



Bonding situation and stability of η^1 - and η^6 -bonded heteroarene complexes $M(\eta^1\text{-EC}_5\text{H}_5)_6$ and $M(\eta^6\text{-EC}_5\text{H}_5)_2$ ($M = \text{Cr, Mo, W}$; $E = \text{N, P, As, Sb, Bi}$)[☆]

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ABSTRACT

Density functional calculations at the BP86/TZ2P level are reported for the pseudo-octahedral heteroarene complexes $M(\eta^1\text{-EC}_5\text{H}_5)_6$ and for the sandwich complexes $M(\eta^6\text{-EC}_5\text{H}_5)_2$ ($M = \text{Cr, Mo, W}$; $E = \text{N, P, As, Sb, Bi}$). The complexes $M(\text{CO})_6$ and $M(\eta^6\text{-C}_6\text{H}_6)_2$ have been calculated for comparison. The nature of the metal–ligand interactions was analyzed with the EDA (energy decomposition analysis) method. The calculated bond dissociation energies (BDE) of $M(\eta^1\text{-EC}_5\text{H}_5)_6$ have the order for $E = \text{P} > \text{As} > \text{N} > \text{Sb} \gg \text{Bi}$ and for $M = \text{Cr} < \text{Mo} < \text{W}$. All hexaheteroarenes bind more weakly than CO in $M(\text{CO})_6$. Except for pyridine, which is the weakest η^6 -bonded ligand, the trend in the BDE of the $M(\eta^6\text{-EC}_5\text{H}_5)_2$ complexes is opposite to the trend of the $M(\eta^1\text{-EC}_5\text{H}_5)_6$ complexes $\text{NC}_5\text{H}_5 < \text{PC}_5\text{H}_5 < \text{AsC}_5\text{H}_5 < \text{SbC}_5\text{H}_5 < \text{BiC}_5\text{H}_5$. The opposite trend is explained with the different binding modes in $M(\eta^6\text{-EC}_5\text{H}_5)_2$ and $M(\eta^1\text{-EC}_5\text{H}_5)_6$. The bonding in the former complexes mainly takes place through the π electrons of the ligand which are delocalized over the ring atoms while the bonding in the latter takes place through the lone-pair electrons of the heteroatoms E. The Lewis basicity of the group-15 heterobenzenes EC_5H_5 becomes weaker for the heavier elements E. The occupied π orbitals of the heterobenzene ring become gradually more polarized toward the five carbon atoms in the heavier arenes EC_5H_5 which induces stronger metal–carbon bonds in $M(\eta^6\text{-EC}_5\text{H}_5)_2$ and weaker metal–E bonds. The EDA calculations show that the nature of the M– EC_5H_5 bonding in $M(\eta^1\text{-EC}_5\text{H}_5)_6$ is similar to the M–CO bonding in $M(\text{CO})_6$. Both types of bonds have a slightly more covalent than electrostatic character. The π orbital interactions in the chromium and molybdenum complexes of CO and heterobenzene are more important than the σ interactions. This holds true also for the tungsten complexes of CO and the lighter heteroarenes while the σ - and π -bonding in the heavier $\text{W}(\eta^1\text{-EC}_5\text{H}_5)_6$ species have similar strength. The EDA results also show that the nature of the bonding in the sandwich complexes $M(\eta^6\text{-EC}_5\text{H}_5)_2$ is very similar to the bonding in the bis-benzene complexes $M(\eta^6\text{-C}_6\text{H}_6)_2$. The orbital interactions contribute for all metals and all arene ligands about 60% of the attractive interactions while the electrostatic attraction contributes about 40%. The largest contribution to the orbital term comes always from the δ orbitals. The calculations predict that the relative stability of the sandwich complexes $M(\eta^6\text{-EC}_5\text{H}_5)_2$ over the octahedral species $M(\eta^1\text{-EC}_5\text{H}_5)_6$ increases when E becomes heavier and it increases from W to Mo to Cr when $E = \text{N, P, As}$.

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1. Introduction

Heteroarenes of the group 15 elements EC_5H_5 ($E = \text{N–Bi}$) [1–4] are ambient ligands which can either bind η^1 via the σ -lone electron pair of atom E or η^6 through the six π electrons of the aromatic ring. The coordination chemistry of this class of ligands has systematically been investigated in experimental studies of

Elschenbroich [5–13] with the focus on the preparation of neutral compounds. The results show that the phosphinine ligand prefers the η^6 -binding mode in complexes with early metals of the first transition metal row while in complexes of late transition metals η^1 coordination via the lone pair is favored [5–7]. The group-6 metals chromium and molybdenum which are in the middle of the transition metals rows are particularly interesting because they exhibit a diverse binding mode with heteroarene ligands. Both coordination modes are experimentally observed for group-6 metals chromium [8–11] and molybdenum [12–14]. So far, for tungsten only η^1 -complexes with phosphinine and arsenine are experimentally verified [12,15]. The arsenine complexes of the group-6 elements are particularly interesting, because they exemplify the dichotomy of the bonding behaviour of the heteroarenes.

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Chromium binds to arsenine in the η^6 -mode exclusively, molybdenum exhibits both options η^1 and η^6 , while for tungsten only the η^1 coordination is observed [8,14].

Previously, we reported on the η^1 -bonding properties of EC_5H_5 in Lewis acid-base complexes with $\text{H}_3\text{B-L}$ and $\text{H}_2\text{B}^+\text{-L}$ and compared them with CO [16]. For EC_5H_5 not only the expected σ -donation in $\text{H}_2\text{B}^+\text{-L}$ was found, but the calculations also suggested a significant amount of out-of-plane π_{\perp} -donation for all heteroarenes which was more than three times as strong as for CO which is a very weak π -donor [17].

In this paper, we expand our studies to transition metal complexes of EC_5H_5 and compare their bonding properties with CO in η^1 -complexes while the η^6 -complexes are compared with benzene as ligand. The group-6 transition metals are ideal candidates for this study as they are known to bind with both binding modes towards the heteroarenes. Firstly, we will discuss the η^1 - and then the η^6 -bonding mode separately. This will be followed by a discussion of the reason for the preference of one mode over the other depending on the metal and/or the heteroatom in EC_5H_5 .

2. Methods

The geometries and bond dissociation energies have been calculated at the non-local DFT level of theory using the exchange functional of Becke [18] and the correlation functional of Perdew [19] (BP86). Scalar relativistic effects have been considered using the zero-order regular approximation (ZORA) [20]. Uncontracted Slater-type orbitals (STOs) were used as basis functions for the SCF calculations [21]. The basis sets for all atoms have triple-zeta quality augmented with two sets of polarization functions, i.e. two p functions on hydrogen, two d functions on the main-group elements and two f functions on the metals. An auxiliary set of s, p, d, f and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle [22]. This level of theory is denoted BP86/TZ2P. The latter calculations were carried out with the program package ADF 2003.01 [23]. All structures which are reported here are energy minima on the BP86/TZ2P potential energy surface by calculations of the Hessian matrices which have no imaginary frequencies.

The nature of the metal–ligand bonding has been investigated through the energy partitioning analysis (EDA) of the program package ADF based on the EDA method of Morokuma [24] and the extended transition state (ETS) partitioning scheme of Ziegler [25]. In the EDA method the bond dissociation energy D_e between the interacting fragments is partitioned into several contributions which can be identified as physically meaningful entities. In the present case the fragments are the naked transition metal M in the electronic reference singlet state with the proper valence configuration (η^1 : $(n)s^0(n-1)[d_{xy} d_{xz} d_{yz}]^6 [d_{z^2}d_{z^2-y^2}]^0$; η^6 : $(n)s^0(n-1)[d_{z^2}d_{z^2-y^2}d_{xy}]^6 [d_{xz} d_{yz}]^0$) and the ligand cages. The latter are $(\text{EC}_5\text{H}_5)_6$ for the η^1 -bonded complexes and $(\text{EC}_5\text{H}_5)_2$ for the η^6 -bonded species. We also calculated the hexacarbonyls $\text{M}(\text{CO})_6$ where the ligand cage is the set of the six CO ligands $(\text{CO})_6$. In the EDA, D_e is first separated into two major components ΔE_{prep} and ΔE_{int} :

$$-D_e = \Delta E_{\text{prep}} + \Delta E_{\text{int}} \quad (1)$$

ΔE_{prep} is the energy which is necessary to promote the fragments from their equilibrium geometry to the geometry which they have in the complex and from the electronic ground state to the reference state. In the present case, the former applies only for the ligand cage while the latter applies only for the metal atoms. ΔE_{int} is the instantaneous interaction energy between the fragments in the molecule. Note that it is ΔE_{int} and not D_e which should be used to identify the nature of the chemical bond. The interaction energy ΔE_{int} can be divided into three components:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{pauli}} + \Delta E_{\text{orb}} \quad (2)$$

ΔE_{elstat} gives the electrostatic interaction energy between the fragments which are calculated with a frozen electron density distribution in the geometry of the complex. It can be considered as an estimate of the *electrostatic* contribution to the bonding interactions. The second term ΔE_{pauli} in Eq. (1) gives the repulsive four-electron interactions between occupied orbitals. ΔE_{pauli} is calculated by enforcing the Kohn–Sham determinant of the molecule which results from superimposing the fragments to be orthonormal through antisymmetrization and renormalisation. The stabilizing orbital interaction term ΔE_{orb} is calculated in the final step of the analysis when the Kohn–Sham orbitals relax to their final form. The orbital term ΔE_{orb} can be considered as an estimate of the *covalent* contributions to the attractive interactions. Thus, the ratio $\Delta E_{\text{elstat}}/\Delta E_{\text{orb}}$ indicates the electrostatic/covalent character of the bond. The latter term can be partitioned further into contributions by the orbitals which belong to different irreducible representations of the interacting system. This makes it possible to calculate e.g. the contributions of σ and π bonding to a covalent multiple bond. More details about the method can be found in Ref. [23b]. Reviews of EDA results for metal–ligand bonds have been reported in reference [26].

3. Geometries and dissociation energies

3.1. $\text{M}(\eta^1\text{-EC}_5\text{H}_5)_6$ complexes

The optimized structures of the $\text{M}(\eta^1\text{-EC}_5\text{H}_5)_6$ ($\text{M} = \text{Cr, Mo, W}$; $\text{E} = \text{N, P, As, Sb, Bi}$) complexes have a pseudo-octahedral geometry with T_h -symmetry. Due to technical restrictions in the ADF package the T_h symmetry group cannot be applied. In the actual geometry optimization we used D_{2h} symmetry for the calculation of the heteroarene complexes. Inspection of the finally optimized geometries showed that they have T_h symmetry. The most important bond lengths and bond angles of $\text{M}(\eta^1\text{-EC}_5\text{H}_5)_6$ are shown in Table 1

Table 1

Calculated bond lengths [Å] and bond angles [°] of $\text{M}(\eta^1\text{-EC}_5\text{H}_5)_6$ with $\text{E} = \text{N, P, As, Sb, Bi}$ at D_{2h} symmetry^a at the BP86/TZ2P level. Experimental values in *italics*.

	N	P	As	Sb	Bi
Cr					
Cr–E	2.081	2.276	2.406	2.594	2.717
		2.265(10) ^b			
E–C2	1.376	1.747	1.867	2.063	2.159
C2–C3	1.386	1.392	1.388	1.388	1.384
C2–C4	1.400	1.399	1.402	1.404	1.406
C2–E–C2'	113.9	101.0	98.6	94.1	91.7
D_e	79.4	135.1	85.4	75.0	15.5
Mo					
Mo–E	2.170	2.410	2.518	2.692	2.793
		2.381 (8) ^c			
E–C2	1.380	1.745	1.866	2.061	2.156
C2–C3	1.386	1.392	1.388	1.388	1.384
C2–C4	1.401	1.399	1.402	1.404	1.406
C2–E–C2'	114.2	101.2	98.7	94.2	91.9
D_e	130.4	191.0	143.6	128.7	72.3
W					
W–E	2.153	2.408	2.512	2.690	2.787
		2.378(10) ^c			
E–C2	1.384	1.745	1.865	2.060	2.155
C2–C3	1.384	1.392	1.388	1.388	1.384
C2–C4	1.402	1.399	1.402	1.404	1.406
C2–E–C2'	114.0	101.4	99.0	94.5	92.2
D_e	177.3	241.1	188.0	169.5	107.1

^a ADF is not able to use T_h symmetry; however, complexes are practically T_h even though D_{2h} symmetry had to be applied.

^b Ref. [8].

^c Ref. [12].

Table 2

Calculated bond lengths [Å] of $M(\text{CO})_6$ at the BP86/TZ2P level and experimental values. Theoretically predicted bond dissociation energies D_e for loss of 6 CO in kcal/mol.

	Cr		Mo		W	
	R(Cr–C)	R(C–O)	R(Mo–C)	R(C–O)	R(W–C)	R(C–O)
R (calc.)	1.905	1.152	2.062	1.152	2.060	1.153
R (exp.)	1.914(3) ^a	1.140(2) ^a	2.063(3) ^b	1.145(2) ^b	2.058(3) ^b	1.148(3) ^b
D_e (calc.)	216.9		261.9		319.9	

^a Ref. [32].

^b Ref. [33].

which gives also the experimental M–P distances of the phosphinine complexes. The theoretical data at BP86/TZ2P and experimental values are in a good agreement. A very good agreement between theory and experiment is also found for the bond lengths of the hexacarbonyls $M(\text{CO})_6$ parent compounds which are given in Table 2.

Table 1 shows that the M–E bond lengths exhibit for all three metals the expected trend for E with $N < P < \text{As} < \text{Sb} < \text{Bi}$. The tungsten complexes have slightly shorter M–E bonds than the molybdenum species while the chromium complexes have clearly the shortest M–E bonds. The bond shortening of the third TM row compounds is due to relativistic effects, which is a well-known phenomenon in transition metal chemistry [27]. The bond dissociation energy (BDE) for all heteroarenes is smaller than for the corresponding carbonyls (Table 2). Phospinine is by far the strongest bonded η^1 ligand among the heteroarenes for all three metals. Pyridine binds weaker than arsine which results in an overall order of $\text{PC}_5\text{H}_5 > \text{AsC}_5\text{H}_5 > \text{NC}_5\text{H}_5 > \text{SbC}_5\text{H}_5 \gg \text{BiC}_5\text{H}_5$. The very weak M–BiC₅H₅ bond is consistent with the very long M–Bi bond distances. The BDE increases for the heavier metal $\text{Cr} < \text{Mo} < \text{W}$ for $M(\text{CO})_6$ and also for the $M(\text{EC}_5\text{H}_5)_6$ complexes.

3.2. $M(\eta^6\text{-EC}_5\text{H}_5)_2$ complexes

The geometry optimizations of the $M(\eta^6\text{-EC}_5\text{H}_5)_2$ complexes with different conformations of the heteroarene ligands gave the *syn* conformation shown in Fig. 1 which has C_{2v} -symmetry as the energetically lowest lying energy minima. The other conformations are <3 kcal/mol higher in energy than the C_{2v} (*syn*) form and shall not be discussed here. The most important bond lengths and angles of the $M(\eta^6\text{-EC}_5\text{H}_5)_2$ complexes which include the benzene complexes where E = CH are shown in Table 3.

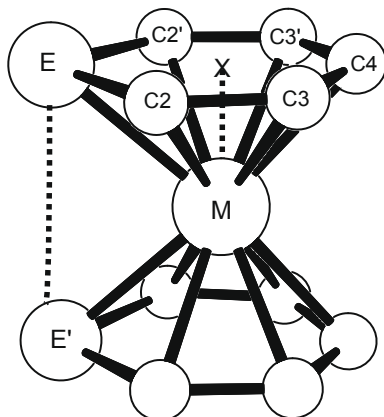


Fig. 1. Schematic representation of the calculated *syn* conformation of $M(\eta^6\text{-EC}_5\text{H}_5)_2$.

Table 3

Calculated bond lengths [Å] and bond angles [°] of $M(\eta^6\text{-EC}_5\text{H}_5)_2$ with E = N, P, As, Sb, Bi at C_{2v} -symmetry at the BP86/TZ2P level. Experimental values in *italics*.

	CH	N	P	As	Sb	Bi
Cr						
M–X	1.626 1.613°	1.631	1.607	1.590	1.569	1.558
M–E	2.159 2.150 ^a	2.159	2.435	2.548	2.749	2.859
E–E'	3.252	3.185	3.243	3.319	3.444	3.495
E–C2	1.420 1.423°	1.370	1.779	1.908	2.117	2.224
C2–C3	1.420	1.423	1.414	1.410	1.406	1.403
C3–C4	1.420	1.417	1.416	1.417	1.417	1.417
E–M–E'	97.7	95.1	83.5	81.3	77.6	75.4
C2–E–C2'	120.0	117.2	97.8	93.6	86.4	82.5
C3'–C3–C2–E	0.0	-0.2	2.0	5.5	11.1	14.9
D_e	67.4	56.4	84.2	85.6	91.4	94.2
Mo						
M–X	1.798	1.806	1.770	1.748	1.710	1.692
M–E	2.293	2.297	2.551	2.654	2.831	2.934
E–E'	3.596	3.544	3.583	3.620	3.555	3.515
C2–C3	1.424	1.374	1.784	1.914	2.132	2.250
C3–C4	1.424	1.425	1.418	1.415	1.413	1.409
C3–C5	1.424	1.420	1.420	1.421	1.422	1.423
E–M–E'	103.3	101.0	89.2	86.0	77.8	73.6
C2–E–C2'	120.0	117.1	98.0	93.8	86.3	82.0
C3'–C3–C2–E	0.0	-0.1	2.5	6.0	12.5	17.0
D_e	101.0	89.0	122.8	125.6	134.0	138.8
W						
M–X	1.798	1.803	1.764	1.739	1.702	1.687
M–E	2.293	2.299	2.555	2.664	2.847	2.951
E–E'	3.596	3.540	3.579	3.609	3.520	3.485
C2–C3	1.424	1.376	1.786	1.918	2.141	2.262
C3–C4	1.424	1.427	1.421	1.418	1.416	1.412
C3–C5	1.424	1.422	1.422	1.422	1.423	1.425
E–M–E'	103.3	100.7	88.9	85.3	76.4	72.4
C2–E–C2'	120.0	117.1	97.8	93.4	85.3	80.9
C3'–C3–C2–E	0.0	-0.1	3.1	7.3	14.4	18.8
D_e	138.9	124.7	160.9	163.8	173.7	179.9

^a Ref. [34].

The distance between the metal and the center point X is a significant parameter which is defined as the middle point of the rectangle with the corners C2, C2', C3 and C3' (Fig. 1). Table 3 shows that the trend of the M–X distance in the heteroarene complexes has the order $N > P > \text{As} > \text{Sb} > \text{Bi}$, i.e. the pyridine complexes have the longest M–X distance while the bismabenzene complexes have the shortest M–X distance. The M–E distances exhibit the expected trend for E: $N < P < \text{As} < \text{Sb} < \text{Bi}$. Note that the heavier heteroarenes are no longer planar. This becomes obvious from the calculated dihedral angle C3'–C3–C2–E which show a significant deviation from the value of 0° for a planar ring, particularly for E = Sb, Bi (Table 3).

The calculated bond dissociation energies follow the same trend as the M–X distances. This means that pyridine is the weakest η^6 bonded ligand while bismabenzene is the strongest bonded ligand. The trend in the BDE of the η^6 bonded heteroarene ligands which are heavier than pyridine is opposite to the trend which is found for the binding in the η^1 -mode. This is a very important result which will be further discussed below. The results in Table 3 show that benzene binds 10–15 kcal/mol stronger than pyridine in the group-6 transition metal complexes.

4. Bonding analysis

4.1. $M(\eta^1\text{-EC}_5\text{H}_5)_6$ complexes

The nature of the donor–acceptor bond in the heteroarene complexes was investigated with the energy decomposition analysis (EDA). The EDA results for the $M(\eta^1\text{-EC}_5\text{H}_5)_6$ complexes and for $M(\text{CO})_6$ which was calculated for comparison are shown in Tables 4–6. The calculations have been performed for the inter-

Table 4
EDA [kcal/mol] results for Cr(CO)₆ and Cr(η¹-EC₅H₅)₆ with E = N, P, As, Sb, Bi; EDA in D_{2h}-symmetrie with fragmentation in [Cr] + [L₆] at the BP86/TZ2P level.

Term	CO	N	P	As	Sb	Bi
ΔE _{int}	-415.6	-317.4	-327.4	-266.9	-242.1	-183.5
ΔE _{Pauli}	376.9	318.0	310.9	232.2	200.5	160.8
ΔE _{elstat} ^a	-303.3	-263.7	-267.4	-209.9	-192.9	-153.5
	(38.3%)	(41.5%)	(41.9%)	(42.0%)	(43.6%)	(44.6%)
ΔE _{orb} ^a	-489.1	-371.8	-370.9	-289.3	-249.7	-190.8
	(61.7%)	(58.5%)	(58.1%)	(58.0%)	(56.4%)	(55.4%)
a _g ^b (σ)	-123.5	-39.6	-72.9	-58.4	-53.9	-33.4
	(25.2%)	(10.7%)	(19.7%)	(20.2%)	(21.6%)	(17.5%)
b _{1g} ^b (π + π _⊥)	-115.1	-106.1	-94.8	-72.0	-60.3	-48.3
	(23.5%)	(28.6%)	(25.6%)	(24.9%)	(24.2%)	(25.3%)
b _{2g} ^b (π + π _⊥)	-115.1	-106.2	-94.8	-72.0	-60.3	-48.3
	(23.5%)	(28.6%)	(25.6%)	(24.9%)	(24.2%)	(25.3%)
b _{3g} ^b (π + π _⊥)	-115.1	-106.2	-94.8	-72.0	-60.3	-48.3
	(23.5%)	(28.6%)	(25.6%)	(24.9%)	(24.2%)	(25.3%)
a _u ^b	0.0	-0.2	-0.1	-0.1	0.0	0.0
	(0.0%)	(0.0%)	(0.0%)	(0.0%)	(0.0%)	(0.0%)
b _{1u} ^b (σ)	-6.8	-4.4	-4.5	-4.9	-4.9	-4.1
	(1.4%)	(1.2%)	(1.2%)	(1.7%)	(2.0%)	(2.2%)
b _{2u} ^b (σ)	-6.8	-4.5	-4.5	-4.9	-4.9	-4.2
	(1.4%)	(1.2%)	(1.2%)	(1.7%)	(2.0%)	(2.2%)
b _{3u} ^b (σ)	-6.8	-4.5	-4.5	-4.9	-4.9	-4.2
	(1.4%)	(1.2%)	(1.2%)	(1.7%)	(2.0%)	(2.2%)
σ	-143.8	-53.0	-86.4	-73.2	-68.7	-45.9
	(29.4%)	(14.3%)	(23.3%)	(25.3%)	(27.5%)	(24.1%)
π	-345.3	-318.6	-284.5	-216.1	-181.0	-144.8
	(70.6%)	(85.7%)	(76.7%)	(74.7%)	(72.5%)	(75.9%)
ΔE _{prep} [Cr] ^c	156.8	156.8	156.8	156.8	156.8	156.8
ΔE _{prep} [L ₆] ^d	41.9	81.2	35.4	24.7	10.4	11.2
ΔE _{prep}	198.7	238.0	192.3	181.6	167.2	168.0
D _e	216.9	79.4	135.1	85.4	75.0	15.5

^a The values in parentheses give the percentage contribution to the total attractive interaction.

^b The values in parentheses give the percentage contribution to the total orbital interactions.

^c Excitation energy of chromium from the ground state 3d⁵4s¹ to the references state 3([d_{xy}d_{xz}d_{yz}]⁶[d_{z²-y²]⁰]⁴s⁰).}

^d Geometrical distortion of the ligands.

actions between the naked transition metal M in the electronic reference state with the proper valence configuration (n)s⁰(n-1)-[d_{xy}d_{xz}d_{yz}]⁶[d_{z²-y²]⁰ and the ligand cage (EC₅H₅)₆ and (CO)₆ in the frozen geometry of the complex. The same procedure has previously been used in our theoretical studies of M(CO)₆ (M = Cr, Mo, W) [28] and Cr(η⁶-C₆H₆)₂ [29].}

The EDA data in Tables 4–6 suggest that the M–EC₅H₅ bonds have a slightly higher electrostatic and less covalent character than the M–CO bonds. This is revealed by comparing the percentage contributions of ΔE_{elstat} with the ΔE_{orb}. However, the differences between the two classes of compounds are not very big.

The orbital contribution ΔE_{orb} was further analyzed in terms of σ- and π-orbital interactions. Tables 4–6 give first the contributions which come from orbitals that belong to different irreducible representations of the D_{2h} point group (a_g, b_{1g}, b_{2g}, b_{3g}, a_u, b_{1u}, b_{2u}, b_{3u}). The latter are then summarized as σ- and π-orbital contributions. There are significant differences in the relative strength of σ- and π-orbital interactions between the chromium compound and the heavier homologues. Table 4 shows that, in the chromium complexes, the π-orbital interactions are much stronger than the σ-interactions which are for all compounds only <30% of the total orbital interactions. This holds for the hexacarbonyl and for the heteroarene complexes where the ΔE_{orb} term has always smaller percentage contributions from the σ-orbitals compared with Cr(CO)₆. The percentage contributions from the σ-orbitals to the ΔE_{orb} term become significantly larger in the molybdenum and tungsten complexes. Tables 5 and 6 show that the σ bonding becomes nearly as important as π bonding in the heavier heteroarene complexes M(η¹-EC₅H₅)₆ where E = P, As, Sb, Bi while the contribution of σ bonding in the pyridine complexes remains small. It holds for all metals that the pyridine ligand has the smallest percentage contribution to the orbital interactions.

The dissociation energies D_e which were discussed above are the sum of the interaction energy ΔE_{int} and the preparation energy ΔE_{prep}. The data in Tables 4–6 give notice of the importance of the preparation energy which is particularly large for the pyridine complexes. The calculated results show that the intrinsic interaction energy between the metal and the pyridine cage (NC₅H₅)₆ is only slightly less weaker than the bonding of the phosphinine ligands (PC₅H₅)₆, but the former has significantly larger preparation energies. However, the very low BDE of the bismabenzene ligands (BiC₅H₅)₆ comes from the intrinsically weak metal–ligand interactions.

The trend in the strength of the attractive terms ΔE_{elstat} and ΔE_{orb} which decrease in M(η¹-EC₅H₅)₆ in the order N > P > As > Sb > Bi [30] rationalizes the overall weakening of the metal–ligand bonds for the heavier heteroarenes. It can be explained with the weaker Lewis donor strength of the electron lone-pairs of heavier elements. Nitrogen as an element of the first octal row plays a particular role. The results in Tables 4–6 show that the very low BDE of the pyridine complexes comes from the large preparation energy, but not from intrinsically weak bonds.

4.2. M(η⁶-EC₅H₅)₂ complexes

The EDA calculations for the M(η⁶-EC₅H₅)₂ complexes were performed with C_{2v}-symmetry. The interacting fragments are the metal atom M with the electron configuration (n)s⁰(n-1)[d_{z²-y²]⁶[d_{xy}]⁰ and the ligands (η⁶-EC₅H₅)₂. The results are shown in Tables 7–9.}

The trend of the total interactions ΔE_{int} of the η⁶-bonded heteroarene complexes M(η⁶-EC₅H₅)₂ shows for E the order N < P < As < Sb < Bi (Tables 7–9). This is different to the trend which is calculated for the η¹-bonded complexes M(η¹-EC₅H₅)₆ where

Table 5EDA [kcal/mol] results for Mo(CO)₆ and Mo(η^1 -EC₅H₅)₆ with E = N, P, As, Sb, Bi; EDA in D_{2h}-symmetry with fragmentation in [Mo] + [L₆] at the BP86/TZ2P level.

Term	CO	N	P	As	Sb	Bi
ΔE_{int}	-404.5	-313.5	-331.6	-277.6	-256.9	-197.8
ΔE_{pauli}	398.7	392.2	352.9	284.0	256.0	219.1
$\Delta E_{\text{elstat}}^{\text{a}}$	-332.3	-319.3	-305.8	-248.8	-233.9	-193.7
	(41.4%)	(45.3%)	(44.7%)	(44.3%)	(45.6%)	(46.6%)
$\Delta E_{\text{orb}}^{\text{a}}$	-470.8	-386.4	-378.8	-312.8	-279.0	-223.2
	(58.6%)	(54.7%)	(55.3%)	(55.7%)	(54.4%)	(53.5%)
$a_{\text{g}}^{\text{b}}(\sigma)$	-153.8	-90.6	-135.3	-117.0	-117.3	-86.6
	(32.7%)	(23.5%)	(35.7%)	(37.4%)	(42.0%)	(38.8%)
$b_{1\text{g}}^{\text{b}}(\pi_{\parallel} + \pi_{\perp})$	97.2	-91.5	-75.0	-58.9	-48.0	-40.4
	(20.6%)	(23.7%)	(19.8%)	(18.8%)	(17.2%)	(18.1%)
$b_{2\text{g}}^{\text{b}}(\pi_{\parallel} + \pi_{\perp})$	97.2	-91.5	-75.0	-58.9	-48.0	-40.4
	(20.6%)	(23.7%)	(19.8%)	(18.8%)	(17.2%)	(18.1%)
$b_{3\text{g}}^{\text{b}}(\pi_{\parallel} + \pi_{\perp})$	97.2	-91.5	-75.0	-58.9	-48.0	-40.4
	(20.6%)	(23.7%)	(19.8%)	(18.8%)	(17.2%)	(18.1%)
a_{u}^{b}	0.0	-0.3	-0.1	-0.1	-0.1	0.0
	(0.0%)	(0.1%)	(0.0%)	(0.0%)	(0.0%)	(0.0%)
$b_{1\text{u}}^{\text{b}}(\sigma)$	-8.8	-7.0	-6.1	-6.3	-5.9	-5.1
	(1.8%)	(1.8%)	(1.6%)	(2.0%)	(2.1%)	(2.3%)
$b_{2\text{u}}^{\text{b}}(\sigma)$	-8.8	-7.0	-6.2	-6.3	-5.9	-5.1
	(1.8%)	(1.8%)	(1.6%)	(2.0%)	(2.1%)	(2.3%)
$b_{3\text{u}}^{\text{b}}(\sigma)$	-8.8	-7.0	-6.2	-6.3	-5.9	-5.1
	(1.8%)	(1.8%)	(1.6%)	(2.0%)	(2.1%)	(2.3%)
σ	-179.3	-111.7	-153.7	-135.9	-135.0	-102.0
	(38.1%)	(28.9%)	(40.6%)	(43.4%)	(48.4%)	(45.7%)
π	291.6	-274.4	-224.9	-176.8	-144.0	-121.2
	(61.9%)	(71.0%)	(59.4%)	(56.5%)	(51.6%)	(54.3%)
$\Delta E_{\text{prep}}[\text{Mo}]^{\text{c}}$	117.2	117.2	117.2	117.2	117.2	117.2
$\Delta E_{\text{prep}}[\text{L}_6]^{\text{d}}$	25.4	65.9	23.4	16.9	11.0	8.3
ΔE_{prep}	142.6	183.1	140.5	134.0	128.2	125.5
D_{e}	261.9	130.4	191.0	143.6	128.7	72.3

^a The values in parentheses give the percentage contribution to the total attractive interaction.^b The values in parentheses give the percentage contribution to the total orbital interactions.^c Excitation energy of molybdenum from the ground state 4d⁵5s¹ to the reference state 4([d_{xy}d_{xz}d_{yz}]⁶[d_{z²-y²]⁰5s⁰).}^d Geometrical distortion of the ligands.**Table 6**EDA [kcal/mol] results for W(CO)₆ and W(η^1 -EC₅H₅)₆ with E = N, P, As, Sb, Bi; EDA in D_{2h}-symmetry with fragmentation in [W] + [L₆] at the BP86/TZ2P level.

Term	CO	N	P	As	Sb	Bi
ΔE_{int}	-475.6	-378.1	-395.1	-335.8	-311.3	-246.3
ΔE_{pauli}	440.3	464.0	393.0	322.1	287.6	251.7
$\Delta E_{\text{elstat}}^{\text{a}}$	-397.0	-391.4	-366.8	-302.0	-282.1	-236.6
	(43.3%)	(46.5%)	(46.5%)	(45.9%)	(47.1%)	(47.5%)
$\Delta E_{\text{orb}}^{\text{a}}$	-518.9	-450.7	-421.3	-355.9	-316.9	-261.5
	(56.7%)	(53.5%)	(53.5%)	(54.1%)	(52.9%)	(52.5%)
$a_{\text{g}}^{\text{b}}(\sigma)$	-174.6	-112.0	-158.1	-141.0	-141.4	-110.2
	(33.7%)	(24.8%)	(37.5%)	(39.6%)	(44.6%)	(42.2%)
$b_{1\text{g}}^{\text{b}}(\pi_{\parallel} + \pi_{\perp})$	-103.9	-103.1	-79.0	-62.7	-50.1	-43.0
	(20.0%)	(22.9%)	(18.8%)	(17.6%)	(15.8%)	(16.5%)
$b_{2\text{g}}^{\text{b}}(\pi_{\parallel} + \pi_{\perp})$	-103.9	-103.2	-79.1	-62.8	-50.2	-43.1
	(20.0%)	(22.9%)	(18.8%)	(17.7%)	(15.9%)	(16.5%)
$b_{3\text{g}}^{\text{b}}(\pi_{\parallel} + \pi_{\perp})$	-103.9	-103.2	-79.1	-62.8	-50.2	-43.1
	(20.0%)	(22.9%)	(18.8%)	(17.7%)	(15.9%)	(16.5%)
a_{u}^{b}	0.0	-0.4	-0.1	-0.1	-0.1	-0.1
	(0.0%)	(0.1%)	(0.0%)	(0.0%)	(0.0%)	(0.0%)
$b_{1\text{u}}^{\text{b}}(\sigma)$	-10.9	-9.6	-8.6	-8.8	-8.2	-7.3
	(2.1%)	(2.1%)	(2.0%)	(2.5%)	(2.6%)	(2.8%)
$b_{2\text{u}}^{\text{b}}(\sigma)$	-10.9	-9.6	-8.6	-8.8	-8.3	-7.3
	(2.1%)	(2.1%)	(2.0%)	(2.5%)	(2.6%)	(2.8%)
$b_{3\text{u}}^{\text{b}}(\sigma)$	-10.9	-9.7	-8.6	-8.8	-8.3	-7.3
	(2.1%)	(2.1%)	(2.0%)	(2.5%)	(2.6%)	(2.8%)
σ	-207.2	-140.9	-183.9	-167.4	-166.2	-132.2
	(39.9%)	(31.2%)	(43.6%)	(47.0%)	(52.4%)	(50.5%)
π	-311.7	-309.5	-237.2	-188.4	-150.6	-129.3
	(60.1%)	(68.7%)	(56.3%)	(52.9%)	(47.5%)	(49.4%)
$\Delta E_{\text{prep}}[\text{Mo}]^{\text{c}}$	130.0	130.0	130.0	130.0	130.0	130.0
$\Delta E_{\text{prep}}[\text{L}_6]^{\text{d}}$	25.7	70.8	24.0	17.9	11.8	9.2
ΔE_{prep}	155.7	200.8	153.9	147.8	141.8	139.2
D_{e}	319.9	177.3	241.1	188.0	169.5	107.1

^a The values in parentheses give the percentage contribution to the total attractive interaction.^b The values in parentheses give the percentage contribution to the total orbital interactions.^c Excitation energy of tungsten from the ground state 5d⁴6s² to the reference state 5([d_{xy}d_{xz}d_{yz}]⁶[d_{z²-y²]⁰6s⁰).}^d Geometrical distortion of the ligands.

Table 7EDA [kcal/mol] results for Cr(*syn*- η^6 -EC₅H₅)₂ with E = CH, N, P, As, Sb, Bi; EDA in C_{2v}-symmetry with fragmentation in [Cr] + [L₂] at the BP86/TZ2P level.

Term	CH	N	P	As	Sb	Bi
ΔE_{int}	-255.3	-245.7	-278.8	-284.2	-299.3	-309.6
ΔE_{Pauli}	385.7	375.5	388.1	388.5	389.6	391.0
$\Delta E_{\text{elstat}}^a$	-257.8 (40.2%)	-239.1 (38.5%)	-266.8 (40.0%)	-272.7 (40.5%)	-279.5 (40.6%)	-282.4 (40.3%)
ΔE_{orb}^a	-383.2 (59.8%)	-382.1 (61.5%)	-400.1 (60.0%)	-400.0 (59.5%)	-409.4 (59.4%)	-418.3 (59.7%)
a_1^b	-185.0 (48.3%)	-183.3 (48.0%)	-202.7 (50.7%)	-209.9 (52.5%)	-223.2 (54.5%)	-232.9 (55.7%)
a_2^b	-30.1 (7.9%)	-31.4 (8.2%)	-26.3 (6.6%)	-25.2 (6.3%)	-24.3 (5.9%)	-23.8 (5.7%)
b_1^b	-138.4 (36.1%)	-136.4 (35.7%)	-142.7 (35.7%)	-140.0 (35.0%)	-140.2 (34.2%)	-141.5 (33.8%)
b_2^b	-29.8 (7.8%)	-31.0 (8.1%)	-28.4 (7.1%)	-24.9 (6.2%)	-21.7 (5.3%)	-20.0 (4.8%)
σ	-46.5 (12.1%)	-46.7 (12.3%)	-60.0 (15.0%)	-69.9 (17.5%)	-83.1 (20.3%)	-91.4 (21.9%)
π	-59.9 (15.6%)	-62.4 (16.4%)	-54.6 (13.6%)	-50.1 (12.5%)	-46.0 (11.2%)	-43.8 (10.5%)
δ	-276.9 (72.3%)	-272.7 (71.4%)	-285.5 (71.4%)	-280.0 (70.0%)	-280.3 (68.5%)	-283.0 (67.7%)
ΔE_{prep}	188.0	189.2	194.6	198.6	207.9	215.4
D_e	67.4	56.4	84.2	85.6	91.4	94.2

^a The values in parentheses give the percentage contribution to the total attractive interaction.

^b The values in parentheses give the percentage contribution to the total orbital interactions.

Table 8EDA [kcal/mol] results for Mo(*syn*- η^6 -EC₅H₅)₂ with E = CH, N, P, As, Sb, Bi; EDA in C_{2v}-symmetry with fragmentation in [Mo] + [L₂] at the BP86/TZ2P level.

Term	CH	N	P	As	Sb	Bi
ΔE_{int}	-230.3	-220.1	-255.4	-261.7	-280.8	-296.1
ΔE_{Pauli}	814.7	765.6	752.0	751.7	757.8	764.8
$\Delta E_{\text{elstat}}^a$	-510.6 (48.9%)	-482.6 (49.0%)	-485.1 (48.1%)	-490.2 (48.4%)	-496.1 (47.8%)	-500.6 (47.2%)
ΔE_{orb}^a	-534.4 (51.1%)	-503.2 (51.0%)	-522.4 (51.9%)	-523.1 (51.6%)	-542.4 (52.2%)	-560.3 (52.8%)
a_1^b	-315.76 (59.1%)	-287.45 (57.1%)	-297.15 (56.9%)	-300.25 (57.4%)	-313.13 (57.7%)	-325.32 (58.1%)
a_2^b	-46.2 (8.6%)	-45.8 (9.1%)	-44.1 (8.4%)	-44.3 (8.5%)	-46.5 (8.6%)	-47.8 (8.5%)
b_1^b	-126.6 (23.7%)	-124.3 (24.7%)	-130.0 (24.9%)	-129.7 (24.8%)	-133.4 (24.6%)	-137.7 (24.6%)
b_2^b	-45.9 (8.6%)	-45.6 (9.1%)	-51.2 (9.8%)	-48.8 (9.3%)	-49.4 (9.1%)	-49.4 (8.8%)
σ	-189.2 (35.4%)	-163.1 (32.4%)	-167.2 (32.0%)	-170.5 (32.6%)	-179.8 (33.1%)	-187.6 (33.5%)
π	-92.0 (17.2%)	-91.4 (18.2%)	-95.3 (18.2%)	-93.1 (17.8%)	-95.9 (17.7%)	-97.2 (17.3%)
δ	-253.2 (47.4%)	-248.6 (49.4%)	-259.9 (49.7%)	-259.5 (49.6%)	-266.7 (49.2%)	-275.5 (49.2%)
ΔE_{prep}	129.2	131.1	132.7	136.0	146.8	157.3
D_e	101.0	89.0	122.8	125.6	134.0	138.8

^a The values in parentheses give the percentage contribution to the total attractive interaction.

^b The values in parentheses give the percentage contribution to the total orbital interactions.

the bond strength increases from N to P but then it strongly decreases with the trend P > As > Sb > Bi (Tables 4–6). The breakdown of the total interaction energies into the repulsive Pauli term ΔE_{Pauli} and the attractive electrostatic interactions ΔE_{elstat} and orbital term ΔE_{orb} shows that the metal–ligand bonding in M(η^6 -EC₅H₅)₂ has a slightly larger electrostatic than covalent character. The percentage contributions of ΔE_{orb} and ΔE_{elstat} to ΔE_{int} in the η^6 -bonded heteroarene complexes M(η^6 -EC₅H₅)₂ are very similar to the values which are calculated for the η^1 -bonded species

Table 9EDA [kcal/mol] results for W(*syn*- η^6 -EC₅H₅)₂ with E = CH, N, P, As, Sb, Bi; EDA in C_{2v}-symmetry with fragmentation in [W] + [L₂] at the BP86/TZ2P level.

Term	CH	N	P	As	Sb	Bi
ΔE_{int}	-299.6	-287.3	-325.4	-332.6	-356.1	-374.0
ΔE_{Pauli}	395.2	374.3	432.6	449.7	494.2	515.5
$\Delta E_{\text{elstat}}^a$	-257.8 (37.1%)	-228.9 (34.6%)	-297.5 (39.2%)	-316.1 (40.4%)	-354.5 (41.7%)	-372.1 (41.8%)
ΔE_{orb}^a	-437.0 (62.9%)	-432.8 (65.4%)	-460.6 (60.8%)	-466.3 (59.6%)	-495.8 (58.3%)	-517.4 (58.2%)
a_1^b	-182.0 (41.7%)	-180.5 (41.7%)	-197.7 (42.9%)	-204.3 (43.8%)	-223.5 (45.1%)	-237.0 (45.8%)
a_2^b	-65.2 (14.9%)	-62.2 (14.4%)	-59.2 (12.8%)	-59.7 (12.8%)	-62.5 (12.6%)	-64.3 (12.4%)
b_1^b	-125.2 (28.6%)	-128.2 (29.6%)	-134.9 (29.3%)	-136.1 (29.2%)	-142.5 (28.7%)	-147.9 (28.6%)
b_2^b	-64.7 (14.8%)	-61.8 (14.3%)	-68.8 (14.9%)	-66.2 (14.2%)	-67.3 (13.6%)	-68.2 (13.2%)
σ	-59.9 (13.0%)	-52.3 (12.1%)	-62.7 (13.6%)	-68.2 (14.6%)	-81.1 (16.3%)	-89.1 (17.2%)
π	-129.8 (29.7%)	-124.0 (28.7%)	-128.0 (27.8%)	-125.9 (27.0%)	-129.8 (26.2%)	-132.5 (25.6%)
δ	-250.3 (57.3%)	-256.5 (59.3%)	-269.9 (58.6%)	-272.3 (58.4%)	-285.0 (57.5%)	-295.7 (57.2%)
ΔE_{prep}	166.7	162.7	164.5	168.8	182.4	194.1
D_e	138.9	124.7	160.9	163.8	173.7	179.9

^a The values in parentheses give the percentage contribution to the total attractive interaction.

^b The values in parentheses give the percentage contribution to the total orbital interactions.

M(η^1 -EC₅H₅)₆. Both classes of compounds show for the total interaction energy of the metal–ligand bonding of the three metals the trend Mo < Cr < W.

The increase in the strength of the attractive terms ΔE_{elstat} and ΔE_{orb} in the sandwich complexes M(η^1 -EC₅H₅)₆ in the order N < P < As < Sb < Bi offers an explanation for the difference to the octahedral complexes M(η^6 -EC₅H₅)₂ which show the opposite order. The bonding in the former complexes mainly takes place through the π electrons of the ligand which are delocalized over the ring atoms while the bonding in the latter takes place through the lone-pair electrons of the heteroatoms E. The occupied π orbitals become gradually more polarized toward the five carbon atoms in the heavier arenes EC₅H₅ which means that the metal–carbon bonds in M(η^6 -EC₅H₅)₂ become stronger while the metal–E bond becomes weaker. Since the former bonds are intrinsically stronger than the latter the polarization yields overall stronger metal–ligand bonding in the heavier sandwich complexes M(η^6 -EC₅H₅)₂.

The C_{2v} symmetry group does not allow for a straightforward analysis of the orbital interactions in terms of σ , π or δ symmetry. A previous EDA analysis of chromium bisbenzene Cr(η^6 -C₆H₆)₂ showed that the δ -orbital interactions are dominating ΔE_{orb} by more than 70% [29]. Hence, it is desirable to estimate the orbital contributions having σ , π or δ symmetry also for the heteroarene complexes M(η^6 -EC₅H₅)₂. This was done in the following way. The four irreducible representations in C_{2v}-symmetry are a_1 , a_2 , b_1 and b_2 . In a_1 there are contributions from σ (s , d_{z^2}), δ ($d_{x^2-y^2}$) and π (p_y); a_2 comprises π (d_{xz}) contributions; b_1 has contributions from δ (d_{xy}) and π (p_z); b_2 includes π (d_{yz}) and σ (p_z) contributions. The σ , π and δ contributions in the *syn*-heteroarene group-6 sandwich complexes may now become estimated with the following assumptions: first, the δ interactions in a_1 and b_1 have the same magnitude. Second, the strength of the σ interactions of the metal p_z orbital with the ligands is negligible. Third, the π interactions in a_1 and b_1 which come from the interactions of the p_x and p_y metal orbital also contribute little to the overall orbital interaction. Therefore, the σ interactions can be approximated as $a_1 - b_1$, the π interactions are approximately the sum of a_2 and b_2 and finally

Table 10

Calculated reaction energies [kcal/mol] for reaction 3 at the BP86/TZ2P level. The ZPE contributions and the thermal and entropy corrections were calculated at BP86/TZVP.

M	E	E				
		N	P	As	Sb	Bi
Cr	ΔE	23.0	50.9	-0.2	-16.4	-78.7
	ΔE^{ZPE}	20.0	47.4	-1.2	-16.9	-78.1
	ΔH^{298}	18.6	45.2	-3.6	-20.7	-82.9
	ΔG^{298}	-31.5	0.3	-46.5	-60.7	-119.1
Mo	ΔE	41.4	68.2	18.0	-5.3	-66.5
	ΔE^{ZPE}	36.8	55.8	16.1	-6.6	-68.2
	ΔH^{298}	36.4	53.5	12.7	-10.4	-71.2
	ΔG^{298}	-14.0	9.4	-28.0	-42.3	-108.3
W	ΔE	52.6	80.2	24.2	-4.2	-72.8
	ΔE^{ZPE}	47.7	65.0	20.9	-5.8	-73.4
	ΔH^{298}	47.5	62.9	17.6	-10.7	-78.4
	ΔG^{298}	-3.7	18.0	-26.5	-49.3	-114.6

the δ interactions are twice as strong as the b_1 interactions. We checked the validity of the above approximations using $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$ which can be analyzed with C_{2v} - and D_{6h} -symmetry. The results are given in Table S1 of Supporting Information. They show that the D_{6h} calculations give values of -46.5 kcal/mol for the σ contribution, -59.1 kcal/mol for the π contribution and -274.5 kcal/mol for the δ contribution. The latter values are very close to the σ , π and δ contributions which are estimated from the C_{2v} calculations (Table 7).

The breakdown of the orbital term ΔE_{orb} into σ , π and δ contributions shows that δ bonding is the most important orbital term in all heteroarene complexes $\text{M}(\eta^6\text{-C}_6\text{H}_6)_2$ as it was previously found in chromium bisbenzene [29]. The σ and π contributions to ΔE_{orb} are significantly smaller. The EDA results for the molybdenum complexes $\text{Mo}(\eta^6\text{-C}_6\text{H}_6)_2$ give somewhat larger σ contributions (Table 8) which are probably the result of a technical problem. The calculation of the bare Mo metal did not yield pure atomic orbitals but a hybrid of the 5s and 4d₂ AOs which yield larger σ and smaller δ bonding. The EDA results suggest that the heteroarene complexes $\text{M}(\eta^6\text{-C}_6\text{H}_6)_2$ are δ bonded molecules like chromium bisbenzene [29].

5. Stability of η^1 - versus η^6 -bonded complexes

A central question which is of uttermost interest for synthetic chemistry concerns the trend of the relative stabilities of the η^1 - and η^6 -bonded complexes $\text{M}(\eta^1\text{-EC}_5\text{H}_5)_6$ and $\text{M}(\eta^6\text{-EC}_5\text{H}_5)_2$ for the metals M and the elements E. In order to address this question we calculated the reaction energies of the interconversion process 3:

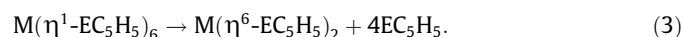


Table 10 shows the calculated reaction energies for reaction (3). Positive values indicate that the reaction is endothermic which means that the $\text{M}(\eta^1\text{-EC}_5\text{H}_5)_6$ complex is more stable than the $\text{M}(\eta^6\text{-EC}_5\text{H}_5)_2$ species. The calculated data give the electronic ener-

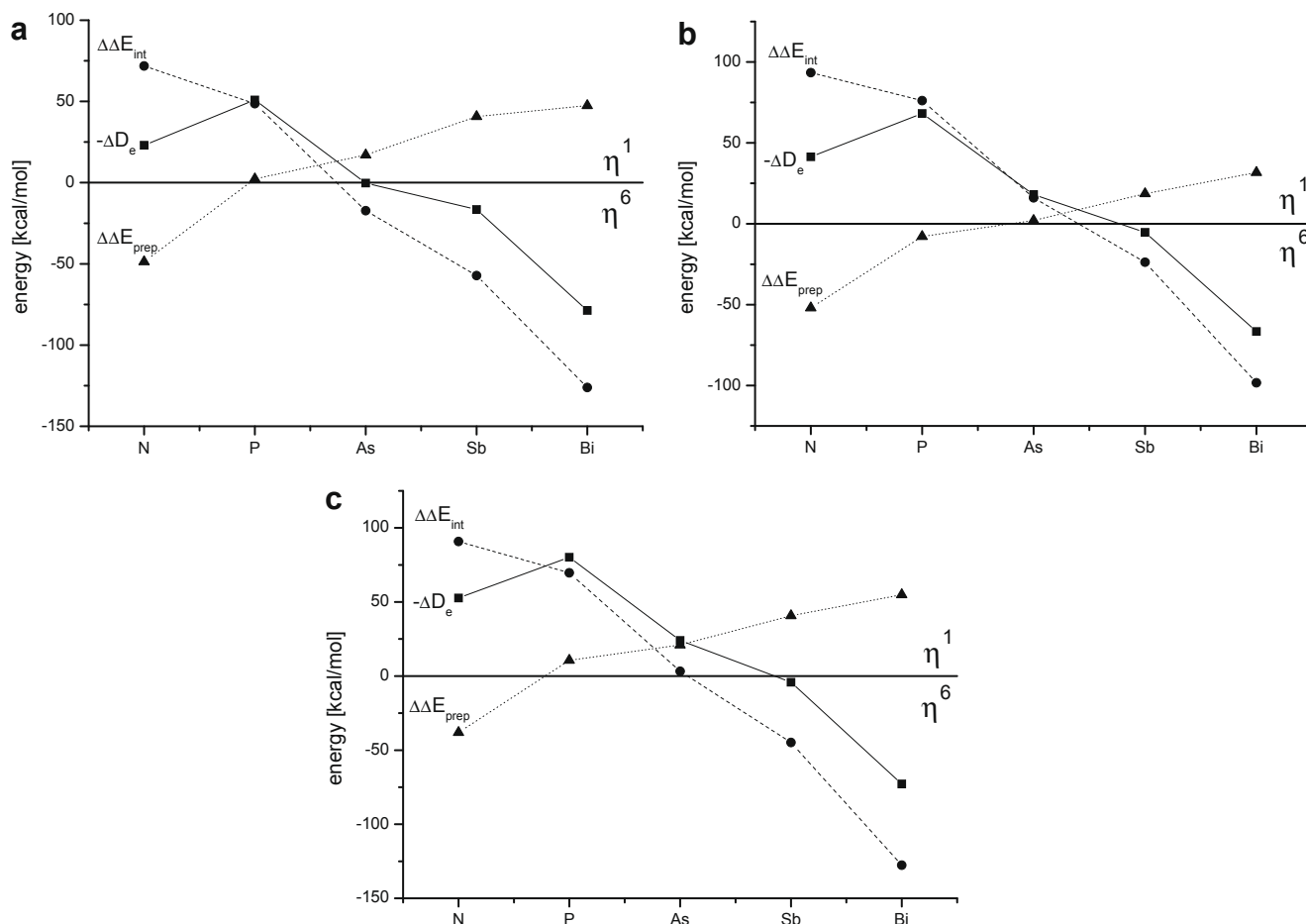


Fig. 2. Trend of the differences in the bond dissociation energies ΔD_e , the interaction energies $\Delta\Delta E_{\text{int}}$ and the preparation energies $\Delta\Delta E_{\text{prep}}$ between the sandwich complexes $\text{M}(\eta^6\text{-EC}_5\text{H}_5)_2$ and the octahedral complexes $\text{M}(\eta^1\text{-EC}_5\text{H}_5)_6$. Negative values indicate that $\text{M}(\eta^6\text{-EC}_5\text{H}_5)_2$ is more stable than $\text{M}(\eta^1\text{-EC}_5\text{H}_5)_6$. (a) Chromium complexes. (b) Molybdenum complexes. (c) Tungsten complexes.

gies E , the zero-point energy corrected values E^{ZPE} , the room-temperature adjusted enthalpies ΔH^{298} and finally the free reaction energies ΔG^{298} . It becomes obvious that the entropy is a very important factor for the driving force of reaction (3). The calculations suggest that the formation of the sandwich complexes $M(\eta^6\text{-EC}_5\text{H}_5)_2$ with $E = \text{N, P, As}$ may become favourable only because of entropy.

The data in Table 10 indicate the following trends for the relative stabilities of $M(\eta^1\text{-EC}_5\text{H}_5)_6$ and $M(\eta^6\text{-EC}_5\text{H}_5)_2$. For the heteroatoms E the stability of the η^1 -bonded species over the η^6 -bonded complexes decreases for all three metals in the order $\text{PC}_5\text{H}_5 > \text{NC}_5\text{H}_5 > \text{AsC}_5\text{H}_5 > \text{SbC}_5\text{H}_5 > \text{BiC}_5\text{H}_5$. The heaviest heteroarenes AsC_5H_5 , SbC_5H_5 and BiC_5H_5 are predicted to preferentially bind as sandwich complexes with the group-6 metals. For the metals M the stability of the $M(\eta^1\text{-EC}_5\text{H}_5)_6$ complexes over the sandwich form $M(\eta^6\text{-EC}_5\text{H}_5)_2$ increases with $\text{Cr} < \text{Mo} < \text{W}$ when $E = \text{N, P, As}$. The trend from Mo to W reverses for $E = \text{Sb, Bi}$ (Table 10). Note that the same trends are predicted by the four sets of energy and enthalpy values given in Table 10.

In order to rationalize the calculated trends for reaction (3) we analyzed the energy components of the EDA calculations in more detail. Fig. 2a–c show the plots of the difference between the calculated dissociation energies $-\Delta D_e$ of $M(\eta^1\text{-EC}_5\text{H}_5)_6$ and $M(\eta^6\text{-EC}_5\text{H}_5)_2$ for the three metals. Note that the $-\Delta D_e$ values are similar to the reaction energies E of reaction (3) (Table 10). Since the contributions of temperature, entropy and ZPE do not change the trend

for the different metals and different heteroarenes it is justified to consider only the $-\Delta D_e$. Fig. 2a–c show that the curves for the differences of the intrinsic interactions energies $\Delta\Delta E_{\text{int}}$ continuously decrease from N to Bi while the curve for the $-\Delta D_e$ values exhibits a maximum at $E = \text{P}$. It becomes obvious that the increase of $-\Delta D_e$ from N to P comes from the difference between the preparation energies $\Delta\Delta E_{\text{prep}}$. The higher propensity for η^1 -bonding of the phosphinine ligand compared with pyridine is thus not an intrinsic effect of the metal–ligand interactions but it comes from the preparation energies of the ligand fragments. As noted before, the $M(\eta^1\text{-NC}_5\text{H}_5)_6$ complexes have particularly large ΔE_{prep} values (Tables 4–6). The data suggest that the $M\text{--}E$ interactions exhibit a systematic trend toward preference for $M(\eta^6\text{-EC}_5\text{H}_5)_2$ when E becomes heavier $\text{N} < \text{P} < \text{As} < \text{Sb} < \text{Bi}$.

Figs. 3a–c give the trend of the energy components of the EDA. It becomes obvious that the sequence of the $\Delta\Delta E_{\text{int}}$ values is determined by the attractive components $\Delta\Delta E_{\text{elstat}}$ and $\Delta\Delta E_{\text{orb}}$ which both favour $M(\eta^6\text{-EC}_5\text{H}_5)_2$ over $M(\eta^1\text{-EC}_5\text{H}_5)_6$ when E becomes heavier. The differences of the Pauli repulsion between the metal atom and the ligands $\Delta\Delta E_{\text{Pauli}}$ show the opposite trend which is compensated by the effect of the attractive forces.

In order to compare the theoretically predicted intrinsic stabilities of the $M(\eta^6\text{-EC}_5\text{H}_5)_2$ and $M(\eta^1\text{-EC}_5\text{H}_5)_6$ complexes with experimental observations we summarize in Table 11 the results of synthetic efforts which have been reported so far. Note that the entries in Table 11 give only results for unsubstituted heteroa-

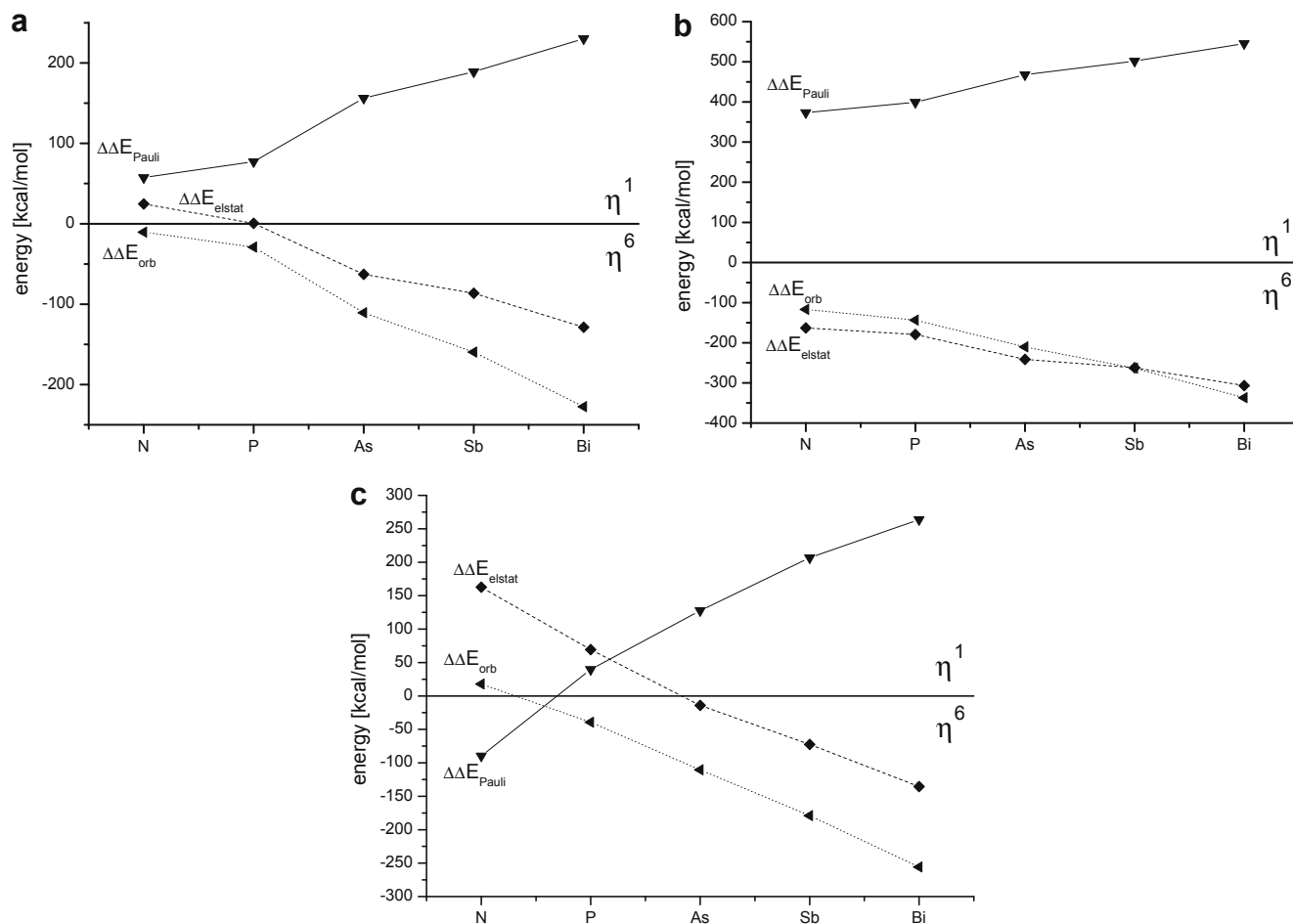


Fig. 3. Trend of the differences in the EDA terms $\Delta\Delta E_{\text{elstat}}$, $\Delta\Delta E_{\text{orb}}$ and $\Delta\Delta E_{\text{Pauli}}$ between the sandwich complexes $M(\eta^6\text{-EC}_5\text{H}_5)_2$ and the octahedral complexes $M(\eta^1\text{-EC}_5\text{H}_5)_6$. Negative values indicate that $M(\eta^6\text{-EC}_5\text{H}_5)_2$ is more favored than $M(\eta^1\text{-EC}_5\text{H}_5)_6$. (a) Chromium complexes. (b) Molybdenum complexes. (c) Tungsten complexes.

Table 11

Overview of the experimentally observed η^1 - and η^6 -bonded homoleptic heteroarene complexes of the group-6 elements.

M	E				
	N	P	As	Sb	Bi
Cr	η^6 [9]	η^1 [8]	η^6 [11]	–	–
Mo	–	η^1 [12]	η^1 [14] η^6 [14]	–	–
W	–	η^1 [12]	η^1 [14]	–	–

rene complexes. Numerous studies have been carried out for substituted analogues which are not considered in our work since they exhibit ligand-specific effect on the relative stability.

The experimentally observed [8,14] change in the binding mode of the arsenine complexes from chromium (η^6) to molybdenum (η^1 and η^6) to tungsten (η^1) agrees with the trend of the calculated energies (Table 10). The theoretical values for the free energy differences ΔG^{298} let one expect that the sandwich complexes $M(\eta^6\text{-AsC}_5\text{H}_5)_2$ should always be more stable than the $M(\eta^1\text{-EC}_5\text{H}_5)_6$ complexes. We think that the difference between theory and experiment comes partly from the effect of intermolecular forces and partly from the intrinsic error in the method. The calculations further suggest that the preference for the η^1 -binding mode over η^6 should be much stronger for phosphinine than for arsenine. This is in agreement with experimental observations. Until today, only $M(\eta^1\text{-PC}_5\text{H}_5)_6$ complexes of the group-6 metals could become isolated [8,12,31]. The only homoleptic group-6 complex with pyridine as ligand which has been synthesized so far is $\text{Cr}(\eta^1\text{-NC}_5\text{H}_5)_6$ [9]. This confers with the calculated ΔG^{298} value which is given in Table 10. In summary, the theoretically obtained energies given here accurately predict the trend of the relative stability of the $M(\eta^6\text{-EC}_5\text{H}_5)_2$ and $M(\eta^1\text{-EC}_5\text{H}_5)_6$ complexes which should be helpful for future experimental work.

6. Summary and conclusion

In this work, we analyzed the nature of the donor-acceptor bond of two possible binding modes of group 6 transition metals with heteroarenes EC_5H_5 (E = N, P, As, Sb, Bi). The η^1 -complexes $M(\eta^1\text{-EC}_5\text{H}_5)_6$ have been compared to the $M(\text{CO})_6$ (M = Cr, Mo, W) complexes and the η^6 -complexes $M(\eta^6\text{-EC}_5\text{H}_5)_2$ were compared with the bisbenzenes $M(\text{C}_6\text{H}_6)_2$.

The calculated bond dissociation energies of the pseudo-octahedral $M(\eta^1\text{-EC}_5\text{H}_5)_6$ complexes have the order for $E = \text{PC}_5\text{H}_5 > \text{AsC}_5\text{H}_5 > \text{NC}_5\text{H}_5 > \text{SbC}_5\text{H}_5 \gg \text{BiC}_5\text{H}_5$ and for $M = \text{Cr} < \text{Mo} < \text{W}$. All hexaheteroarenes bind weaker than CO in $M(\text{CO})_6$. Except for pyridine, which is the weakest η^6 -bonded ligand, the trend in the BDE of the sandwich $M(\eta^6\text{-EC}_5\text{H}_5)_2$ complexes is opposite to the trend of the $M(\eta^1\text{-EC}_5\text{H}_5)_6$ complexes $\text{NC}_5\text{H}_5 < \text{PC}_5\text{H}_5 < \text{AsC}_5\text{H}_5 < \text{SbC}_5\text{H}_5 < \text{BiC}_5\text{H}_5$. The opposite trend is explained with the different binding modes in $M(\eta^6\text{-EC}_5\text{H}_5)_2$ and $M(\eta^1\text{-EC}_5\text{H}_5)_6$. The bonding in the former complexes mainly takes place through the π electrons of the ligand which are delocalized over the ring atoms while the bonding in the latter takes place through the lone-pair electrons of the heteroatoms E. The Lewis basicity of the group-15 heteroarenes EC_5H_5 becomes weaker for the heavier elements E. The occupied π orbitals of the heterobenzene ring become gradually more polarized toward the five carbon atoms in the heavier arenes EC_5H_5 which means that the metal–carbon bonds in $M(\eta^6\text{-EC}_5\text{H}_5)_2$ become stronger while the metal–E bond becomes weaker. Since the former bonds are intrinsically stronger than the latter the polarization yields overall stronger metal–ligand bonding in the heavier sandwich complexes $M(\eta^6\text{-EC}_5\text{H}_5)_2$.

The EDA calculations show that the nature of the $M\text{-EC}_5\text{H}_5$ bonding in $M(\eta^1\text{-EC}_5\text{H}_5)_6$ is similar to the $M\text{-CO}$ bonding in $M(\text{CO})_6$. Both types of bonds have a slightly more covalent than

electrostatic character. The π orbital interactions in the chromium and molybdenum complexes of CO and heterobenzene are more important than the σ interactions. This holds true also for the tungsten complexes of CO and the lighter heteroarenes while the σ - and π -bonding in the heavier $W(\eta^1\text{-EC}_5\text{H}_5)_6$ species have similar strength. The EDA results also show that the nature of the bonding in the sandwich complexes $M(\eta^6\text{-EC}_5\text{H}_5)_2$ is very similar to the bonding in the bisbenzene complexes $M(\eta^6\text{-C}_6\text{H}_6)_2$. The orbital interactions contribute for all metals and all arene ligands about 60% of the attractive interactions while the electrostatic attraction contributes about 40%. The largest contribution to the orbital term comes always from the δ orbitals.

The calculations predict that the relative stability of the sandwich complexes $M(\eta^6\text{-EC}_5\text{H}_5)_2$ over the octahedral species $M(\eta^1\text{-EC}_5\text{H}_5)_6$ increases when E becomes heavier and it increases from W to Mo to Cr when E = N, P, As.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.10.018](https://doi.org/10.1016/j.jorganchem.2008.10.018).

References

- [1] A.J. Ashe III, J. Am. Chem. Soc. 93 (1971) 3293.
- [2] A.J. Ashe III, J. Am. Chem. Soc. 93 (1971) 6690.
- [3] A.J. Ashe III, M.D. Gordon, J. Am. Chem. Soc. 93 (1972) 7596.
- [4] A.J. Ashe III, Tetrahedron Lett. (1976) 415.
- [5] C. Elschenbroich, M. Nowotny, B. Metz, W. Massa, J. Graulich, K. Biehler, W. Sauer, Angew. Chem., Int. Ed. Engl. 30 (1991) 547.
- [6] C. Elschenbroich, M. Nowotny, A. Behrendt, K. Harms, S. Wocadlo, J. Pebler, J. Am. Chem. Soc. 116 (1994) 6217.
- [7] C. Elschenbroich, M. Nowotny, A. Behrendt, W. Massa, S. Wocadlo, Angew. Chem. 104 (1992) 1388.
- [8] C. Elschenbroich, M. Nowotny, J. Kroker, A. Behrendt, W. Massa, S. Wocadlo, J. Organomet. Chem. 459 (1993) 157.
- [9] C. Elschenbroich, J. Koch, M. Wünsch, W. Massa, G. Baum, G. Stork, Chem. Ber. 121 (1988) 1983.
- [10] C. Elschenbroich, F. Bär, E. Bilgar, D. Mahrwald, M. Nowotny, B. Metz, Organometallics 12 (1993) 3373.
- [11] (a) C. Elschenbroich, J. Kroker, W. Massa, M. Wünsch, A.J. Ashe III, Angew. Chem. 98 (1986) 562; (b) C. Elschenbroich, Angew. Chem., Int. Ed. Engl. 25 (1986) 571; (c) C. Elschenbroich, J. Kroker, M. Nowotny, A. Behrendt, B. Metz, K. Harms, Organometallics 18 (1999) 1495.
- [12] C. Elschenbroich, S. Voß, O. Schiemann, A. Lippek, K. Harms, Organometallics 17 (1998) 4417.
- [13] J. Six, Diploma Thesis, Marburg, 1999.
- [14] C. Elschenbroich, J. Six, K. Harms, Dalton Trans. 92 (2008).
- [15] C. Elschenbroich, personal communication.
- [16] S. Erhardt, G. Frenking, Chem. Eur. J. 12 (2006) 4620.
- [17] A. Diefenbach, F.M. Bickelhaupt, G. Frenking, J. Am. Chem. Soc. 122 (2000) 6449.
- [18] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
- [19] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.
- [20] (a) C. Chang, M. Pelissier, Ph. Durand, Phys. Scr. 34 (1986) 394; (b) J.-L. Heully, I. Lindgren, E. Lindroth, S. Lundquist, A.-M. Martensson-Pendrill, J. Phys. B 19 (1986) 2799; (c) E. van Lenthe, E.J. Baerends, J.G. Snijders, J. Chem. Phys. 99 (1993) 4597; (d) E. van Lenthe, E.J. Baerends, J.G. Snijders, J. Chem. Phys. 105 (1996) 6505; (e) E. van Lenthe, R. van Leeuwen, E.J. Baerends, J.G. Snijders, Int. J. Quantum Chem. 57 (1996) 281.
- [21] J.G. Snijders, E.J. Baerends, P. Vernooijs, At. Nucl. Data Tables 26 (1982) 483.
- [22] J. Krijn, E.J. Baerends, Fit Functions in the HFS-Method, Internal Report (in Dutch), Vrije Universiteit Amsterdam, The Netherlands, 1984.
- [23] (a) F.M. Bickelhaupt, E.J. Baerends, Rev. Comput. Chem. 15 (2000) 1; (b) G. te Velde, F.M. Bickelhaupt, E.J. Baerends, S.J.A. van Gisbergen, C. Fonseca Guerra, J.G. Snijders, T. Ziegler, J. Comput. Chem. 22 (2001) 931.
- [24] K. Morokuma, J. Chem. Phys. 55 (1971) 1236.
- [25] T. Ziegler, A. Rauk, Theor. Chim. Acta 46 (1977) 1.

- [26] (a) G. Frenking, K. Wichmann, N. Fröhlich, C. Loschen, M. Lein, J. Frunzke, V.M. Rayón, *Coord. Chem. Rev.* 238–239 (2003) 55;
(b) M. Lein, G. Frenking, *Theory and Applications of Computational Chemistry: The First 40 Years*, in: C.E. Dykstra, G. Frenking, K.S. Kim, G.E. Scuseria (Eds.), Elsevier, Amsterdam, 2005, p. 367.
- [27] N. Fröhlich, G. Frenking, *Chem. Rev.* 100 (2000) 717.
- [28] A. Diefenbach, F.M. Bickelhaupt, G. Frenking, *J. Am. Chem. Soc.* 122 (2000) 6449.
- [29] V.M. Rayón, G. Frenking, *Organometallics* 22 (2003) 3304.
- [30] The ΔE_{elstat} value of $\text{Cr}(\eta^1\text{-NC}_5\text{H}_5)_6$ is slightly smaller than that of $\text{Cr}(\eta^1\text{-PC}_5\text{H}_5)_6$ but otherwise the trend is the same.
- [31] P. Le Floch, *Coord. Chem. Rev.* 250 (2006) 627.
- [32] P.S. Braterman, *Metal Carbonyl Spectra*, Academic, London, 1979.
- [33] L.H. Jones, R.S. McDowell, M. Goldblatt, *Inorg. Chem.* 8 (1969) 2349.
- [34] A. Haaland, *Acta Chem. Scand.* 19 (1965) 41.