituent effects. The following substituents were taken into consideration: NO, NO₂, CN, CHO, F, H, CH₃, OCH₃, OH and NH₂. Additionally, the Cr–N and Cr–C bonds were characterized on the basis of *Atoms in Molecules* topological analysis of electron density. It has been found that the substituents in position 4 of the pyridine ring influence the Cr–N bond of Cr(CO)₅–pyridine complex in a systematic manner, as a result of with, the pyridine moiety has a diversified ability of participating in the interaction with the Cr atom of Cr(CO)₅ moiety. It has also been found, that the electron withdrawing substituents additionally stabilize the Cr–N bond, whereas the electron donating ones weaken it. The substituent effect mainly affects the π-component of the Cr–N bond. This effect proceeds in the whole Cr–pyridine–R moiety, and it is additionally reflected in the corresponding changes in metal–carbonyl bonds, particularly the *trans* Cr–CO bond.
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1. Introduction

The chemistry of M(CO)₅–L transition metal complexes is thoroughly explored because of unique properties of the compounds belonging to this organometallic species. This kind of compounds are used in industry as important homogeneous and heterogeneous catalysts [1]. The photochemistry of M(CO)₅–L complexes (M = Cr, Mo, W) was recognized and characterized in the early 70s of the previous century [2]. Moreover, these compounds were found to exhibit non-linear optical properties [3]. Processes of displacement of coordinated N₂ by H₂ in unstable compounds using low-temperature/high-pressure techniques were also investigated for the M(CO)₅–L (M = Cr, Mo, W) complexes [4]. The M(CO)₅–L derivatives are the attractive model systems for many investigations carried out by

means of quantum-chemistry modeling. For instance, the systematic M–L bond characterization in M(CO)₅–L, where M = Cr, Mo, W and L were different simple ligands, was carried out using computational methods [5].

It is well known that the introduction of a substituent into the suitable position of the molecule of a given chemical compound results in changes in chemical and physical properties of this compound [6]. Thus, the controlled substitution is a commonly used tool in the synthesis of chemical compounds having specified properties. An excellent example from the field of chemistry of the M(CO)₅–L compounds can be a case of the W(CO)₅–L complexes, where L is a pyridine-type nitrogen [7]. It was found that electronic excitation of such complexes leads to ligand field or metal-to-ligand charge transfer excited states. The latter becomes the lowest excited state when the pyridine ligand bears the electron-withdrawing substituents in position 4. Another example of substituent effect analysis in related organometallic species that can be mentioned here is the systematic

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analysis of different reactivities of Fisher and Schrock $Cr(CO)_5$–L carbine complexes [8].

Pyridine belongs to a group of typical heterocyclic aromatic compounds and is widely applied in experimental organic and organometallic chemistry. The nitrogen atom in the pyridine ring is endowed with a lone electron pair. This electron pair can be involved in different interatomic interactions, including H-bonding in which the N atom plays the role of the acceptor of proton [9–12] or in the ligand–metal interaction. Thus, pyridine belongs to Lewis bases and in organometallic chemistry is considered as a common and relatively strong σ-donating ligand [13]. It was shown by Krygowski and co-workers [14] that the pyridine moiety is relatively weakly sensitive to substituent resonance effect, when the N atom is involved in H-bond creation. In this work quantum chemical methods were used in order to gain a deeper insight into the phenomenon of the substituent effect in a series of *para* substituted $Cr(CO)_5$–pyridine complexes. The obtained results were related to the experimentally estimated substituent constants [15]. Additionally, the metal–ligand bonds were characterized by means of the *Atoms in Molecules* [16] topological analysis of electron density function.

2. Methodology

A set of simple and most common substituents, having possibly different properties in resonance effect according to the values of substituents constants [15] were chosen in order to simulate the influence of substitution in the *para*-position of pyridine ring in $Cr(CO)_5$–pyridine. The following substituents were taken into consideration: NO, NO_2, CN, CHO, F, H, CH_3, OCH_3, OH and NH_2. The geometries of all the molecular systems were optimized without any restrains using DFT-B3LYP functional [17–19] in combination with 6-31+G(3df) basis set (Pople's 6-31+G(3df) basis set for O, N, C and H [20–23] and 6-31+G basis containing additional three f and one g polarization functions for the Cr atom) implemented in GAUSSIAN-03 set of codes [24]. The obtained geometries are generally in agreement with the previously reported geometry of $Cr(CO)_5$–pyridine molecule in the crystal state [25]. A graphical representation of the optimized geometry of unsubstituted $Cr(CO)_5$–pyridine is shown in Fig. 1a. Electron densities estimated for fully optimized systems were used to AIM-based analysis of electron density [16]. Topological analysis of electron distribution was performed using AIM-2000 package [26]. The number of critical points found for all the analyzed systems is in agreement with the Poincaré-Hopf rule [27]. The electron density at *bond critical point* ($\rho_{(BCP)}$), its Laplacian $\nabla^2\rho_{(BCP)}$, total electron energy density (H) and its components, kinetic (G) and potential (V) electron energy densities were analyzed in order to characterize metal–ligand bonding. A molecular graph with positions of critical points is shown in Fig. 1b. Additionally, the energies of LUMO orbitals in free pyridine derivatives were estimated at the same level
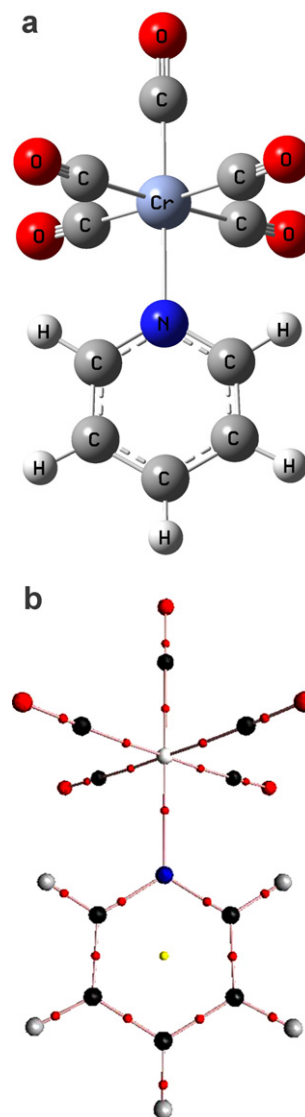

Fig. 1. Graphical representation of the optimized geometry of $(CO)_5$Cr–pyridine (a), and corresponding to this system molecular graph with the bond and ring critical points as small red circles for BCPs and small yellow circles for RCPs (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of approximation as that present above. A set of experimentally estimated substituent constants [15] were taken into account in order to investigate the substituent effect in *para* substituted $Cr(CO)_5$–pyridine. The following substituent constants were taken into account: σ^+, σ^-, F, R^+ and R^-. As it is known, substituent constants numerically quantify mutual electron interaction between a given substituent and the *para*-placed reactivity centre, spaced by the aromatic ring. The constants selected for these studies can be characterized as follows.

The σ^+ is the substituent constant estimated for the *para*-placed reactivity centre (in respect to a given substituent, see Chart 1, where X is the reactivity centre and R is the considered substituent), which could effectively delocalize a positive charge, e.g. $C(CH_3)_2Cl$ [28]. In other words,

Chart 1.

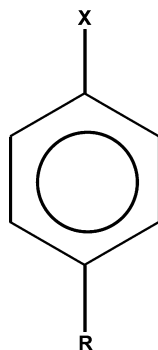the σ^+ values are estimated for the centre which introduces a positive charge onto its carrier ring. The values of σ^- are estimated for the centre having lone electron pairs, e.g. the OH or NH_2 group, so the centre which introduces a negative charge onto its carrier ring [29]. The F values reflect field/inductive properties of a given substituent, while R^+ and R^- are the resonance constants obtained for suitable centers of reactivity. The large positive value of a given constant implies high electron-withdrawing power by inductive and/or resonance effect, relative to the hydrogen atom; while the large negative value of a given constant implies high electron-releasing power relative to the hydrogen atom. The choice of five different type constants is due to the fact that the metal centre can interact with a given ligand both as the electron donating and electron withdrawing centre. It is known that M–L bonding is considered as a simple lone-pair-donor–acceptor bond (as for instance in M–NH_3 bond) or as a more complex interaction in which the metal atom plays the role of accepting and/or donating centre (e.g. the case of *back-bonding* or π-electron ligand-to-metal donation).

3. Results and discussion

As it was already mentioned, the pyridine moiety is relatively weakly sensitive to substituent resonance effect in the case when the N atom is involved in H-bond creation. It was shown by Krygowski and co-workers [14] that the influence of substituents on H-bridge is relatively weak. According to those authors, the most probable reason of this is that the 2p-type electron in the nitrogen atom is weakly involved in the mesomeric and π-electron delocalization due to H-bond formation. This is obviously related to the fact that the 2p orbital of the H atom is only slightly accessible during the complexation. In fact, it was reported on the basis of UHF/cc-pVQZ calculations that the energy of hydrogen 2p orbital is 14.48 eV as compared with 0.53 eV and 1.6 eV energies of Li and BeH 2p orbitals, respectively [30]. Therefore, it is worth taking a closer look on the case of the M–$N_{(pyridine)}$ bond, where M is the transition metal atom. In M–$N_{(pyridine)}$ bond not only σ, but also the π component of the bond should be considered. This is because, being distinct from the hydrogen atom,

the transition metals form bonds through the d-type orbital having a more complex three-dimentional geometry than the s-type orbital on the H atom. For instance, carbonyl ligands are known as both σ-donating and π-accepting species [13]. The M–CO σ-bond is formed by the donation of a lone pair of the carbon atom into empty d orbital of the metal. When the metal atom has the d^2 or higher configuration, its filled d orbital is overlapping with the empty CO π^* orbital, which results in the so-called *back-bonding*. It should be emphasized here that this *back-bond* is usually considered as a main force linking the transition metal and CO ligand [5,31–34]. For this reason, metals with d^0 configuration seldom form stable carbonyl complexes. Another example can be the anionic maleimidato ligand. The maleimidato ligand exhibits significant σ-donating properties, however, being distinct from the CO ligand, it is a π-donating moiety due to the filled p-type orbital on coordinating nitrogen atom [35]. For this reason the efficient π-electron donation can be observed in the case of complexes containing maleimidato fragment [36,37]. In the case of the N atom in pyridine the σ-donating component occurs as it takes place in the maleimidato ligand. Also a filled p-type orbital is present on the pyridine N atom, however, it can be expected that its availability in M–N bond formation is limited due to the fact that p-electrons are strongly involved in the formation of a stable aromatic system within the pyridine ring. Therefore, the π-donating properties of pyridine ligand should be strongly restricted when compared with the anionic η^1-N maleimidato ligand. The situation should become even more complicated when a set of variably *para* substituted pyridine ligands are considered. As it can be seen in Table 1, the M–$N_{(pyridine)}$ bond length in substituted $Cr(CO)_5$–pyridine is changing due to the presence of the substituent in position 4 of the pyridine ring. For the strongest electron withdrawing substituents (these having large positive values of substituent constants, e.g.: NO, NO_2) the M–N bond is shorter than in the unsubstituted $Cr(CO)_5$–pyridine system, whereas for the electron donating substituents (these having large negative values of substituent constants, e.g. NH_2, OH) this bond is, respectively, longer. Therefore, the electron withdrawing substituents additionally stabilize the Cr–N bond, while the electron donating ones weaken it. This can be surprising, considering the fact that the surplus of negative charge on the N atom should result in stronger bassic properties of the pyridine ligand and therefore, it should additionally stabilize the bond under discussion. It should be pointed out, however, that in the case of pyridine system the substituents do not affect the σ-donating component of the M–N bond, or at least this component is affected very weakly, as it can be concluded on the basis of H-bond investigations [14]. Therefore, it can be supposed that the substituents in *para*-position of pyridine affect the π-component of the Cr–$N_{(pyridine)}$ bond. It is also worth taking a closer look on the possible canonical structures of the substituted pyridine. It has been shown in Fig. 2c and d, that the substituent effect for electron

Table 1
Substituent constants, LUMO energies of the free pyridine system and selected AIM based parameters of organometallic species; electron densities, ρ, its laplacians, $\nabla^2\rho$, total electron energy density, $H(\rho)$, and its components, kinetic, $G(\rho)$, and potential, $V(\rho)$, electron densities

	Substituent constants					Cr–N bond						trans Cr–C bond						cis Cr–C bond						LUMO
	σ^+	σ^-	F	R^+	R^-	d(N–Cr)	ρ	$\nabla^2\rho$	$H(\rho)$	$G(\rho)$	$V(\rho)$	d(Cr–C)	ρ	$\nabla^2\rho$	$H(\rho)$	$G(\rho)$	$V(\rho)$	d(Cr–C)	ρ	$\nabla^2\rho$	$H(\rho)$	$G(\rho)$	$V(\rho)$	
NH₂	-1.30	-0.15	0.08	-1.38	-0.23	2.210	0.051	0.294	2.373	0.070	-0.066	1.861	0.123	0.575	-20.886	0.177	-0.210	1.911	0.109	0.521	-15.335	0.155	-0.179	-0.0195
OCH₃	-0.78	-0.26	0.29	-1.07	-0.55	2.212	0.051	0.294	2.446	0.070	-0.066	1.862	0.122	0.574	-20.819	0.177	-0.210	1.911	0.109	0.521	-15.259	0.154	-0.179	-0.0252
OH	-0.92	-0.37	0.33	-1.25	-0.70	2.214	0.051	0.293	2.495	0.069	-0.065	1.862	0.122	0.574	-20.793	0.177	-0.210	1.911	0.109	0.522	-15.341	0.155	-0.179	-0.0283
F	-0.07	-0.03	0.45	-0.52	-0.48	2.214	0.050	0.296	2.609	0.070	-0.066	1.863	0.122	0.572	-20.630	0.176	-0.209	1.912	0.109	0.521	-15.255	0.155	-0.179	-0.0390
CH₃	-0.31	-0.17	0.01	-0.32	-0.18	2.208	0.052	0.299	2.456	0.071	-0.067	1.863	0.122	0.573	-20.691	0.176	-0.209	1.911	0.109	0.521	-15.281	0.155	-0.179	-0.0351
H	0.00	0.00	0.00	0.00	0.00	2.208	0.052	0.300	2.512	0.071	-0.067	1.863	0.122	0.572	-20.607	0.176	-0.209	1.911	0.109	0.521	-15.259	0.155	-0.179	-0.0400
CN	0.66	1.00	0.51	0.15	0.49	2.198	0.052	0.311	2.663	0.073	-0.069	1.868	0.121	0.567	-20.194	0.174	-0.206	1.913	0.108	0.520	-15.124	0.154	-0.178	-0.0895
CHO	0.73	1.03	0.33	0.40	0.70	2.194	0.053	0.313	2.564	0.074	-0.070	1.867	0.121	0.567	-20.204	0.174	-0.206	1.913	0.108	0.519	-15.079	0.154	-0.178	-0.0985
NO₂	0.79	1.27	0.65	0.14	0.62	2.193	0.053	0.316	2.677	0.075	-0.070	1.869	0.120	0.565	-20.038	0.173	-0.205	1.914	0.108	0.520	-15.065	0.154	-0.178	-0.1217
NO	–	0.49	–	–	1.14	2.184	0.054	0.321	2.530	0.076	-0.072	1.870	0.120	0.563	-19.949	0.173	-0.204	1.914	0.108	0.519	-15.086	0.154	-0.178	-0.1325

Both LUMO energies and all AIM-based parameters are in atomic units. The only exception is $H(\rho)$ expressed in kcal mol⁻¹ bohr⁻¹ (conversion factor: 627.509). For NO group some of substituent constants are unavailable.
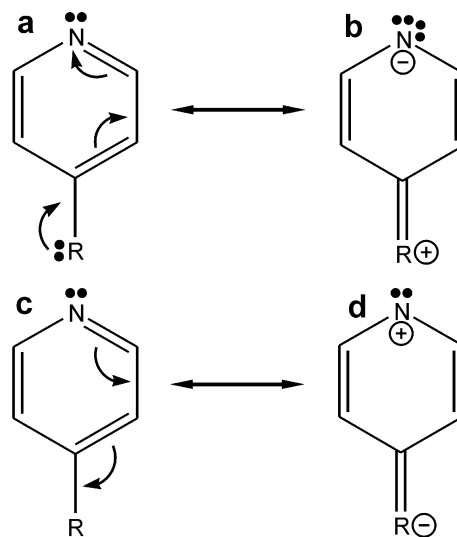

Fig. 2. Selected resonance structures of pyridine substituted with electron donating (a) and (b), and electron withdrawing (c) and (d), substituent.

withdrawing substituents results in a partial lack of π-electrons on the N atom. This leads to a decrease of the π-donating, or an increase of the π-accepting properties of pyridine moiety. The latter can result in additional stabilization *via* back-bonding effect in the M–N bond. When the electron withdrawing substituent is replaced with the electron donating one (Fig. 2a and b), the π-donating properties of the pyridine ligand increase (or π-accepting properties decrease) which in the case of the analyzed systems seems to destabilize the interaction between pyridine ligand and the rest of the complex. The postulate, according to which the substituents mainly affect the π-component of the Cr–N_(pyridine) bond, can be additionally proved by performing an analysis of LUMO energies in free pyridine derivatives. Table 1 presents the values of energies of the LUMO orbitals estimated for free pyridine molecule substituted in the *para*-position with respect to the hetero-atom. Additionally, graphical representations of these orbitals are shown in Fig. 3. As it can be seen, the LUMO orbital can be involved in π-electron interaction with d-orbitals of the transition metals. Thus it can be expected that in the case of electron-withdrawing substituents the energy of the LUMO orbital should be lowered, which should favour back-donation. In the case of electron-donating substituents an opposite effect should be observed. In fact, the data collected in Table 1 is in excellent agreement with the above statement. For significantly electron-withdrawing substituents the LUMO energy is considerably lower when compared with the case of the substituents considered as electron-donating ones. There is even a direct relation between the LUMO energy and Cr–N distance (cc. = 0.964). Therefore, it can be stated that in the Cr(CO)₅–pyridine complexes the *back-bonding* effect is the one which additionally stabilizes the Cr–N_(pyridine) bond, similarly as it occurs in the case of M–CO bond. The interdependences between the
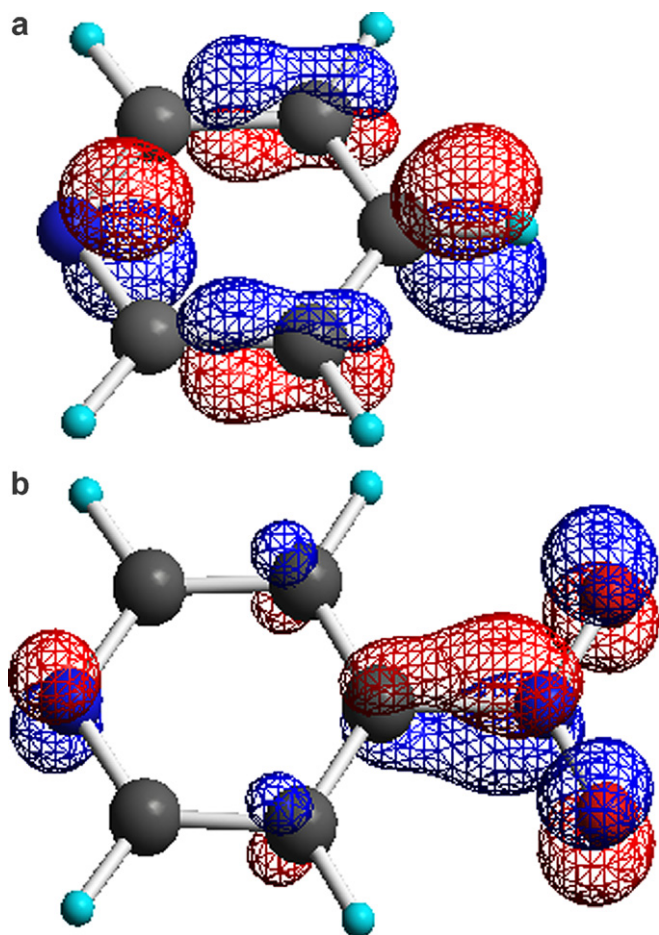
Fig. 3. Graphical visualization of LUMO orbital in (CO)$_5$Cr–pyridine (a) and its derivative (b) substituted in *para*-position of pyridine ring by the NO$_2$ group.

Cr–N$_{(pyridine)}$ bond length and selected substituent constants are presented in Fig. 4. There is a close to linear interdependence between d(Cr–N) and R^-, whereas there is a lack of such relation between d(Cr–N) and R^+. A similar situation can be found if one considers the values of σ^- and σ^+. It seems therefore that the communication between the substituents and the Cr(CO)$_5$ moiety through the pyridine ring has the same character as the interaction between a given substituent and the centre which introduces the electrons onto the aromatic ring due to communication with this substituent (see the definition of substituted constants used in this work). This observation additionally corroborates the stabilizing effect of the *back-donation*. The clearest interdependence observed for R^- can additionally prove that the main factor influencing the Cr–N bonding within the investigated set of Cr(CO)$_5$–pyridine systems is connected with the π-electron effects, particularly as it is difficult to find a clear relationship between the field/inductive substituent constant F and the considered bond lengths. It is worth mentioning here that the introduction of a given substituent into position 4 of the pyridine ring results in small but systematic changes in the Cr–C$_{(carbonyl)}$ bonding. This results from an obvious connection between the back-donations in the

Cr–N$_{(pyridine)}$ and Cr–C$_{(carbonyl)}$ bonds. An increase in Cr–N back-donation goes with a reduction in Cr–CO$_{trans}$ back-donation, since the same occupied orbital of the metal is involved in both these π-electronic effects [38]. The changes in Cr–C distances are relatively lower than in the case of Cr–N bond, nevertheless the trends in these changes seem to be equally systematic. As it can be seen from Table 1, there is a relation between the substituent constants and the length of *trans* placed Cr–C bond. Clearly, the greater electron withdrawing properties of the given substituent, the longer is the *trans* Cr–C$_{(carbonyl)}$ bond. This can be a valuable observation, since it potentially allows one to modulate the Cr–C$_{(carbonyl)}$ bonding *via* substitution of pyridine in the *para*-position with the appropriate chemical group. It is also worth emphasizing, that this effect seems to be exactly the same for *trans* as well as *cis* placed carbonyls. However, for *cis* carbonyl ligands these changes are smaller. The *trans* Cr–C bond length adopts the values in the range of 1.860–1.870 Å, whereas in the case of *cis* placed carbonyls this value is in the range of 1.910–1.914 Å. In addition to that, the *cis* Cr–C bonds are relatively longer than their *trans* counterparts. This can be explained by the presence of the pyridine ligand, which, as a lower field ligand than the CO one, weakens the *cis*-placed Cr–CO bonds.

It has been proved, that the AIM-based analysis of electron density can provide valuable information on many physical and chemical properties of the molecular systems [39–43]. (It is fair to mention here some criticism of *AIM Quantum Theory*. For this criticism see Ref. [44].) It has been found for instance that the value of electron density (ρ) and its laplacian ($\nabla^2\rho$) estimated at bond critical point (BCP) of a given bond correlate very well with the strength of this bond, as well as with its length, since, as it is well known, both the strength and the length of a given bond are mutually dependent [45–48,39,49,50]. Also in this case such a relationship can be observed and the linear regression can be found between ρ(N–Cr) and d(N–Cr) (c.c. = 0.982). Similarly, the laplacian of ρ(N–Cr), $\nabla^2\rho$, fulfils such a linear relationship (c.c. = 0.989).

Additional valuable information on chemical bond properties is available from the total electron energy density, $H(\rho)$, and its components; kinetic electron energy density, $G(\rho)$, positive by definition, and potential electron energy density, $V(\rho)$, negative by definition. The following relation is known for $H(\rho)$ and its components [16]:

$$H(\rho) = G(\rho) + V(\rho).$$

It is known that in the region of the bond CP of weak closed-shell interatomic interactions the kinetic energy density dominates, with $G(\rho)$ magnitude being slightly greater than the potential energy density $|V(\rho)|$ which implies the total energy density $H(\rho) > 0$ and close to zero, whereas for strong covalent interactions $V(\rho)$ dominates over the kinetic energy density and $H(\rho) < 0$. This is usually accompanied by $\nabla^2\rho > 0$ for the proper case and $\nabla^2\rho < 0$ for the latter one (there is one exception mentioned in the further
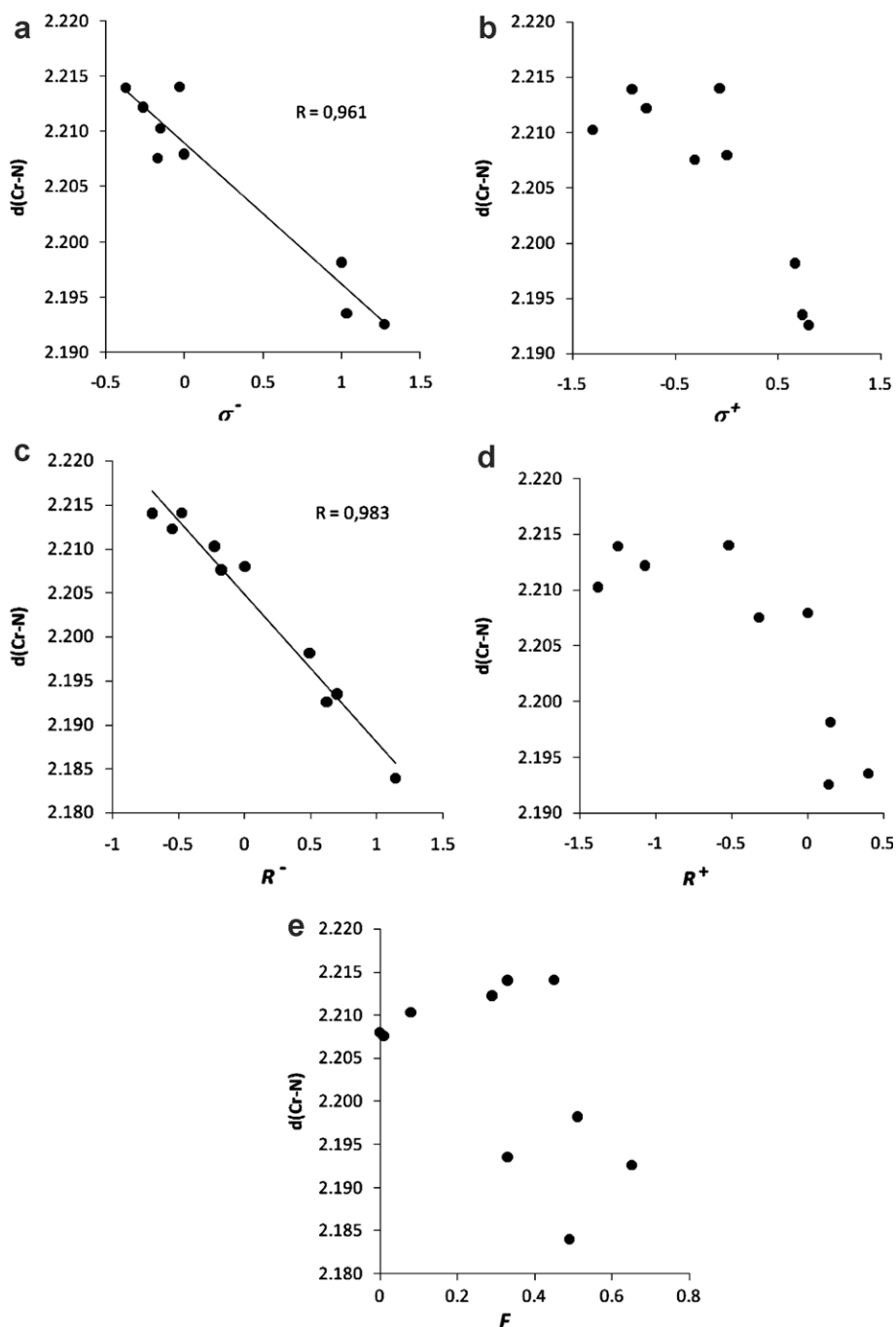
Fig. 4. Mutual interrelation between Cr–N distance (in Å) and substituent constants under discussion. Only linear regressions for which c.c. > 0.8 are present.

part of the discussion). Interestingly, both $G(\rho)$ and $|V(\rho)|$ values increase with electron-withdrawing properties of substituents in the *para*-position of the pyridine ring. However, $H(\rho)$ is invariably positive and very close to zero. Probably, this could be due to the changes in the Cr–N bond length. As already mentioned, the Cr–N$_{(pyridine)}$ distance decreases with an increase of electron-withdrawing properties of the attached substituents. It can thus be expected that the shorter is the bond, the more covalent is its character, which implies an increase of $|V(\rho)|$ magni-

tude. However, this is compensated by an increase of $G(\rho)$ which is related with Pauli repulsion between two closed shells. As a result, the $H(\rho)$ varies within a very small range. These changes are relatively small because of a limited possibility of the influence of substituents on the Cr–N$_{(pyridine)}$ bond, and can be more significant in the case of a larger spectrum of variability of a given bond. The above-described relations have a more variable, but still systematic character if following from hydrogen bond to covalent bond, as shown for the proton transfer reaction
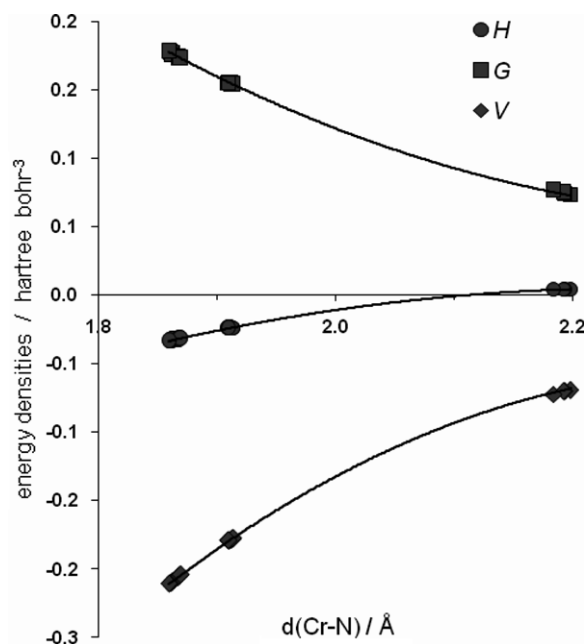
Fig. 5. Total electron energy density (H) and its components, kinetic (G) and potential (V) electron energy densities as functions of Cr–X distance (where X = N, C). All electron densities are expressed in hartree/bohr^3. General trends are illustrated with the polynomial regressions.

[51] or in AIM characterization of bonding in a series of DMAN complexes and Schiff bases [52]. However, if one summarize the data for the Cr–N and both *cis* and *trans* Cr–C$_{(carbonyl)}$ bonds, as it was done in Fig. 5, then some general trends are well represented. (It should be emphasized, that within a large range of bond length the values of energy densities should form two independent trends for the Cr–N and Cr–C bond, separately. These two trends have been merged only by purposes of illustration of the one general trend.) It can be seen that for shorter M–L bonds $V(\rho)$ predominate over $G(\rho)$, as a result of which $H(\rho)$ adopts negative values. (For illustration purposes polynomial regressions are shown in Fig. 5. These relations can also be expressed by logarithmic regressions. C.c. for both polynomial and logarithmic regressions practically equals 1.) Interestingly, in the case of all the Cr–C$_{carbonyl}$ bonds, both *trans* and *cis* placed, $\nabla^2\rho$ values at corresponding BCPs are positive, as it was found for closed-shell interactions, but with $H(\rho) < 0$, as found for shared interactions. This is in agreement with observations made for the Ti–C bonds in titanium complexes [53], in the case when the metal–ligand bonding has a characteristics that represents a mix of the closed-shell and shared parameters. Moreover, the $H(\rho)$ values are more negative for trans Cr–C bonds, which is directly connected with relative greater predominance of $|V(\rho)|$ magnitude over the $G(\rho)$ magnitude. This suggests a more covalent character of the *trans* Cr–C$_{carbonyl}$ bond as compared with the *cis* ones, and is also in line with general knowledge, according to which low-field ligands (e.g. pyridine) weaken the *cis*-placed M–carbonyl bonds. Generally, the grater value of

$|H(\rho)|$ (with negative sign), the more covalent character of the bond. It seems therefore that the covalent character of the Cr–C$_{carbonyl}$ bonds increases with electron donating properties of the substituent attached to the pyridine ring. This can be partially connected with the *trans-effect* and the fact that a relatively greater contribution of structure (b) in Fig. 2 should lead to an increase of back-donation in the *trans* placed Cr–C$_{carbonyl}$ bond. Summarizing this paragraph, it can be said that in the analyzed organometallic species the Cr–C$_{(carbonyl)}$ bonding has a more covalent character than the Cr–N$_{(pyridine)}$ bonding. Moreover, the *trans* placed carbonyl ligand forms a more covalent bond than its *cis* counterparts.

4. Conclusions

In conclusion, the substituents in position 4 of the pyridine ring affect the Cr–N$_{(pyridine)}$ bond in the Cr(CO)$_5$–pyridine complex in a systematic manner. It seems, that due to substitution the pyridine moiety has a diversified ability of participating in the interaction with the Cr atom of the Cr(CO)$_5$ moiety. Mutual interrelation between geometrical and electronic properties of the Cr–N bond and the considered substituent constants shows the complexity of the metal–ligand bonding. Unlike in the H-bonded complexes, in transition metal complexes the pyridine moiety is a relatively effective transferring moiety for π-electron effects. The substituent effect mainly affects the π-component of the Cr–N bond and moreover, the pyridine moiety exhibits π-accepting properties. The electronic effect proceeds in the whole Cr–pyridine–R moiety. The changes occurring in the Cr–N$_{(pyridine)}$ bond are revealed as slight changes of the Cr–CO bonds, particularly the *trans* Cr–CO bond. This property can potentially be used for modulation of the Cr–CO bond by substitution of the Cr(CO)$_5$–pyridine complex in *para* position of the pyridine ring.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem. 2007.05.029.

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