Russian Chemical Bulletin, International Edition, Vol. 54, No. 9, pp. 2055—2066, September, 2005

Lithiation of tricarbonylchromium complexes with polyaromatic carbo- and heterocyclic ligands. DFT study*

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The reactions of tricarbonylchromium complexes of polyaromatic carbo- and heterocyclic derivatives with Bu^nLi was studied by the density functional theory. The kinetic and thermodynamic factors for controlling the direction and selectivity of metallation were calculated for the model biphenylenetricarbonylchromium complex. Both approaches indicate that lithiation occurs exclusively at the aromatic ring bonded to the transition metal, which agrees with experimental data, while the selectivity inside this ring is determined more exactly by the thermodynamic factor. The solvation effects were simulated for the lithium salt of the tricarbonylnaphthalenechromium complex in which the lithium atom is localized in position 1 of the coordinated ring. The simulation showed the stable coordination of the lithium atom with two THF molecules, and the addition of the next THF molecule is thermodynamically unfavorable. The results of calculation of the relative energies for all possible THF-solvated lithium salts of the tricarbonylchromium complexes of biphenyl, naphthalene, biphenylene, and dibenzothiophene indicate that the difference in energies $\Delta E \leq 1$ kcal mol^{-1} corresponds to the experimentally observed absence of selectivity, while the difference more than 2.5 kcal mol^{-1} corresponds to the selectivity of the reaction. No additional coordination of the lithium atom to the free electron pair of the heteroatom was observed for the sulfur-containing dibenzothiophene complex. Similar calculations show that double metallation in the dibenzothiophene complex occurs at positions 1 and 4. The developed approach enables one to predict the direction and selectivity of metallation reactions of transition metal complexes with different arenes.

Key words: arenetricarbonylchromium complexes, polyaromatic and heterocyclic ligands, lithiation, quantum chemical calculations, density functional theory.

Tricarbonylchromium π-complexes with aromatic carbo- and heterocyclic ligands are widely used currently in the organic and organometallic chemistry for both catalytic and synthetic purposes. Their use provides fine regio- and stereochemical control of organic reactions, including that in the synthesis of optically active compounds, due to the activating influence of the $Cr(CO)_3$ group with specific steric and electronic properties.

This important and large class of organometallic compounds were studied in most detail for carbocyclic monoaromatic ligands and, to a less extent, for polyaromatic carbo- and heterocyclic ligands. All available data are discussed in detail in numerous reviews.[1]

One of the most important synthetic reactions of arenetricarbonylchromium complexes is their lithiation, *i.e.*, replacement of the hydrogen atom by the lithium atom in the reaction of the complexes with alkyllithium compounds RLi.

This reaction[2] for the monocyclic complexes occurs with classical organolithium bases (most frequently, with butyllithium) at low temperatures (–78 °C) in ethereal solvents.

Further, the organolithium derivative (without intermediate isolation) reacts with an electrophilic agent RX (R = D, Me, Me_3Si, Me_3Sn, *etc.*). Depending on the stated synthetic problem, the complex decomposes under the action of light or using oxidants to form R-substituted complexes or free ligands. The R substituent in both the complex that formed and ligand is directed to the same position as lithium.[3]

The most important feature of lithiation of the tricarbonylchromium π-complexes with polyaromatic carbocyclic ligands is regioselectivity, namely, lithiation is rigidly directed to the aromatic ring, which is bonded to the transition metal. This occurs because the pK_a of the aromatic ring activated due to linking with the electrone-

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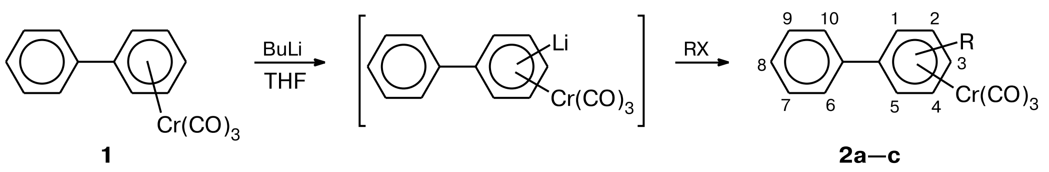
* Dedicated to Academician N. S. Zefirov on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1993—2003, September, 2005.

Scheme 1



gative bond $Cr(CO)_3$ is nearly seven units lower[1a] than that of the non-coordinated moiety of the polycycle.

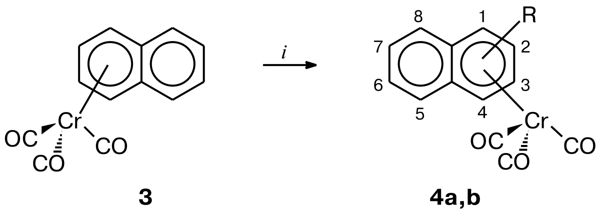
However, within the metal-coordinated aromatic ring, lithium—carbon bond formation is non-regioselective in the general case, *i.e.*, occurs at all possible positions of the coordinated aromatic ring.

Lithiation followed by the interaction of the lithium derivative of η^6-biphenyltricarbonylchromium **1** with an electrophilic agent (RX = D_2O, MeI) proceeds at all of the three possible positions (*ortho*, *meta,* and *para*) of the coordinated ring to form compounds **2a**, **2b**, and **2c**, respectively[4] (Scheme 1).

As a whole, the regularities of lithiation of the tricarbonylchromium complexes of condensed aromatic ligands[5—10] are similar. For instance, tricarbonylnaphthalenechromium complex **3** is metallated also regioselectively, *i.e.*, only at the coordinated aromatic ring.[7,8]

However, if exotic sterically hindered organolithium derivatives[7] are not used for the lithiation of **3**, then no regioselectivity is observed inside the coordinated ring and, as a result, the interaction with electrophile RX produces a mixture of both possible α- and β-R-derivatives **4a** and **4b** with some predomination of the β-isomer (see Schemes 1 and 2; Table 1).

Scheme 2



i. 1) BuLi, THF, –78 °C; 2) RX

R = D, Me, Me_3Si, Me_3Sn, *etc*.

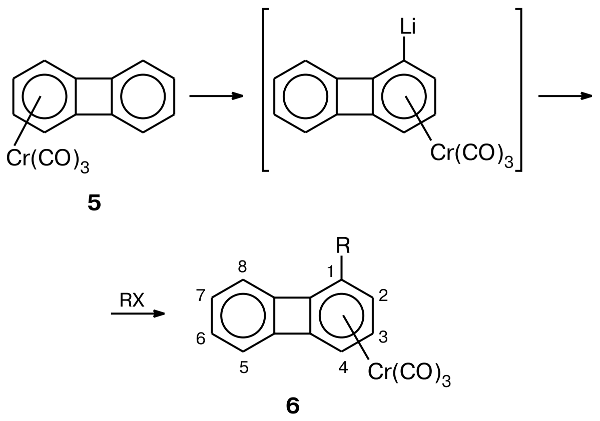
However, the rigidly regioselective metallation (BuLi, THF, –78 °C) of the tricarbonylchromium complex of polyaromatic carbocyclic biphenylene **5** [5,10] is also known (Scheme 3), when metallation proceeds exclusively to position 1 to form complex **6**. Nowadays, reasons for this difference between the tricarbonylchromium complexes of biphenylene, on the one hand, and biphenyl and naphthalene, on the other hand, remain unclear.

Table 1. Yield and selectivity of the reactions of the lithium salts of tricarbonyl-η^6-diphenyl- and tricarbonyl-η^6-naphthalenechromium with electrophilic agents at –78 °C in THF

RX	Yield of **4a**+**4b** (%)	Ratio **4a** : **4b**	Yield of **2a**+**2b**+**2c** (%)	Ratio **2a** : **2b** : **2c**
D_2O	87	44 : 56	84	10 : 65 : 25
CH_3I	66	36 : 64	18	12 : 58 : 30
Me_3SnCl	74	30 : 70		
Me_3SiCl	45	34 : 76		
I_2	20	*		

* Only isomer **4b** is formed.

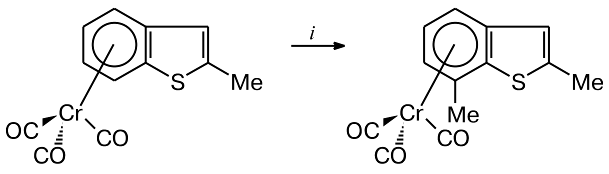
Scheme 3



R = D, Me

The situation changes dramatically in the presence of a heteroatom (N, S, O, *etc.*) as the substituent in the coordinated six-membered ring of the complex. In this case, the coordinated ring is metallated exclusively at the *ortho*-position relative to the heteroatom, if the substituent creates no significant steric hindrance.[11,12] It is commonly accepted that this selectivity is explained by an additional stabilizing interaction of the lithium atom, which attacks the complex of an organolithium compound, with a free electron pair of the heteroatom. An example of lithiation at the *ortho*-position relative to the heteroatom for the 2-methylbenzothiophenetricarbonylchromium complex[11d] is presented in Scheme 4.

Scheme 4



i. 1) BuLi, THF, –78 °C; 2) MeI

We have previously[13] shown that the lithiation of the tricarbonylchromium complex of heterocyclic polyaromatic dibenzothiophene **7** is rigidly regioselective. It occurs at the coordinated ring only and, in this ring, at position 4 only to form compound **8** (Scheme 5).

Although the existence of lithium derivatives of arenetricarbonylchromium complexes were reliably proved by IR[14,15] and NMR spectroscopy,[15] they are very unstable and reactive, which prevented their isolation and study by different physicochemical methods, including X-ray diffraction analysis. We found no published data on the X-ray determination of the structure of a lithium derivative of the tricarbonylchromium complex with an aromatic ligand, although simple lithium derivatives of organic mono- and polyaromatic[16] compounds, including those containing a heteroatom,[17] were intensely studied by different methods (including X-ray diffraction) in both the absence and presence of additional coordinating ligands (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, THF, diethyl ether, *etc.*).

Thus, it is evident that alternative, in particular, quantum chemical, methods should be used to study the structure and reactivity of lithium derivatives of the arenetricarbonylchromium complexes.

Analysis shows that the DFT calculation of the geometric, conformational, and energy parameters of the tricarbonylchromium complexes with polyaromatic ligands, such as naphthalene,[8] dibenzothiophene,[13] biphenylene,[10] and fluoranthene,[18,19] gives results that agree well with the experimental data. Such parameters as distances and angles between atoms (*cf.* X-ray diffraction data), rotation barriers to the tricarbonylchromium group, and ^{1}H and ^{13}C NMR chemical shifts are reliably described.

The density functional theory has well recommended itself for the description of the kinetic and thermodynamic parameters of several chemical reactions and processes that occur in these complexes (metallotropic and rebound rearrangements, elimination of ligands, complex formation, *etc.*).[8,10,13,18–20]

The purpose of this work is to develop the DFT-based calculated criterion for determining the direction of lithiation of the tricarbonylchromium complexes with aromatic ligands and to study the structure of the resulting lithium salts. This approach can be a theoretical basis for further experimental studies of the reactivity and structural features of this important class of very unstable compounds.[21]

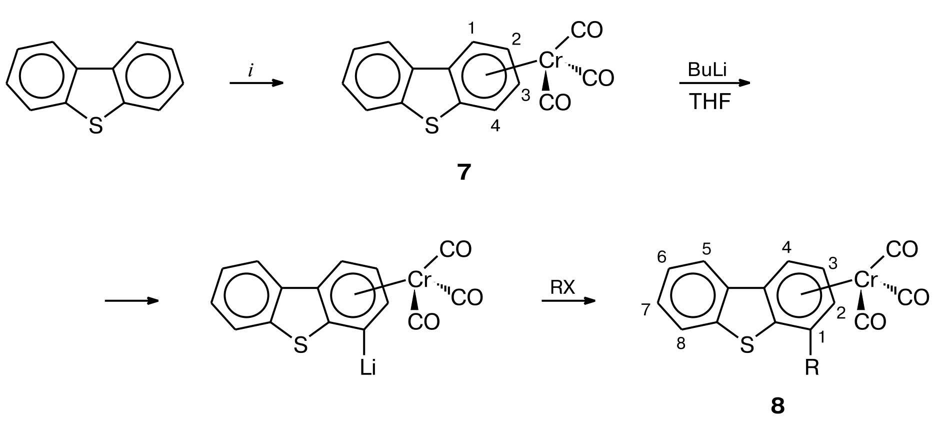
Calculation Method

All calculations were performed with the non-empirical non-local PBE functional[22] in the extended split TZ2p basis set using the PRIRODA program complex[23] on an MVS 1000M computer cluster at the Interdepartment Supercomputer Center (Moscow). Corrections for zero-point vibration energies were calculated in the harmonic approximation. The types of stationary points (minima and transition states (TS) on the potential energy surface (PES)) were determined by analysis of Hessians. Reaction routes were plotted by the intrinsic reaction coordinate (IRC) method.[24]

Results and Discussion

When assuming that the interaction of the lithium derivative with an electrophile does not change the site of

Scheme 5



i. $L_3Cr(CO)_3$; L = NH_3, MeCN, Py

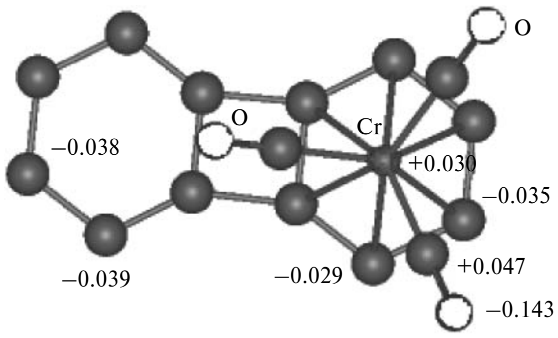


Fig. 1. Charge distribution in a molecule of **5**.

incorporation of substituent R,[3,25] which substitutes the lithium atom, we have to determine the parameter, whose numerical value shows that one of the positions in the coordinated ring of the ligand is preferentially attacked by a Bu^{n}Li molecule. As a result, the lithium atom and then substituent R enter into this position. In this case, this parameter can be considered as a criterion for the direction of metallation.

Complex **5** was chosen as a testing compound, because it is metallated exclusively at position 1 of the coordinated ring. This facilitates considerably data interpretation and search for the calculated criterion.

At the first stage, we considered the optimized electronic structure of compound **5** to determine a possible direction of the attack of Bu^{n}Li (Fig. 1).

The presented electron density distribution (see Fig. 1) calculated by the Hirshfeld method[26] shows that the negative charge is mainly concentrated on the carbonyl groups, while the negative charges on the carbon atoms of the non-coordinated and coordinated rings are similar. Therefore, the electron density on different atoms cannot serve as a criterion for Li$^+$ localization in the corresponding lithium salt and cannot thus determine the regioselectivity of metallation.

At the next stage, we calculated the structure and energy parameters of all molecular systems (pre-reaction complex **PC**, transition state **TS**, and reaction products **Pr**), which represent stationary points on the coordinate of the reaction of **5** with butyllithium resulting in the cleavage and formation of new bonds. Different types of energies (E_{tot} is the total energy, E^0 is the energy with allowance for the correction for the zero-point vibration energy, and G is the free Gibbs energy under normal conditions) were determined during the calculation of the reactants, pre-reaction complexes, transition states, and reaction products.

Table 2. Calculated energy parameters for the reaction of complex **5** with Bu^{n}Li affording 1-Li-**5**, 2-Li-**5**, and 5-Li-**5** for the pre-reaction complexes (**PC**), transition states (**TS**), and products (**Pr**)

Molecular system	E_{tot}/au	ΔE	ΔE^0	ΔG
		kcal mol^{-1}		
PC1	−2010.929340	0.0	0.0	0.0
TS1	−2010.911340	11.30	8.66	7.85
Pr1	−2010.955472	−16.40	−15.41	−16.33
PC2	−2010.928972	0.23	0.12	−0.19
TS2	−2010.909401	12.51	9.67	9.31
Pr2	−2010.951005	−13.60	−12.75	−11.84
PC5	−2010.931041	−1.07	−1.44	−1.65
TS5	−2010.901236	17.64	14.64	14.06
Pr5	−2010.940539	−7.03	−6.24	−7.78

Note: E_{tot} is the total energy; ΔE is the relative total energy ignoring zero-point vibrations; ΔE^0 is the relative energy with allowance for zero-point vibrations; ΔG is the relative free Gibbs energy under normal conditions; ΔE, ΔE°, and ΔG are the energies relative to **PC1**.

The data of calculation for the lithiation of **5** to positions 1, 2, and 5 with formation of lithium derivatives 1-Li-**5**, 2-Li-**5**, and 5-Li-**5** (see Fig. 2) are given in Table 2. In all cases, the pre-reaction complex is a structure with an additional coordination interaction of the lithium atom and oxygen atom of one of the carbonyl groups (Fig. 1). This stabilizing interaction is retained further in the corresponding final lithium derivatives. The interaction of alkaline metal cations with the carbonyl groups in the tricarbonylchromium complexes of aromatic anions is well known and was studied in detail using IR spectroscopy.[14,21] The transition states exhibit a gradual elongation of the attacked C—H bond and then removal of the H atom from the C atom and its replacement by the Li atom to form an organolithium derivative and butane. To avoid the considerable complication of calculations, we ignored a possible solvation of the structures involved in this reaction by solvent molecules.

It is seen that the activation barrier of lithiation to positions 1 and 2 of the coordinated ring is ~9 kcal mol^{-1} for all types of energies (**TS1—PC1** and **TS2—PC2**, respectively). This value remains virtually unchanged at different reaction directions (barrier of the reaction to position 1 is lower than that of the reaction to position 2 only by ~1 kcal mol^{-1}). For lithiation at position 5 of the non-coordinated ring, the activation barrier is ~16 kcal mol^{-1}. Calculation for another possible position of the lithium atom in the non-coordinated ring (position 6) gave an increase in the barrier by ~1 kcal mol^{-1} (omitted in Table 2).

Therefore, the kinetic factor determined by the activation barrier of the lithiation reaction rather well predicts the regioselectivity of metallation at the coordinated ring but is poorly appropriate for predicting the lithiation position in this ring.

The relative energies of different types for isomeric 1- and 2-lithium derivatives **5** (ΔE, ΔE^0, and ΔG, *i.e.*,

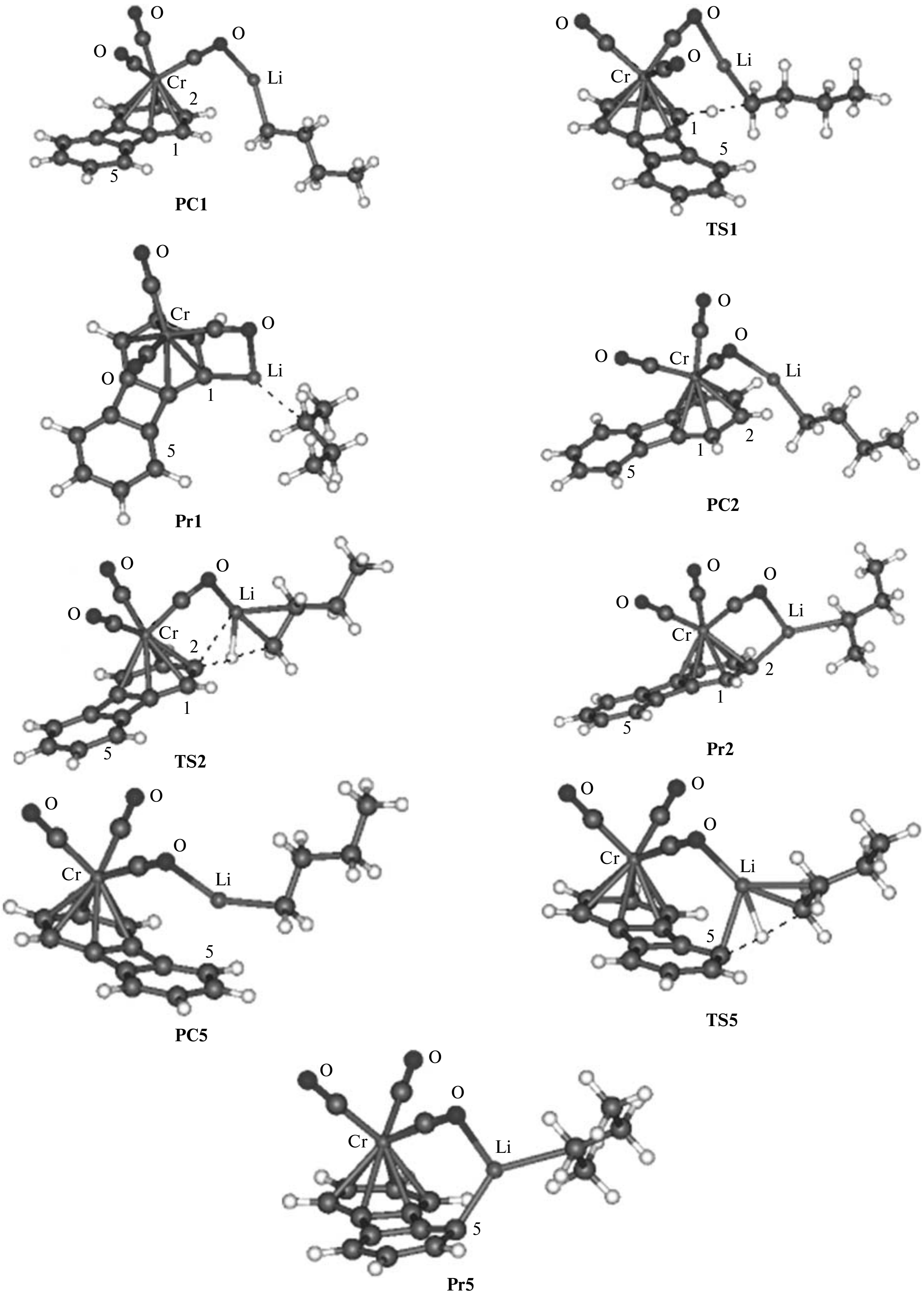


Fig. 2. Data of the DFT calculation of structures **PC**, **TS**, and **Pr** for the reaction of **5** with Bu^{n}Li at the C(1), C(2), and C(5) atoms, respectively (ΔE, ΔE^0, and ΔG are the energies relative to **PC1**).

parameters calculated with and without allowance for zero-point vibrations and the entropy factor) differ more considerably (~3 kcal mol^{-1}). This indicates that the ratio of the isomers should be determined to a greater extent by the thermodynamic rather than kinetic factor. This conclusion makes it possible to simplify significantly further calculations, determining the energy parameters of the reaction products only and ignoring the transition states.

Taking into account these facts, as well as considerable errors in the calculation of the free energies ΔG in the framework of the program used, we have chosen the relative energy with allowance for zero-point vibrations ΔE^0 as a criterion of the lithiation direction.

Another important problem for choosing the calculation model is a considerable association of lithium derivatives in solution. Depending on the polarity of solvent molecules, the lithium derivatives, for example, PhLi, can exist in solution as dimers, tetramers, hexamers, and (or) even larger associates.[27] Monomers as contact ion pairs (CIP, the formation of solvate-separated ion pairs seems improbable for these systems) without Li—C bond cleavage can exist in polar solvents. In these monomers, the lithium cation is additionally coordinated to several solvent molecules.[28] The lithium derivatives in the solid state are often crystallized as dimers in which the lithium cation is additionally bound to several solvent molecules.[29]

However, dimer formation in polar THF is poorly probable for the sterically hindered and electron-deficient lithium derivatives of the arenetricarbonylchromium complexes due to coordination to the strong acceptor, *viz.*, tricarbonylchromium group. In addition, the lithium derivatives without coordination to a transition metal are characterized by the Li—C covalent bond,[30] which distinguishes them from ionic compounds, such as fluorenyllithium, *etc.*,[28,31] capable of forming solvate-separated ion pairs. Taking into account the aforesaid, we considered only monomeric molecules, whose lithium cation in contact ion pairs is covalently bonded to one carbon atom and additionally binds several THF molecules, as a model in the theoretical analysis of the lithiated complexes.

As known, in the lithium salts of polyaromatic ligands non-coordinated by a transition metal in both solution (NMR data) and solids (X-ray diffraction data), the lithium atom is additionally coordinated to solvent molecules (ether, THF)[32] or other coordinating agents (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, crown ethers, *etc.*).[33] Therefore, calculations for the lithium salt of the tricarbonylnaphthalenechromium complex 1-Li-**3** were performed with one, two, and three THF molecules (THF is a standard solvent for lithiation) involved in solvation and localized near the lithium atom (see Fig. 3). The results of calculations are given in Table 3.

It follows from the data in Table 3 that, when the entropy factor is necessarily taken into account[34] by the calculation of the free Gibbs energy, the successive addition of one and then the second THF molecule decreases the free energy of the system ΔG for tricarbonylchromium complex 1-Li-**3** in THF, while the further addition of the third molecule increases ΔG.

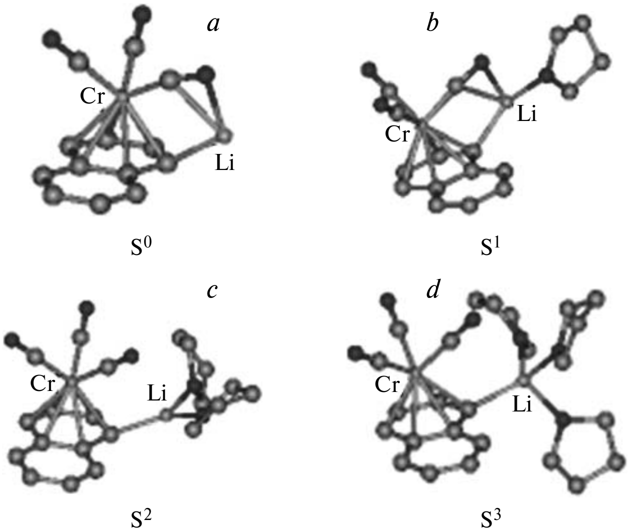


Fig. 3. Calculated structures for 1-Li-**3** without lithium cation solvation (*a*) and for solvation with one (*b*), two (*c*), and three (*d*) THF molecules.

Table 3. Results of calculations of the energies of solvation of the lithium cation in 1-Li-**3** with THF molecules

Structure*	E_{tot}/au	ΔE	ΔE^0	ΔG
		kcal mol^{-1}		
THF	−232.241240			
S^0	−1776.581511			
S^1	−2008.853684	−19.41	−18.62	−7.23
S^2	−2241.114888	−12.53	−11.55	−0.74
S^3	−2473.369981	−8.69	−8.05	3.49

* The structure of the lithium salt for the solvation of the lithium cation with THF molecules.

Thus, we can conclude that a monomer in which the lithium atom covalently bonded to one carbon atom is additionally coordinated to two THF molecules can be accepted as a model for further calculations of the lithium derivatives of the arenetricarbonylchromium complexes. Note that the additional coordination of the lithium atom with already two solvent molecules results in the disappearance of the coordination interaction of the latter with the carbonyl group.

Then, based on this model, we calculated different possible lithium derivatives of complexes **1**, **3**, **5**, and **7** solvated by two THF molecules. These data are presented in Table 4. The structures of the lithium salts are shown in Fig. 4.

The data in Table 4 show that for the lithium derivatives of the tricarbonylchromium complexes of biphe-

Table 4. Energies ΔE^0 of the isomeric lithium salts of complexes **1**, **3**, **5**, and **7** additionally coordinated to two THF molecules*

Lithium salt	E_{tot}/au	ΔE^0/kcal mol^{-1}
1-Li-**1**	−2318.460627	0
2-Li-**1**	−2318.459286	0.48
3-Li-**1**	−2318.458925	0.52
6-Li-**1**	−2318.448580	6.98
1-Li-**3**	−2318.460627	0
2-Li-**3**	−2318.459286	0.48
5-Li-**3**	−2241.107876	4.24
6-Li-**3**	−2241.103112	6.94
1-Li-**5**	−2317.206279	0
2-Li-**5**	−2317.201080	3.09
1-Li-**7**	−2715.333058	0
2-Li-**7**	−2715.328984	2.37
3-Li-**7**	−2715.326695	3.79
4-Li-**7**	−2715.328574	2.78
6-Li-**7**	−2715.309552	14.25
5-Li-**7**	−2715.328574	13.81

* The structures with lithium localization to the non-coordinated ring were not calculated. For comparison, see Table 2.

nyl **1**, naphthalene **3,** biphenylene **5**, and dibenzothiophene **7** the DFT method predicts very well the regioselectivity of lithiation, *i.e.*, preferential formation of the derivatives in which the lithium atom is localized near the coordinated ring, when the difference in energies with allowance for zero-point vibrations ΔE^0 is used. For example, lithium derivatives **1**, **3**, **5**, and **7** exhibit a considerable increase in ΔE^0 (up to 14 kcal mol^{-1}) for lithium localization in the non-coordinated ring compared to the derivatives with lithium localization to the ring bound to the chromium atom, which is consistent with the experimental data on the absence of this lithiation direction.

It is characteristic that for complexes **1** and **3**, whose lithiation to the coordinated ring is not selective, the difference in energies of the isomeric lithium derivatives to the coordinated ring is low (for the lithium derivatives of complex **1**, the ΔE^0 values for the *ortho*-, *meta*-, and *para*-isomers of lithium salts 1-Li-**1**, 2-Li-**1**, and 3-Li-**1** differ not more than by 0.6 kcal mol^{-1}, whereas for isomers 1-Li-**3** and 2-Li-**3** they differ by 1.15 kcal mol^{-1}), while for selectively metallated complexes **5** and **7** this difference between different positions is at least 2.37 kcal mol^{-1}.

For **3**, the ΔE^0 values for the isomers describe correctly the preferential formation of isomers **4b**, while very small differences in ΔE^0 for complex **1** do not allow one to predict the ratio of complexes [**2a**]/[**2b**]/[**2c**] substituted to different positions (see Table 1).

It is interesting that for 1-lithium derivative **7** the DFT calculation indicates no stabilizing coordination interaction with the heteroatom (sulfur atom), which was assumed in many works on the metallation of the aromatic heterocycles and their tricarbonylchromium complexes.

The formation of solvate-separated ion pairs for lithium derivatives **1**, **3**, **5**, and **7**, in which the lithium cation is separated from the negatively charged ligand and further does not covalently interact with this ligand, is highly improbable. The formation of solvate-separated ion pairs is usually characteristic of salts of aromatic anions, such as cyclopentadienyl, indenyl, and fluorenyl anions,[25] where the ligand is stabilized due to the formation of an aromatic structure.

Nevertheless, we performed the DFT calculation for a possibility of formation of these hypothetical anions due to the formation of solvate-separated ion pairs for anions 1-H$^-$-**5**, 2-H$^-$-**5**, 5-H$^-$-**5**, and 6-H$^-$-**5** (the first figure means the position of complex **5** from which H$^+$ was removed). The data of calculations for the anions (**5**-H$^-$) (Fig. 5) are presented in Table 5.

It follows from the data in Table 5 that lithiation to the non-coordinated ring is thermodynamically unfavorable in spite of the substantially simplified model for lithium salts **5**, because the corresponding anion has a very high energy. The selectivity of lithiation at position 1 is determined by a higher energy of the aromatic anion without a proton in position 2. A similar calculation was carried out for complex **7**. In this case, the relative energies ΔE^0 for positions 1, 2, 3, and 4 in the coordinated ring are 0, 4.14, 6.01, and 0.97 kcal mol^{-1}, respectively, while they range from 11.46 to 19.83 kcal mol^{-1} for the non-coordinated ring. Thus, the parallel calculation of the energies of the corresponding hypothetical "free" anions can be considered, probably, as a preliminary estimation, which decreases considerably the time expenses.

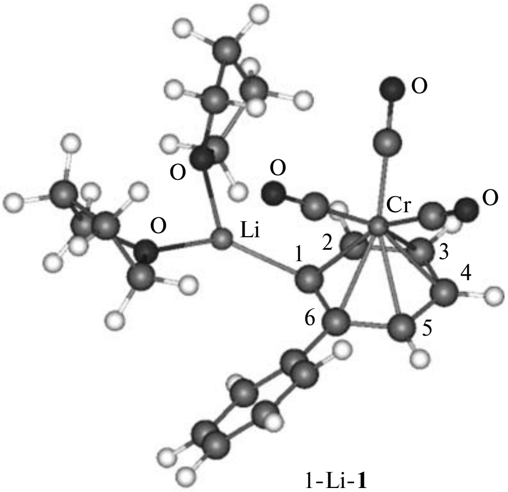
We have previously[13] shown than in excess BuLi complex **7** is doubly metallated to form dilithium derivative **9**. In this case, double metallation occurs at positions 1 and 4. This is also indicated by the fact that the reaction of dilithium derivative 1,4-Li$_2$-**9** with electrophiles RX (R = Me, SiMe$_3$, SnMe$_3$) affords only 1,4-R$_2$-derivatives **10—12** (Scheme 6).

The energies of different possible dilithium derivatives Li$_2$-**9** were also calculated by the DFT method (see Table 6 and Fig. 6).

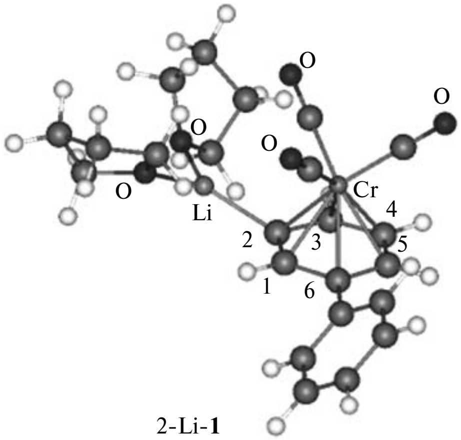
As follows from the data in Table 6, the energy of derivative 1,4-Li$_2$-**9** is minimum and differs considerably

Table 5. Calculation of the energies of anions 1-H$^-$-**5**, 2-H$^-$—**5**, 5-H$^-$—**5**, and 6-H$^-$-**5** in solvate-separated pairs of lithium salts **5**

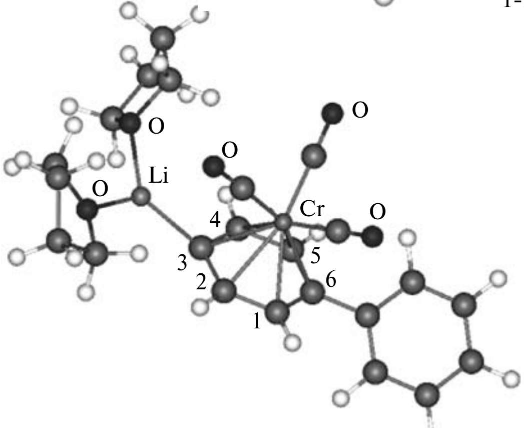
Anion	E_{tot}/au	ΔE^0/kcal mol^{-1}
1-H$^-$-**5**	−1845.180061	0
2-H$^-$-**5**	−1845.173752	3.70
5-H$^-$-**5**	−1845.162053	10.95
6-H$^-$-**5**	−1845.154464	15.34



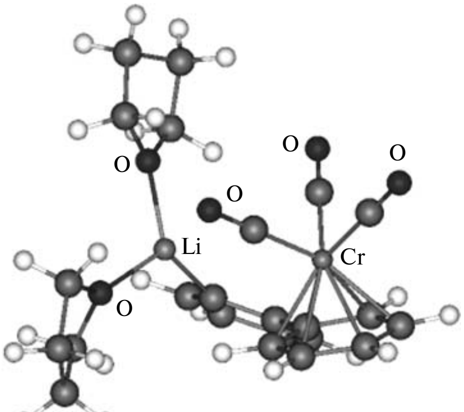
1-Li-**1**



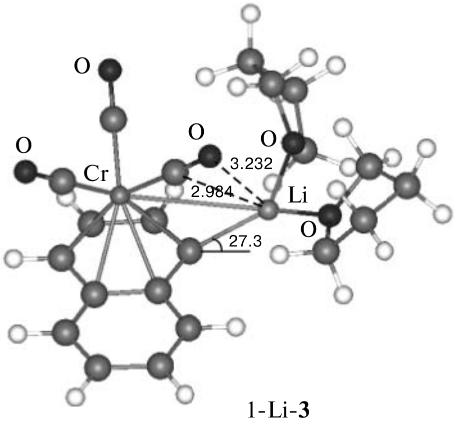
2-Li-**1**



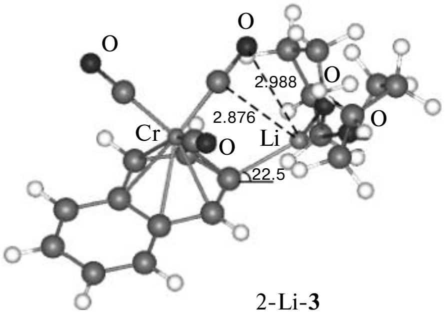
3-Li-**1**



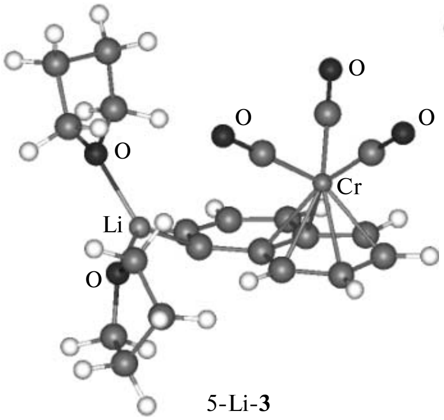
6-Li-**1**



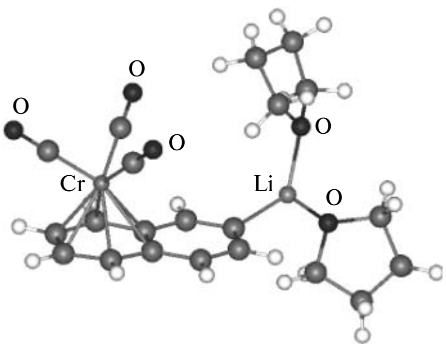
1-Li-**3**



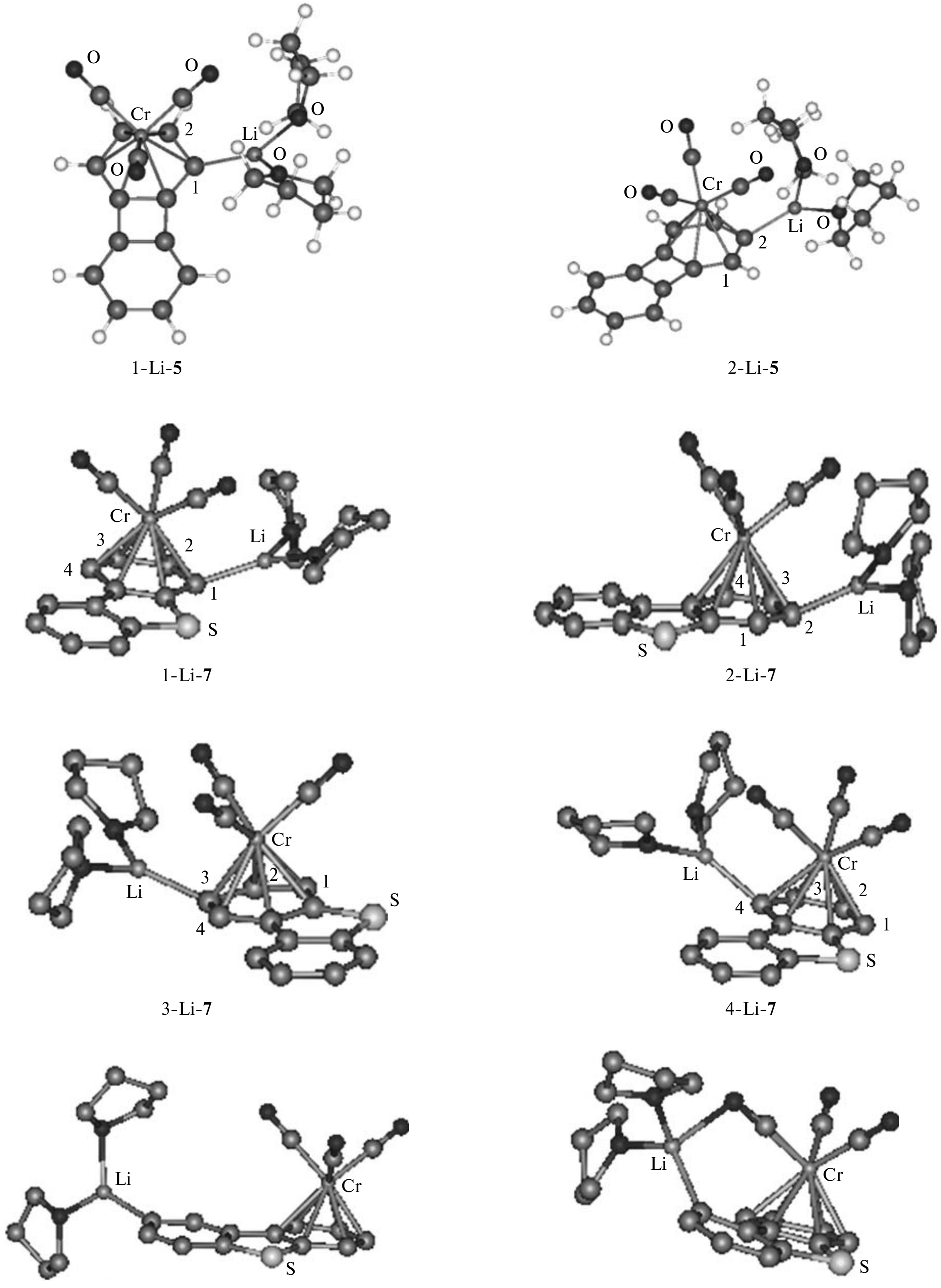
2-Li-**3**



5-Li-**3**



6-Li-**3**



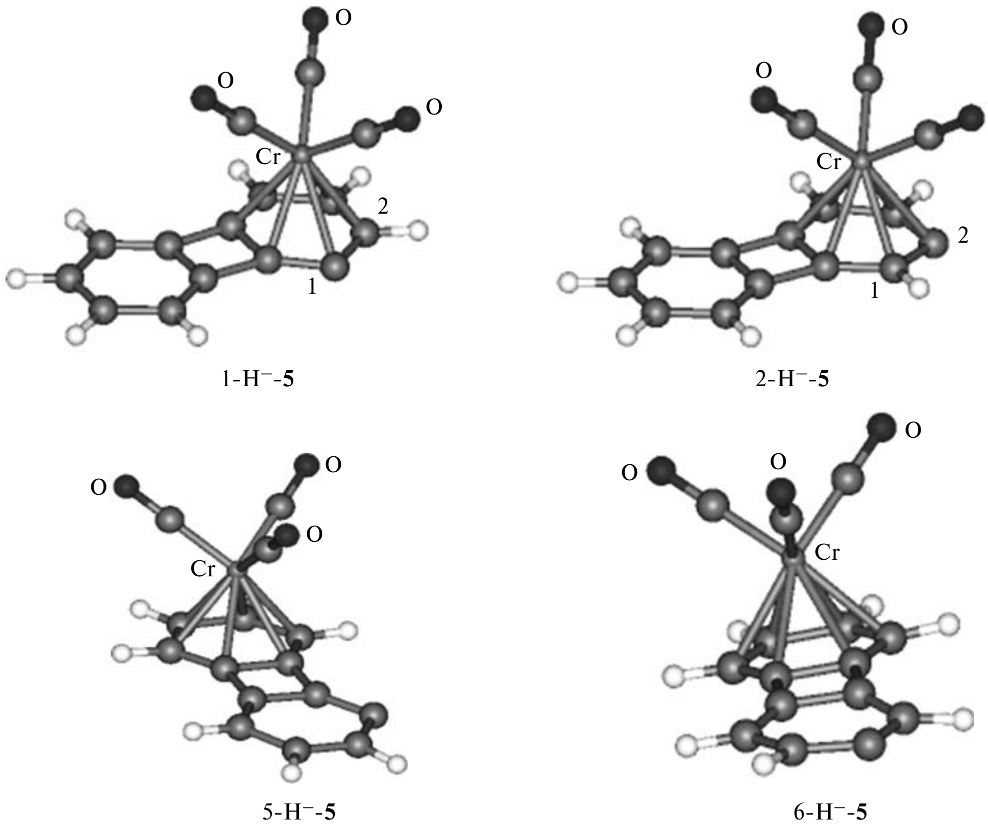
1-Li-**5** 2-Li-**5**

1-Li-**7** 2-Li-**7**

3-Li-**7** 4-Li-**7**

6-Li-**7** 5-Li-**7**

Fig. 4. Structures of lithium salts **1**, **3**, **5**, and **7** solvated by two THF molecules.



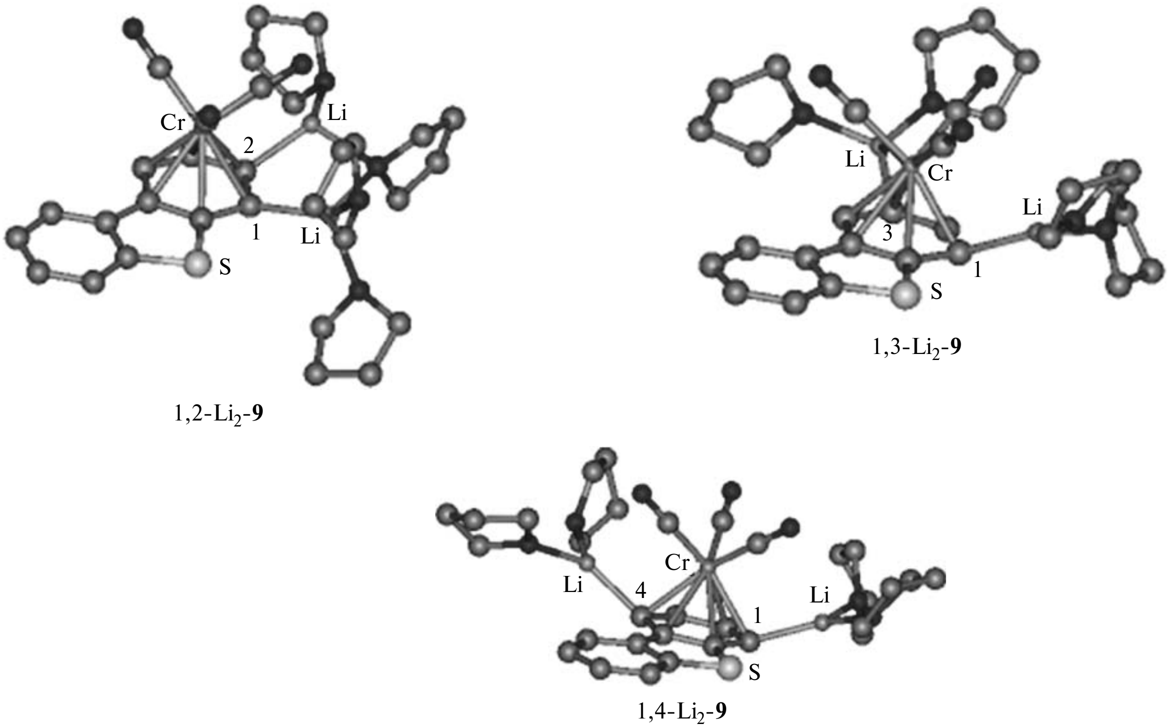
1-H$^-$-**5**

2-H$^-$-**5**

5-H$^-$-**5**

6-H$^-$-**5**

Fig. 5. Structures of anions 1-H$^-$-**5**, 2-H$^-$-**5**, 5-H$^-$-**5**, and 6-H$^-$-**5** in solvate-separated ion pairs of lithium salts **5**.



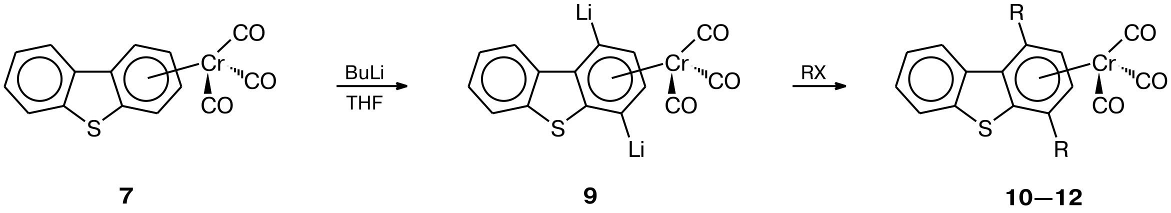
1,2-Li$_2$-**9**

1,3-Li$_2$-**9**

1,4-Li$_2$-**9**

Fig. 6. Structures of possible dilithium derivatives **9** for the metallation of **7** at the coordinated ring.

Scheme 6



R = Me (**10**), $SiMe_3$ (**11**), $SnMe_3$ (**12**)

Table 6. Calculated energies of possible dilithium derivatives **9** for the metallation of **7** at the coordinated ring

Structure*	E_{tot}/au	ΔE^0/kcal mol^{-1}
1,2-Li_2-**9**	−3186.742549	8.96
1,3-Li_2-**9**	−3186.750596	3.91
1,4-Li_2-**9**	−3186.756825	0

* The structure of dilithium derivative **9**.

from the energies of other possible structures, which results in the formation of precisely 1,4-disubstituted complexes **10—12**. We did not consider double lithiation at the non-coordinated ring, because this reaction should be *a priori* thermodynamically unfavorable.

Thus, the DFT method was shown to describe adequately the reactions of the arenetricarbonylchromium complexes with alkyllithium compounds. The thermodynamic factor is the main criterion for the lithiation direction to the coordinated aromatic ring and selectivity of C—Li bond formation in this ring.

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Received June 2, 2005;
in revised form September 15, 2005