



# Isonitrile ligand properties as studied by He I/He II photoelectron spectroscopy

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## ABSTRACT

A new series of isonitrile-substituted cobalt tricarbonyl nitrosyl ( $\text{Co}(\text{CO})_2(\text{NO})\text{CNR}$ ,  $\text{R} = \text{Me, Et, } ^n\text{Pr, } ^i\text{Pr, } ^n\text{Bu, } ^n\text{Pe, CH}_2\text{Si}(\text{CH}_3)_3$ ) has been synthesized, and their He I ultraviolet photoelectron spectra are reported. The assignment of the bands in the low energy part of the spectra was performed with the aid of DFT calculations. The first vertical ionization energies of the complexes were found to be 7.73 (CNMe), 7.58 (CNEt), 7.59 (CN<sup>n</sup>Pr), 7.70 (CN<sup>n</sup>Bu), 7.67 (CN<sup>n</sup>Pe), 7.77 (CN<sup>i</sup>Pr), and  $7.54 \pm 0.03$  eV (CNCH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>). In the case of <sup>n</sup>Pr- and CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>- substitutions, He II photoelectron spectra were also recorded. The relative importance of electronic and steric effects of the isonitrile ligands, as a function of the size of group –R, is discussed.

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## 1. Introduction

Transition-metal complexes are widely used as chemical vapor deposition (CVD) precursors and as catalysts in numerous reactions of biological and industrial importance. The catalytic activity and stability of these complexes are mainly determined by the ligands attached to the metal center.

In the past few years, we have embarked on an experimental program to investigate the electronic and steric effects of various ligands on the electronic structure of transition metal model compounds [1–4].

He I photoelectron spectroscopy (PES) along with the threshold photoelectron photoion coincidence (TPEPICO) technique have already provided important data on the electronic structure and ionic bond energies of phosphine and isonitrile-substituted cobalt tricarbonyl nitrosyl complexes ( $\text{Co}(\text{CO})_2(\text{NO})\text{L}$ ,  $\text{L} = \text{PMe}_3, \text{PEt}_3, \text{P}^n\text{Pr}_3, \text{P}^n\text{Bu}_3, \text{PCy}_3, \text{PPh}_3, \text{P}(\text{OMe})_3$  [5], *t*-BuNC [6]).

The use of isonitrile ligands as catalysts [7–9], as precursors in surface chemistry [10], their structural chemistry [11] and photochemistry [12] shows that the isonitrile substitution may have an important effect on the electronic structure and steric properties of the transition metal complexes. That is why the (RNC)Co(CO)<sub>2</sub>(NO) (R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu, *n*-Pe, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>) series seemed to be an ideal set of compounds in order to study systematically the influence of aliphatic isonitrile on the electronic structure of an organometallic complex.

Our recent UPS and electron transmission spectroscopy (ETS) study on free isonitrile [13] molecules showed that aliphatic isoni-

triles are good  $\sigma$ -donor, but poor  $\pi$ -acceptors. The electron donor properties are expected to be tuned by varying the alkyl group, which can be reflected by the ionization energy (IE) of the molecule orbitals localized around the central metal atom in the (RNC)Co(CO)<sub>2</sub>(NO) complexes.

In this study, we present the complete set of He I and some He II spectra of the series (RNC)Co(CO)<sub>2</sub>(NO) (R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu, *n*-Pe, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>). The assignment of the low energy part of the spectra – supported by quantum chemical calculations – makes possible a more precise description of the isonitrile ligand effect.

## 2. Experimental details

### 2.1. Synthesis

Isonitrile ligands MeNC, EtNC, *n*-PrNC – commercially not available – were prepared from *N*-alkyl-formamides by the method of Casanova et al. [14]. Other ligands, namely *i*-PrNC, *n*-BuNC, *n*-PeNC, (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>NC, as well as Co(CO)<sub>3</sub>(NO) were purchased from Sigma-Aldrich, and from Strem Chemicals, respectively, and were used without further purification.

The synthesis was based on an earlier procedure found in the literature [15]. The solution of the isonitrile (RNC, 10.0 mmol) in tetrahydrofuran (THF, 10 mL) was added in small portions at room temperature to the solution of Co(CO)<sub>3</sub>(NO) (2.076 g, 12.0 mmol) in THF (5 mL), in 1 h under nitrogen atmosphere. The reaction mixture was then stirred for over 3 h, followed by the evaporation of the solvent and the excess reactant under reduced pressure. In the case of (MeNC)Co(CO)<sub>2</sub>(NO) and (EtNC)Co(CO)<sub>2</sub>(NO), lower temperatures (0 °C, and –20 °C, respectively) were used. All the products were isolated as dark-red viscous liquids with a yield of 60–80%. They

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were identified by IR spectroscopy and were stored under nitrogen at  $-25\text{ }^{\circ}\text{C}$ . The solvent (THF) was dried over  $\text{CaH}_2$ , refluxed with sodium and benzophenone, then distilled under argon [16].

## 2.2. Ultraviolet photoelectron spectroscopy

He I photoelectron spectra were recorded on an ATOMKI ESA 32 instrument described elsewhere [17]. The instrument was operated at a resolution of 30 meV measured on the  $^2\text{P}_{3/2}$  peak of Ar. The samples were introduced at room temperature into the ionization chamber via a direct inlet system. Samples of  $[(\text{CH}_3)_3\text{SiCH}_2\text{NC}]\text{Co}(\text{CO})_2(\text{NO})$ , and  $(n\text{-PeNC})\text{Co}(\text{CO})_2(\text{NO})$  were evaporated at  $70\text{ }^{\circ}\text{C}$ . Argon ( $^2\text{P}_{3/2}$  peak, 15.759 eV) and nitrogen ( $^2\Sigma_g^+$  peak, 15.60 eV) were used as internal standards for calibrating the electron-energy scale.

## 2.3. Quantum chemical calculations

Quantum chemical calculations at the density functional theory (DFT) level were carried out in order to help the assignment of the photoelectron spectra, and to obtain the infrared spectra needed to identify the products. For the geometry optimization and the ionization energy calculations, Becke's three parameter hybrid functional (B3) [18] was combined with the correlation functional of Lee, Yang, and Parr (LYP) [19] and utilized with the 6-311++G(2df,p) basis set, as implemented in the GAUSSIAN 03 (rev. C. 02) [20] quantum code package. The optimized geometries of the neutral molecules were justified to be minima by the absence of imaginary vibrational frequencies.

The application of Koopmans's theorem to determine vertical ionization energies, which equates the negative of the Hartree-Fock orbital energies with the ionization energy, is known to be subject to considerable error. As shown by Baerends et al. [21–25], and Politzer et al. [26] Kohn–Sham orbital energies can be taken as approximate vertical ionization energies. In the present study, the first vertical ionization energy was determined at the same level of theory from the difference in the ground-state energy of the ion at the neutral molecule geometry and that of the neutral molecule. The negatives of the Kohn–Sham orbital energies were

then shifted so that the negative of the HOMO energy matched with the  $\Delta\text{DFT}$  value described above. This method provides a reliable assignment in the case of transition-metal complexes, as shown by a recent study [27].

## 3. Results and discussion

As a first step we consider the He I spectra of the above mentioned series together with that of the unsubstituted parent compound ( $\text{Co}(\text{CO})_3\text{NO}$ ) [28]). The previously published He I spectrum of  $(t\text{-BuNC})\text{Co}(\text{CO})_2(\text{NO})$  [6] is also included here for comparison. The recorded spectra are shown in Fig. 1. Experimental ionization energies were extracted by fitting a sum of pseudo-Voigt functions [29] and Shirley background [30] on the experimental points. The determined ionization energies are listed in Table 1.

The spectra of the isonitrile derivatives show very similar outlook feature: they start with two low intensity bands (A;  $B \sim 7.8$ ; 8.4 eV, respectively) and after a Franck–Condon gap there is a band (C  $\sim 12$  eV) followed by an unresolved broad envelope ( $D > 12$  eV). The length of alkyl groups of the isonitrile ligands has some influence on the spectra. The position of bands A and B varies in a small energy range ( $\sim 0.2$  eV), while that of band C varies in a range of 1 eV (Table 1). It is also clearly seen that peak area under band D increases with the size of the alkyl chain.

As far as orbital characters are concerned both correlation with the parent molecule and quantum chemical calculations are informative. Comparison to the He I spectrum of the  $\text{Co}(\text{CO})_3(\text{NO})$  suggests that the first two bands can be assigned to the ionization of molecular orbitals with high  $\text{Co}(d)$  character [6]. In addition, the quantum chemical calculations show that the two bands belong to the ionization of five molecular orbitals. Selected calculated ionization energies along with the corresponding MO characters are listed in Table 2. Each of them consists of a remarkable metal  $d$ -character and a contribution from  $\pi$ -antibonding ligand orbitals (CO, NO, CNR).

More detailed analysis of the low energy part of the spectra shows that bands A and B are shifted to lower energies in the isonitrile substituted complexes compared to the parent molecule. This fact indicates that the isonitrile ligands increase the electron

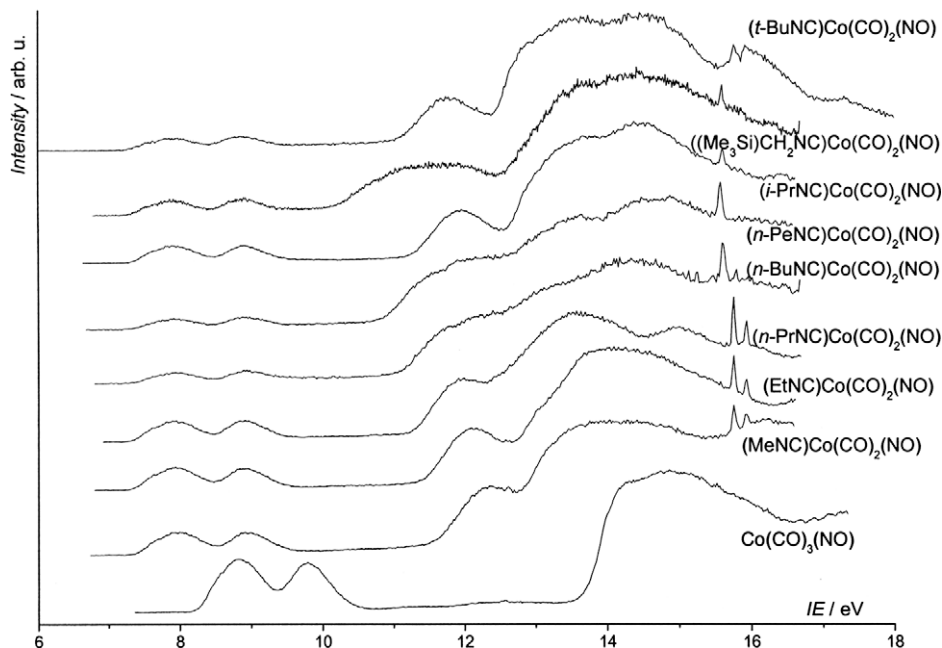


Fig. 1. He I spectra of the  $\text{Co}(\text{CO})_3(\text{NO})$  [Ref. [28)] and its isonitrile derivatives,  $(\text{RNC})\text{Co}(\text{CO})_2(\text{NO})$  (In case of  $\text{R} = t\text{-Bu}$ , the spectrum was taken from Ref. [6]).

**Table 1**  
Measured vertical ionization energies of the  $\text{LCo}(\text{CO})_2(\text{NO})$  complexes (eV).

Band	L							
	MeNC	EtNC	<i>n</i> -PrNC	<i>n</i> -BuNC	<i>n</i> -PeNC	<i>i</i> -PrNC	<i>t</i> -BuNC <sup>a</sup>	(Me <sub>3</sub> Si)CH <sub>2</sub> NC
A	7.7	7.6	7.6	7.7	7.7	7.8	7.7	7.5
	8.1	8.0	8.0	8.0	8.0	8.1	8.0	7.9
B	9.0	8.9	8.9	9.0	8.9	8.9	8.9	8.9
C	12.1	11.9	11.8	11.6	11.5	11.9	11.7	11.0
	12.4	12.2	12.3	12.2	12.1	12.3		11.6
D onset	12.6	12.5	12.2	12.3	12.3	12.5	12.3	12.0
								12.3

<sup>a</sup> Taken from Ref. [6].

**Table 2**  
Experimental and calculated ionization energies: methyl- and silaneopentylisocyanide derivatives.

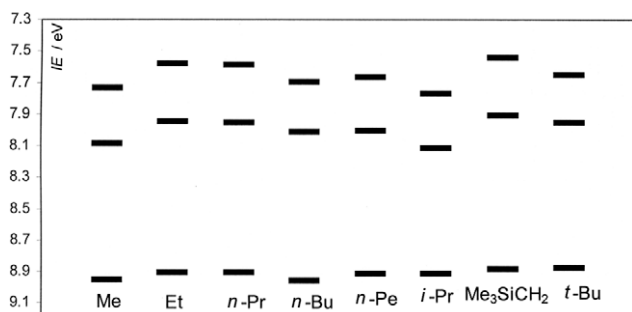
	Exp./eV	B3LYP/6-311+G(2df,p) <sup>a</sup> /eV	Orbital character
$\text{Co}(\text{CO})_3(\text{NO})^*$	8.75	8.75	Co- <i>d</i> + CO ( $\pi^*$ )
	9.11	9.27	Co- <i>d</i> + CO, NO ( $\pi^*$ )
	9.82	10.23	Co- <i>d</i> + CO, NO ( $\pi^*$ )
	14.14	14.19	CO- <i>d</i> + CO( $\sigma$ )
$(\text{CH}_3\text{NC})\text{Co}(\text{CO})_2(\text{NO})$	7.7	7.80	Co- <i>d</i> + CO, NO, CNR ( $\pi^*$ )
		7.82	
	8.1	8.29	Co- <i>d</i> + CO, NO, CNR ( $\pi^*$ )
	9.0	9.25	Co- <i>d</i> + CO, NO, CNR ( $\pi^*$ )
		9.26	
	12.1	11.81	C-N ( $\pi$ ) + Co- <i>d</i>
$[(\text{CH}_3)_3\text{SiCH}_2\text{NC}]\text{Co}(\text{CO})_2(\text{NO})$		11.81	
	7.5	7.58	Co- <i>d</i> + CO, NO, CNR ( $\pi^*$ )
		7.63	
	7.9	8.09	Co- <i>d</i> + CO, NO, CNR ( $\pi^*$ )
	8.9	9.01	Co- <i>d</i> + CO, NO, CNR ( $\pi^*$ )
		9.07	
	11.0	10.19	C-N ( $\pi$ ) + Co- <i>d</i>
	10.32		
	10.41		

\* Taken from Ref. [5].

<sup>a</sup> See details in the text.

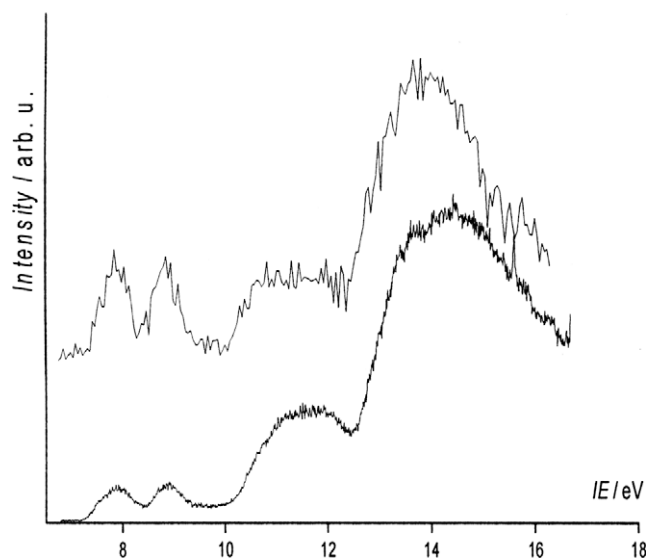
density on the metal center with respect to the carbonyl ligand. The first three ionization energies of the compounds do not change systematically with the electron-donor capability of the alkyl groups, instead they seem to vary randomly in a narrow, 0.2 eV range. This is shown in Fig. 2 where the three lowest vertical ionization energies ( $IE_{1-3}$ ) of the investigated compounds are depicted. Based on the ionization energies of the carbon lone pair ( $n_C$ ) in the free ligands [13], the order of *t*-BuNC ( $IE = 10.76$  eV) > *i*-PrNC ( $IE = 10.90$  eV) > MeNC ( $IE = 11.27$  eV) was expected for the electron donor capabilities. In the corresponding complexes, however, the IEs from the MOs with mainly metal character do not follow such a trend.

In order to help assignment further, He II spectra of (*n*-PrNC)Co(CO)<sub>2</sub>(NO), and [(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>NC]Co(CO)<sub>2</sub>(NO) were also re-



**Fig. 2.** The three lowest ionization energies of the  $(\text{RNC})\text{Co}(\text{CO})_2(\text{NO})$  complexes (values for R = *t*-Bu were taken from Ref. [6]).

corded. These are shown in Figs. 3 and 4 along with the corresponding He I spectra. In the He II spectra it is clearly seen that the relative intensity of the first two bands increases substantially confirming that they are associated with MOs with mainly Co *d* character. Band C, in the same time, does not show any change in the relative ionization cross section. This spectral feature



**Fig. 3.** He I (lower) and He II (upper) spectra of  $[(\text{CH}_3)_3\text{SiCH}_2\text{NC}]\text{Co}(\text{CO})_2(\text{NO})$ .

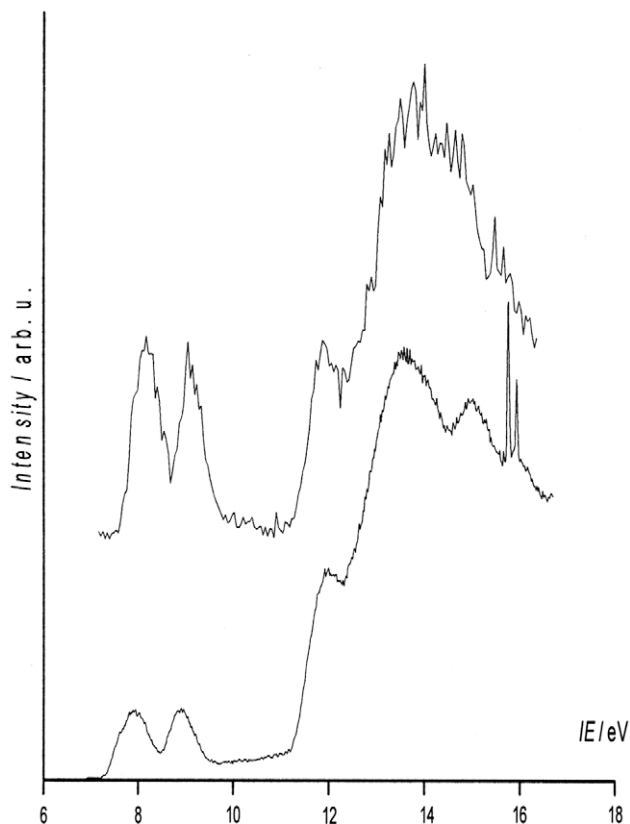


Fig. 4. He I (lower) and He II (upper) spectra of  $(n\text{-PrNC})\text{Co}(\text{CO})_2(\text{NO})$ .

together with the fact that this band is not present in the spectrum of the parent molecule,  $\text{Co}(\text{CO})_3(\text{NO})$ , suggests electron removal from molecular orbitals localized on the isonitrile ligand.

Considering the above facts one can say that the size of the alkyl-chain on the isonitrile-ligand has a minor electronic effect on the first ionization energy. Consequently, at a more or less constant electronic effect, it is the steric demand which may influence the properties of the complex such as stability and reactivity at the transition metal centre. For example, the  $(\text{CH}_3\text{NC})\text{Co}(\text{CO})_2(\text{NO})$  decomposes rapidly in vacuo at room temperature, while the  $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NC})\text{Co}(\text{CO})_2(\text{NO})$  is more stable and can be stored for a day under the same conditions. As a limiting case of electron releasing effect we investigated the complex  $[(\text{CH}_3)_3\text{SiCH}_2\text{NC}]\text{Co}(\text{CO})_2(\text{NO})$  where the +I effect of the silaneopentyl group should cause a substantial decrease in the lowest ionization energies. The silaneopentyl group is known to have a large +I effect, as it was shown by Tsvetkov et al. [31]. But its complex does not match up to the expectations: the ionization energies are in line with the ionization energies of the alkyl-isonitrile complexes.

#### 4. Conclusions

The He I and He II photoelectron spectra and related DFT calculations of new monosubstituted isonitrile derivatives of  $\text{Co}(\text{CO})_3(\text{NO})$  provided valuable information concerning the ligand effects of the isonitrile group.

In agreement with other experimental findings [13] it is well demonstrated – also by the corresponding ionization energies – that alkyl-isonitriles are stronger electron donors than the carbonyl ligand. Upon substitution, the lowest ionization energies, which can be considered as a measure of the electron density on the metal center, decrease by over 1 eV. However, on further changing the alkyl

chain in the isonitrile ligand, the lowest vertical ionization energies vary only in a narrow range of 0.2 eV, and the changes are not in line with the expected electron donor capabilities of the isonitrile ligands. Even the effect of the silaneopentyl group with its strong electron releasing property can not be observed.

Therefore, it can be concluded that in the case of alkyl-isonitrile substitution the steric component of the ligand effect is normally controlled by the size and bulkyness of the alkyl group, while its electronic component remains approximately constant and does not depend on the +I effect of the alkyl group. As a result, complex properties – like stability, and reactivity – can be influenced mainly by the steric demand of the alkyl-isonitrile ligand.

This is in a sharp contrast to the properties of the phosphine ligands. In our recent study we found that the electron density on the metal center largely depends on the length of the alkyl chain bound to the phosphorus atom [5].

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#### References

- [1] A. Nagy, L. Szepes, G. Vass, L. Zanathy, *J. Organomet. Chem.* 485 (1995) 215–218.
- [2] B. Sztáray, E. Rosta, Zs. Böcskey, L. Szepes, *J. Organomet. Chem.* 582 (1999) 267–272.
- [3] G. Vass, B. Sztáray, L. Szepes, *J. Organomet. Chem.* 560 (1998) 7–13.
- [4] B. Sztáray, L. Szepes, T. Baer, *J. Phys. Chem. A* 107 (2003) 9486–9490.
- [5] Zs. Gengeliczki, A. Bödi, B. Sztáray, *J. Phys. Chem. A* 108 (2004) 9957–9961.
- [6] Zs. Gengeliczki, L. Szepes, B. Sztáray, T. Baer, *J. Phys. Chem. A* 111 (2007) 7542–7550.
- [7] S. Braune, U. Kazmaier, *J. Organomet. Chem.* 641 (2002) 26–29.
- [8] S. Branue, U. Kazmaier, M. Pohlman, *J. Organomet. Chem.* 69 (2004) 468–474.
- [9] D. Villemin, A. Jullien, N. Bar, *Tetrahedron Lett.* 48 (2007) 4191–4193.
- [10] T.J. Matheison et al., *Chem. Commun.* 37 (1998) 1–372.
- [11] J.H. Paek et al., *Inorg. Chem. Commun.* 46 (2007) 2787–2796.
- [12] A.J. Esswein, J.L. Dempsey, D.G. Nocera, *Inorg. Chem. Commun.* 46 (2007) 2362–2364.
- [13] I.P. Csonka, L. Szepes, A. Modelli, *J. Mass Spectrom.* 39 (2004) 1456–1466.
- [14] J. Casanova, R.E. Schuster, N.D. Werner, *J. Chem. Soc.* (1963) 4280–4281.
- [15] E.M. Thorsteinson, F. Basolo, *J. Am. Chem. Soc.* 88 (17) (1966) 3929–3936.
- [16] W.L.F. Armarego, C.L.L. Chai, *Purification of Laboratory Chemicals*, fifth ed., Butterworth Heinemann, 2003.
- [17] B. Csákvári et al., *Magy. Kem. Foly.* 98 (1992) 415.
- [18] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [19] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [20] GAUSSIAN 03, Revision C.02, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian Inc., Wallingford CT, 2004.
- [21] E.J. Baerends, O.V. Gritsenko, *J. Phys. Chem. A* 101 (1997) 5383.
- [22] D.P. Chong, O.V. Gritsenko, E.J. Baerends, *J. Chem. Phys.* 116 (2002) 1760.
- [23] O.V. Gritsenko, E.J. Baerends, *J. Chem. Phys.* 117 (2002) 9154.
- [24] O.V. Gritsenko, B. Bra, E.J. Baerends, *J. Chem. Phys.* 119 (2003) 1397.
- [25] O.V. Gritsenko, E.J. Baerends, *J. Chem. Phys.* 120 (2004) 8364.
- [26] P. Politzer, F. Abu-Awwad, *Theor. Chem. Acc.* 94 (1998) 83.
- [27] Zs. Gengeliczki, Cs.I. Pongor, B. Sztáray, *Organometallics* 25 (2006) 2553.
- [28] I.H. Hillier et al., *Mol. Phys.* 27 (1974) 215–223.
- [29] M.P. Seah, I.S. Gilmore, *Phys. Rev. B* 73 (17) (2006).
- [30] D.A. Shirley, *Phys. Rev. B* 5 (12) (1972) 4709.
- [31] E.N. Tsvetkov, G.K. Semin, D.I. Lobanov, M.I. Kabachnik, *Dokl. Akad. Nauk. SSSR* 161 (1965) 1102.