Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 1379–1395
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

A combined experimental and theoretical study of metallic salts of thiapentadienyl, sulfinylpentadienyl and butadienesulfonyls

Prócoro Gamero-Melo [a], Manuel Villanueva-García [b], Juvencio Robles [b], Rosalinda Contreras [a], M. Angeles Paz-Sandoval [a,*]

[a] *Departamento de Química, Centro de Investigación y de Estudios Avanzados del I.P.N., Apartado Postal 14-740, México D.F. 07000, Av. IPN # 2508, Col. San Pedro Zacatenco, D.F. 07360, Mexico*
[b] *Facultad de Química, Universidad de Guanajuato, Col. Noria Alta S/N, Guanajuato 36050, Guanajuato, México*

Received 2 October 2004; accepted 7 December 2004
Available online 7 February 2005

Abstract

Alternative methods for the synthesis of the following acyclic salts ($CH_2CHCHCHS$)M [M = K, **1**(bf K); Na, **1**(**Na**); Li, **1**(**Li**)], ($CH_2CHCHCHSO$)M [M = K, **2**(**K**); Na, **2**(**Na**)], ($CH_2CHCHCHSO_2$)M [M = K, **3**(**K**); Na, **3**(**Na**); Li, **3**(**Li**)], (CH(Me)CHC-(Me)$CHSO_2$)M [Me5-*syn*, M = K, **9**(**K**); Na, **9**(**Na**); Li, **9**(**Li**), (CH(Me)CHCHC(Me)S)M [Me5-*syn*, M = K, **10**(**K**); Na, **10**(**Na**); Me5-*anti*, M = K, **11**(**K**); Na, **11**(**Na**)] are described, as a result of the activation of C–S bond in dihydrothiophenes by deprotonation with different bases. The effect of methyl substituents in the dihydrothiophenes is significant, which modifies considerably the choice of the base. The influence of the reaction conditions, type of solvent, base and dihydrothiophenes is analyzed. The NMR spectroscopy, including NOESY, ROESY and difference NOE establish the preferred U conformation for all derivatives, and support a delocalization of charge on the thiapentadienyl (**1M**) and sulfinylpentadienyl (**2M**) complexes. However, a conjugated diene structure is proposed on the butadienesulfonyl compounds (**3M**), in which the negative charge is delocalized in the SO_2 fragment and stabilized with the corresponding cations (M = K, Na and Li). In presence of traces of base, compounds **3M** suffer a rearrangement, to the most stable S conformer, **13M**. The stability of **3M** depends on the size of the cation, the greater the size, the greater stability. Furthermore, a theoretical study shows that electronic and geometrical properties (energy conformers, charge distributions and relative stabilities) of the thiapentadienyl, sulfinylpentadienyl and butadienesulfonyl anions and their corresponding metal salts **1M**–**3M** (M = Li, Na and K) shows to be in good agreement with the experimental findings.

Keywords: Heterodienes; Anions; Alkaline metals; S,O Ligands; Thiapentadienyl

1. Introduction

While the synthetic utility of pentadienyl anion [1], oxopentadienyl anion [2] and azapentadienyl anion [3] chemistry is well established, the thiapentadienyl anion (**1**) [4] and their corresponding oxidized derivatives, such as the sulfinylpentadienyl (**2**) [5] and the butadienesulfonyl (**3**) [6] anions are scarce. An extensive review of anionic heteroallylic compounds [7] reports the synthesis of allylic-SR, -S(O)R and -SO_2R and their reactivity with electrophiles. Contrastingly, only a few synthetic procedures are reported for the extended sulfur-dienyl analogous [4a], some of them with inconsistent results as far as the structural aspects and spectroscopic studies are concerned.

According to Kloosterziel et al. [4a] and Bleeke et al. [4b–e] the thiapentadienyl anion has a delocalized charge, but they propose different conformations, S

* Corresponding author. Tel.: +52 55 506 13717; fax: +52 55 574 77113.
E-mail address: mpaz@mail.cinvestav.mx (M.A. Paz-Sandoval).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.12.014

and U shape in NH_3 and THF-d_8, respectively. Kloosterziel et al. [4a] also propose an anionic butadienylsulfone in NH_3, with a delocalized charge along the molecule, while Burger et al. [6a] propose a localized charge for the diene fragment and an ionic bond between K and the delocalized SO_2 fragment for potassium *Z*-2-methyl-1,3-butadienyl-sulfinate in DMSO-d_6. Crumbie [5] reports that 2,5-dihydrothiophene-1,1-dioxide (**4**) does not react with *n*-BuLi or LDA at temperatures from −78 to 30 °C, while Ta-Shue Chou [6b] reports ring opening of compound **4** at −78 °C. Because of the high reactivity at the anionic intermediate **2** and **3**, the addition of alkyl halides to 3-sulfolenes has also been studied immediately after and previously to the deprotonation reaction, according to Crumbie [5] and Chou, [6b], respectively. Given this uncertainty and the lack of well defined methodologies to prepare dienesulfonyl and heteropentadienyl salts, it was necessary to investigate the reactions of 2,5-dihydrothiophenes (**5**), [8–13] (**8**) and the corresponding 2,5-dihydrothiophene-1-oxide (**6**) [13] and 2,5-dihydrothiophene-1,1-dioxide (**4**), [13] (**7**) derivatives with Lewis bases, such as hydride reagents MH (M = Li, Na, K) as well as LDA (lithium diisopropylamide), *n*-BuLi, Et_3BHLi, *t*-BuOK and $Me(SO)CH_2K$.

Electronic structure calculations have been performed to determine the nature of the structure and bonding in metalated aldimines, where the lithium atom is π-coordinated to the azaallylic system [14]. It has also been found that the lithium-enolate of acetaldehyde shows less π-coordination capability once solvent molecules are incorporated [15]. Theoretically [3a] it has been found for the azapentadienyl anion conjugated systems that the minimum energy geometry is the W-form, whereas the preferred conformer for azapentadienyllithium is the U-form. Other studies on azapentadienyl anions [3b] have shown that the C3 and C5 atoms in the main chain are the most favorable sites for an electrophilic attack, and that the charge density is distributed in an alternate manner along the chain.

There are several theoretical studies on pentadienyl radicals [16], cations [17], anions [1p,17] and their corresponding alkali metal complexes [1p,17]. The study of the pentadienyl radical has established the energetic preference for the W and S isomers over the U-shaped conformer. More recently, Pratt and Streitwieser [17] reported a thorough theoretical study on most stable structures, geometrical parameters and charge distributions in the lower energy conformers of pentadienyl anion, cation, as well as in pentadienyl-lithium and pentadienyl-sodium complexes. They showed, at different levels of theory and numerical accuracy, that for the pentadienyl anion, there are three preferred conformers, all of them with plane geometry. The most stable corresponds to the W-shaped conformer, followed by the S-shaped and finally the less stable U-shaped conformer. The pentadienyl-lithium and sodium compounds may exist in several conformations but the lower energy is U form for both.

As far as we know, theoretical studies on the anions of thiapentadienyl, sulfinylpentadienyl and butadienesulfonyl and their corresponding metal salts with Li, Na and K have not been published. Then, the purposes of the present work is to perform, on one hand, a systematic theoretical study on these series of species to understand and rationalize some of the experimental findings and, on the other hand, to clarify the structural aspects of compounds **1**–**3**, **9**–**11** and, either, to establish or to improve their synthetic methods. Also, the effect of methyl substituents on the 2,5-dihydrothiophenes, such as 2,4-dimethyl-2,5-dihydrothiophene-1,1-dioxide (**7**) and the corresponding 2,5-dimethyl-2,5-dihydrothiophene (**8**), and 2,5-dimethyl-2,3-dihydrothiophene (**8′**) were studied and will be discussed.

2. Results and discussion

2.1. Synthesis of the alkali metal salts of butadienesulfonyl, thiapentadienyl and sulfinylpentadienyl

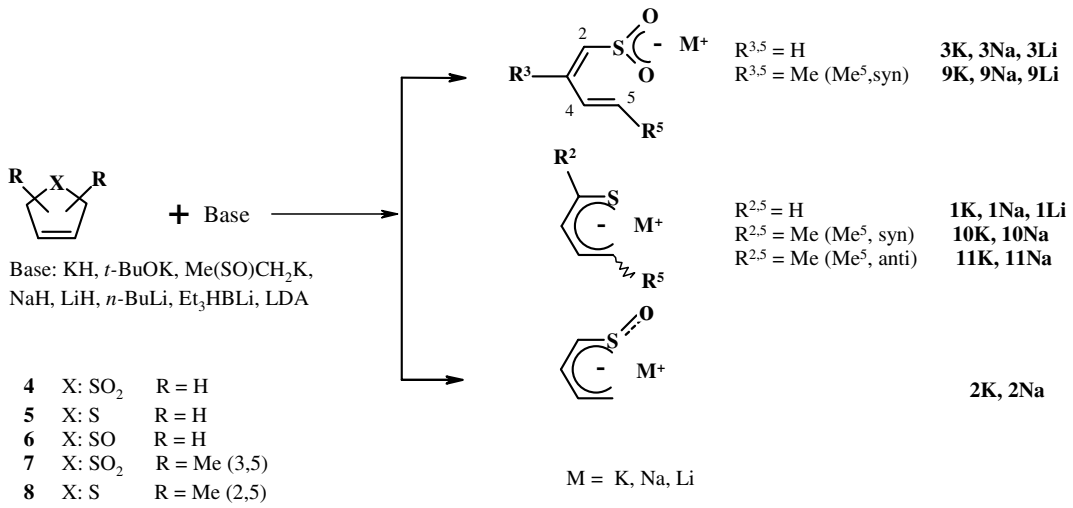
A general method for the synthesis of the following salts ($CH_2CHCHCHSO_2$)M [M = K, **3**(**K**); Na, **3**(**Na**); Li, **3**(**Li**)], (CH(Me)CHC(Me)$CHSO_2$)M [Me5-*syn*, M = K, **9**(**K**); Na, **9**(**Na**); Li, **9**(**Li**), ($CH_2CHCHCHS$)M [M = K, **1**(**K**); Na, **1**(**Na**); Li, **1**(**Li**)] (CH(Me)-CHCHC(Me)S)M [Me5-*syn*, M = K, **10**(**K**); Na, **10**(**Na**); Me5-*anti*, M = K, **11**(**K**); Na, **11**(**Na**)] and (CH_2CHCH-CHSO)M [M = K, **2**(**K**); Na, **2**(**Na**)] is described in Scheme 1. Ultrasonic treatment is used when cleavage of the C–S heterocycle bond is relatively slow.

2.1.1. Potassium, sodium and lithium butadienesulfonyls

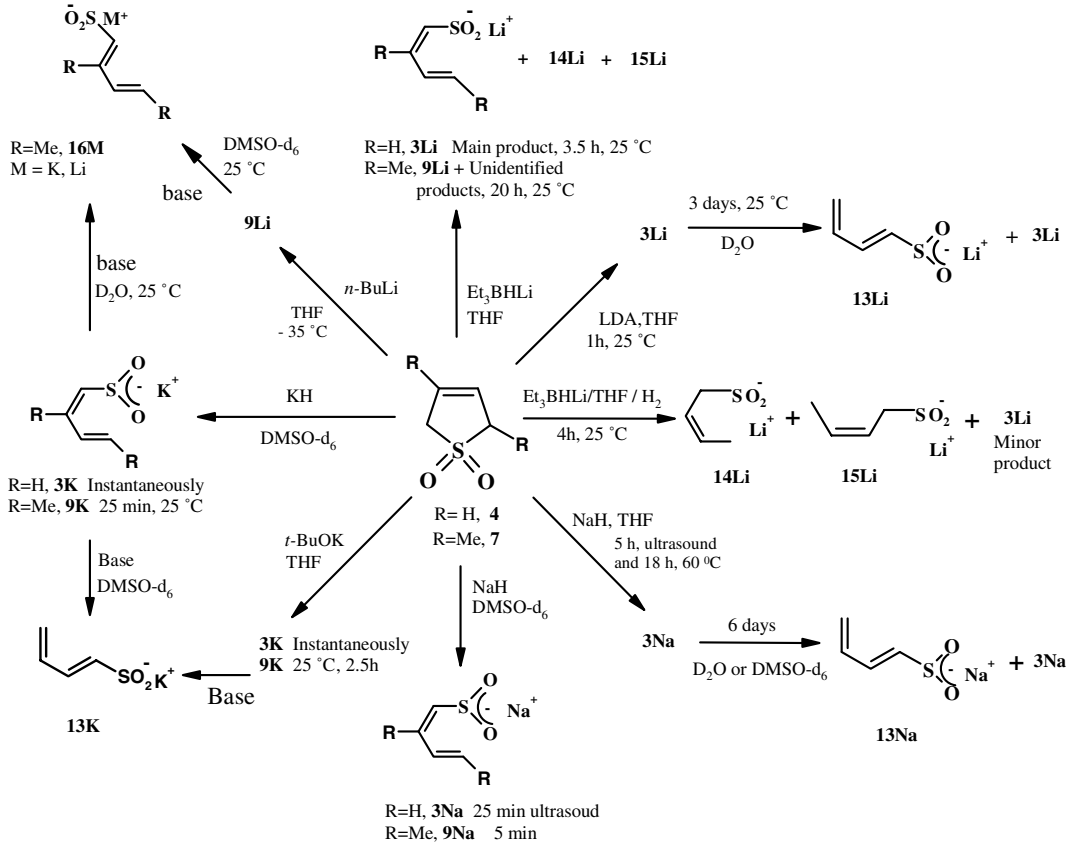
Deprotonation of the 2,5-dihydrothiophene-1,1-dioxide (**4**) with one equivalent of *t*-BuOK in THF affords a pale-yellow complex **3K** in quantitative yield, (Scheme 2).

The reaction gives firstly a mustard-yellow solid, which after 1 h at room temperature goes to a pale yellow; according to these observations it is proposed that there is an initial formation of a cyclic deprotonated intermediate 3-sulfolene **12K**, which transforms into the acyclic salt **3K**, according to Scheme 3. Analogous sulfolenes have been reported by others [5,6b,6c].

KH reacts with DMSO affording $Me(SO)CH_2K$, which acts as a base reacting with **4** in a quite exothermic reaction; however, the purification of **3K** is not straightforward because traces of KH are present and it is difficult to remove the DMSO. Even more, if traces of KH are present, compound **3K** isomerizes from the U to the S conformer **13K**, as described in Scheme 2.



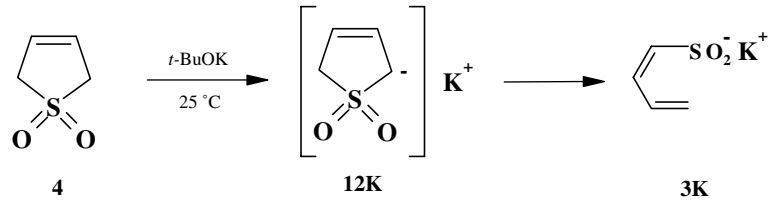
Scheme 1. General procedure for synthesis of the potassium, sodium and lithium salts of butadienesulfonyl, thiapentadienyl and sulfinylpentadienyls.



Scheme 2. Synthesis of metallic salts of butadienesulfonyls, hydrogenated derivatives and 3,5-dimethylbutadiensulfonyls.

The ultrasound synthesis of **3Na** was carried out with NaH and **4** in different solvents, showing that the speed of the reaction increases with the dielectric constant (ε) of the solvent: DMSO ($\varepsilon = 48.9$; 25 min, ultrasound), MeCN ($\varepsilon = 37.5$; 5 h, ultrasound and 12 h at 55 °C) and THF ($\varepsilon = 7.4$; 5 h, ultrasound and 18 h at ~60 °C), respectively. Nevertheless, even though MeCN is a better solvent than THF, the filtration of **3Na** is easier after washing the cream powder with THF (see experimental section).

3Li can be prepared using different bases. Stoichiometric reaction of **4** and LDA in THF at low temperature



Scheme 3. Synthesis of the potassium butadienesulfonyl **3K**.

(−110 °C) gives an initial purple solution which after 1 h at room temperature, affords a yellow solid in 67% yield. The reaction of **4** with Et_3BHLi in THF, after 3.5 h at room temperature, affords compound **3Li** along with lithium *Z*-3-methyl-2-propen-1-sulfonyl (**14Li**) and **15Li** in a 1.6:1:1 ratio, respectively. If the reaction is carried out bubbling H_2, after 4 h at room temperature, the ratio changes to 1:6:6, respectively. (Scheme 2).

In order to compare the reactivity of the metal hydrides, compound **4** was dissolved in DMSO and LiH was added. After 72 h at room temperature and 4.5 h under ultrasound there was no reaction and **4** was recovered. For compound **4** the reactivity of the metal hydrides decreases in the following order: KH > NaH ≫ LiH.

As estimated from ^{1}H NMR spectroscopy, a comparative study of the conversion of compounds **3K**, **3Na** and **3Li** into the corresponding **13K**, **13Na** and **13Li** shows that the stability depends on the size of the cation, the greater size, the greater stability of the corresponding salt. Meanwhile, traces of base transform **3K** into **13K** (1:1 ratio) after 14 days at room temperature in DMSO-d_6 or D_2O; the corresponding sodium salt takes 6 days, at room temperature, to get a mixture of 1:0.74 ratio of **3Na** and **13Na**, and in the case of lithium it takes 3 days, at room temperature, to show a 1:1.5 ratio of **3Li**:**13Li**.

The ^{1}H and ^{13}C NMR data of compounds **3**, **13**, **14** and **15** are reported in the experimental section. Even though chemical shifts and coupling constants of compounds **3M** (M = K, Na, Li) are quite similar to those corresponding to the analogous potassium salt reported by Kloosterziel [4a] as an S conformer (in NH_3 at −60 °C), we proposed for compound **3K** (in DMSO-d_6 or D_2O at 25 °C) the U conformation. According to the COSY experiment, the assignment of all resonances indicates the presence of cross-peaks between H2 and H3, H3 and H4, H4 and H5 and H5′ (for numbering see Scheme 1). Significant ROESY cross-peaks are also observed between H2 and H3 and between H3 and H4, suggesting the U conformation. This is also in agreement with only one *trans* coupling constant for $J_{4,5}$ = 17.2 Hz. Further support for the assignment comes from the ^{13}C NMR which suggests a conjugated diene structure, as deduced from the observation of the terminal vinylic carbon which appears at higher frequency (118.8 ppm) compared to a delocalized vinylic carbon in the pentadienyl complex $(C_5H_7)^-M^+$ (79.9 ppm, M = K; 66.2 ppm, M = Li) [3a]. The corresponding vinylic protons are in the case of butadienesulfonyl metal **3M** at higher chemical shifts than 5.0 ppm, which is characteristic of terminal olefin protons, such as butadiene [18a], bis-allylsulfide [18b], bis-allylsulfinyl [18c] or bis-allylsulfone [18c], and these contrast with those lower frequency values observed for delocalized terminal protons in complexes with pentadienyl (<3.55 ppm) [1c,18d], oxopentadienyl (<4.52 ppm) [2b], azapentadienyl (<4.35 ppm) [3] and thiapentadienyl (<4.87 ppm) [4a] anions.

The analogy between the spectroscopic data for **3M** (M = K, Na, Li) is indicative that the metal is interacting exclusively with the sulfonyl group. This is in agreement with a conjugated diene in which the charge is delocalized along the oxygen–sulfur–oxygen atoms.

A complementary NOE study on compound **3Na** shows that the ratio between the integrals are equal to 11.2% and 19.1% when H3 is irradiated respect to H2 and H4, respectively. Irradiation on H4 resonance at 7.01 leads to the collapse of the triplet at 6.00 ppm to a doublet of doublets with coupling constants of $^3J_{2,3}$ = 9.9 Hz and $^4J_{5',3}$ = 5.3 Hz due to a typical W allylic coupling [19].

The ^{1}H NMR spectra of **3K**, **3Na** and **3Li** in D_2O or DMSO solutions show that they are quite stable for at least 15 days. However, if a small amount of base is added, there is evidence of a slow transformation to the corresponding isomers **13K**, **13Na** and **13Li**, which adopt an S conformation, as indicated, by the *trans* and *cis* coupling patterns, (e.g., **13Na** in D_2O): $J_{4,5}$ = 16.6, $J_{2,3}$ = 15.7 and $J_{4,5'}$ = 9.9, $J_{3,4}$ = 10.4 Hz, respectively. Each couple of isomers **3** and **13** have a cis-diene arrangement according to their similar coupling constants, such as $J_{3,4}$ = 10.6 (**13Na**) and 11.0 Hz (**3Na**). The similarity in the spectra of **3K**, **13K** and **3Li**, **13Li** suggests the same structures for all these species, where the transformation from the kinetic products **3M** to the thermodynamic ones **13M** depends on the size of the cation. The fastest isomerization is observed for **3Li** to **13Li** (15 days at room temperature), after this time, it reaches equilibrium in 1:5 ratio, respectively. Whereas the most stable potassium salt gives a 1:1 ratio of **3K**:**13K** after 14 days at room temperature and a 1:13

ratio after 16 days at room temperature and 2 days at 60 °C. After this time, a small amount of different new species appears in the ^{1}H NMR spectrum.

The ^{1}H-NOESY experiment for the mixture of compounds **3Li**, **14Li** and **15Li** shows that the CH_2 and CH_3 protons in **14Li** are in the same side.

A theoretical conformational analysis for the butadienesulfonyl anion results in nine conformers, the three lower-energy ones adopt an S-conformation, another one has higher energy, and the other five with higher energies, possess a U-shape. In Scheme 4 the lowest energy S (0.00 kJ/mol) and U (5.27 kJ/mol) conformers are displayed, along with bond distances and charge distributions; it can be noticed that the double bonds are localized forming a diene with the negative charge located at the sulfonyl group. Both conformers are close in energy. Then, it should be expected the coexistence of certain amount of both conformers.

Thereafter, plausible structures for complexes **3Li**, **3Na** and **3K** were modeled beginning from the computed butadienesulfonyl anion, with three S-conformers and three U-conformers, all with the lower energy. Regardless of the initial anion conformer geometry, the full geometry optimization of the derived complexes always converge to an S-conformation. This result indicates that the kinetic U-conformer experimentally observed is transformed to the S-shaped thermodynamic conformer. The calculated bond lengths and charge distributions in the optimized structures of complexes **3Li**, **3Na** and **3K** are shown in Scheme 5. It can be noted that distances from atoms C5, C4, C3 and C2 to cations K^+, Na^+, Li^+ are in a range from 3.484 to 6.357 Å, so there is no interaction or bonding between those C atoms and the cations. From the bond lengths in C5–C4 and C3–C2 it can be suggested that in both, the anion and its derived metal salts, the hydrocarbon fragment is a conjugated diene. Meanwhile, the calculated charge distributions indicate that the amount of charge transferred from the butadienesulfonyl anion to the cations is inversely related to the cation size and that the charge is concentrated in the sulfonyl group in agreement with the ^{1}H and ^{13}C NMR experimental observations (vide supra). The highest stability is found in the potassium complex and the lowest in lithium (vide supra).

2.1.2. Potassium, sodium and lithium 3,5-dimethylbutadienesulfonyls

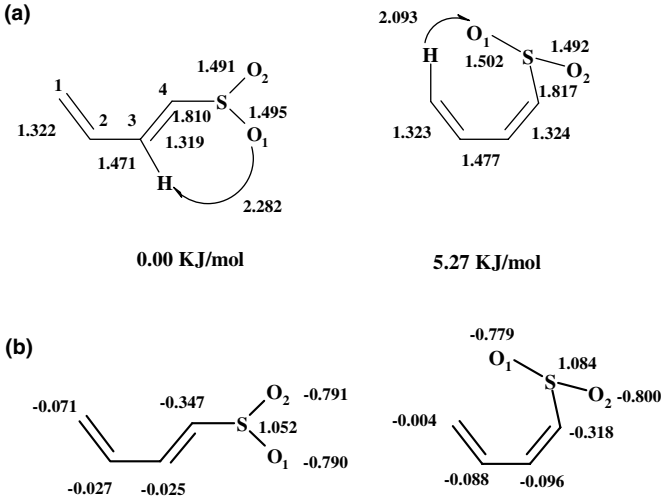
A series of **9K**, **9Na** and **9Li** were prepared by deprotonation of **7** with KH, *t*-BuOK, NaH, Et_3BHLi and n-BuLi in THF and DMSO, as described in Scheme 2.

Reaction of **7** with KH in DMSO affords **9K** in quantitative yield, while *t*-BuOK in THF gives a poor yield (15%), apparently from the bulky substituent of the base. The results contrast with the efficient synthesis of **3K** from *t*-BuOK and the unmethylated **4**.

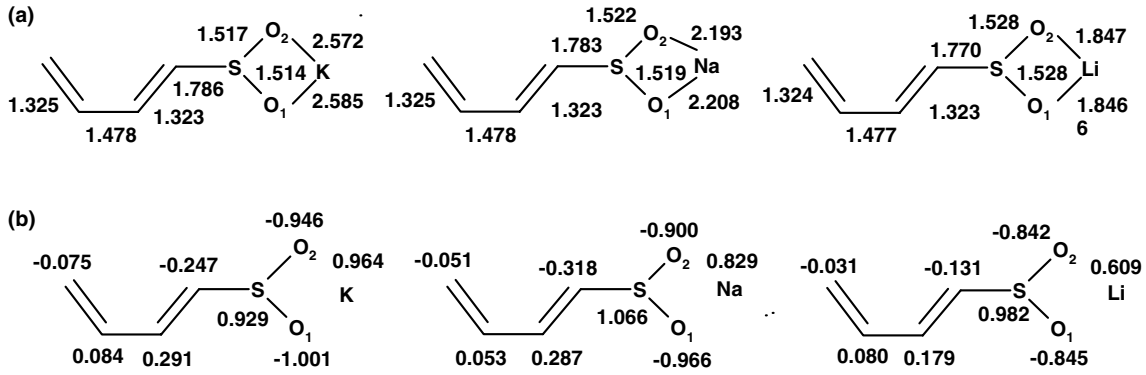
The analogous **9Na** and **9Li** can be prepared efficiently (quantitatively and 88.4%, respectively) when a DMSO and THF solutions of **7** are treated at room temperature and at −35 °C with NaH and *n*-BuLi, respectively.

The use of Et_3BHLi in THF leads to a non-selective reaction with **7**, to give **9Li** in low yield. From the different synthetic routes it can be observed that **9Li**, prepared from **7** and *n*-BuLi in THF, appear to be the most suitable method because **9Li** it is easily prepared and purified, and it can be obtained from less strong coordinated solvents than DMSO.

Compounds **9K**, **9Li** can be stored at 25 °C without decomposition and their stability in solution is also high. These complexes can slowly isomerize, in the presence of a base, to the corresponding **16K** (270 days) and **16Li** (60 days) in a (1:1.4) and (1:0.14) **9M**:**16M** ratio,



Scheme 4. Butadienesulfonyl anion conformations at the HF/3-21G//3-21G level of theory. (a) Relative energies (kJ/mol) and bond distances in Angstroms. (b) Mulliken charges distributions with all of the hydrogen charges summed to the attached heavy atoms.



Scheme 5. Optimized geometries of **3K**, **3Na** and **3Li** at the HF/6-31+G(d)//HF/6-31+G(d) level of theory. (a) Bond distances in Angstroms, (b) Mulliken charges distributions with all of the hydrogen charges summed to the attached heavy atoms.

respectively, (Scheme 2). When longer reaction times are used, both compounds **9** and **16** are transformed to other products which were not identified. These transformations are significantly slower than those observed for **3** and **13**, which suggests that the methyl substituents confer higher stability. This trend has also been observed for several pentadienyl [1a,20] and heterodienyl ligands [21].

The ^{1}H and ^{13}C NMR data of compounds **9K**, **9Na** and **9Li** are described in Section 4 and they are consistent with a U conformation and a butadienesulfonyl structure, as described for compounds **3Li**, **3Na** and **3K** (vide supra). Irradiation in **9Li** of H4 gives a NOE of 13.4% for Me5 and 15.1% for Me3, confirming that the methyl groups are in the same side of the molecule. U conformation is confirmed when H2 is irradiated and a NOE effect of 13.3% is observed for Me3.

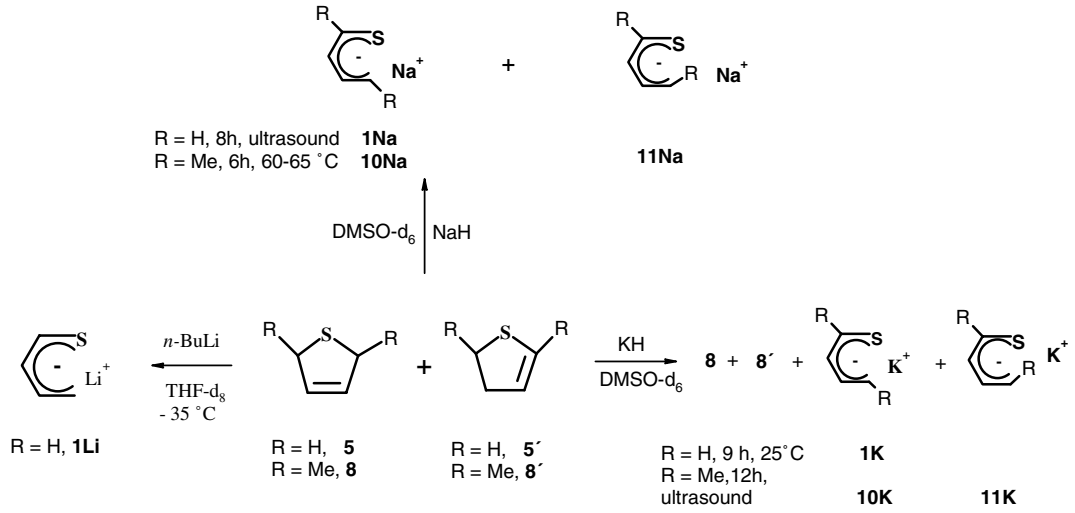
The reactions of **3Li** and **9Li** with $[Cp^{*}IrCl_2]_2$ have been shown the interesting formation of the dinuclear intermediates $[Cp^{*}Ir(Cl)_2\{(5\text{-}\eta)\text{-}SO_2CH{=}CRCH{=}CHR\}(Li)(THF)]_2$ (R = H, Me), while **3K**, **9K** with $[Cp^{*}IrCl_2]_2$ afford the mononuclear complexes $Cp^{*}IrCl[(1,2,5\text{-}\eta)\text{-}SO_2CH{=}CRCH{=}CHR]$ (R = H, Me), which are the first examples with a butadienesulfonyl ligand coordinated to a transition metal [22].

2.1.3. Potassium, sodium and lithium thiapentadienyls

Potassium thiapentadienyl salt has been synthesized with **5** and KNH_2 in liquid ammonia by Kloosterziel et al. [4a] and used as a ligand by Bleeke et al. [4c–e]. An easy alternative, to prepare compounds **1M** in quantitative yields, is the reaction of compound **5** with NaH (8 h) or KH (1 h) in DMSO-d_6, at room temperature under an ultrasound bath. Even more, there is an alternative method to get **1K** or **1Na** starting from a mixture of 2,5- and 2,3-dihydrothiophenes (**5**) and (**5′**) and KH or NaH, respectively, in DMSO at room temperature in ultrasound bath, (Scheme 6). Both compounds **1K** and **1Na** are indefinitely stable in DMSO solution. The same mixture **5** and **5′** can be used with *n*-BuLi in TDF-d_8 at −35 °C, to afford complex **1Li**, which is only stable below this temperature. However, it was not possible to isolate these three salts **1M** (M = K, Na, Li), because once the solvent is removed for **1K** and **1Na** or the temperature increases for **1Li**, insoluble solids of polymeric appearance are obtained [23]. Attempts to deprotonate efficiently **5** and **5′** with *t*-BuOK in THF were unsuccessful.

The deprotonation of the 2,5-dihydrothiophene (**5**) with a base is much faster than the corresponding conversion of the 2,3-dihydrothiophene (**5′**). A stoichiometric reaction of a mixture of **5** and **5′** in dry DMSO-d_6 with KH was monitored, through ^{1}H NMR. After the first hour, compound **5** was totally consumed; while **5′** is still present, along with **1K**. Then, an excess of KH is required in order to get the complete deprotonation of compound **5′**. Three equivalents of KH in a DMSO solution of **5** and **5′**, under ultrasound for 9 h, afford **1K** in a quantitative yield. According to these results, a mixture of thiophenes can be used as precursors of acyclic thiapentadienides, requiring only an excess of base and longer times than when **5** is used as the only precursor. According to these results, the deprotonation is more efficient when performed in the following order: 2,5-dihydrothiophene-1,1-dioxide (**4**) > 2,5-dihydrothiophene (**5**) > 2,3-dihydrothiophene (**5′**).

The effect of changing the reaction solvent was investigated trying to avoid the high boiling point of DMSO. Therefore, THF and 1,2-dimethoxyethane (DME) were used with the mixture of **5** and **5′** with NaH. There is evidence of formation of **1Na** in very low yield only after refluxing THF for 24 h or stirring the mixture of reactants in DME for 20 h. The present results show that the success of the synthesis of these anions requires the use of DMSO as a solvent. Previous studies have shown that the methylsulfinyl carbanion is easily formed when DMSO is in presence of a metal hydride [24]. And it is precisely this anion which promotes the deprotonation of the dihydrothiophenes **5**, **5′**, or the corresponding dihydrothiophene-1,1-dioxide **4**. An experiment was



Scheme 6. Synthesis of potassium, sodium and lithium thiapentadienyls and 2,5-dimethyl derivatives.

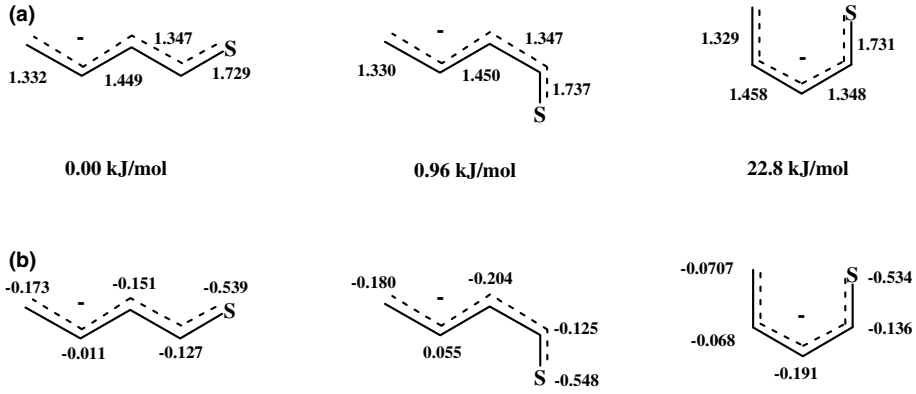
carried out mixing DMSO with NaH, LiH and KH. The formation of the methylsulfinyl carbanion is significantly faster with KH compared to NaH and LiH. The reactivity of **4** in DMSO with the corresponding hydrides is decreasing as follows: KH > NaH ≫ LiH and in summary, the most effective deprotonation of the cyclic dihydrothiophenes is carried out in DMSO as a solvent and KH as a base.

The formation of lithium thiapentadienyls is favored below −35 °C, and they can be prepared in more accessible solvents, such as THF, in order to be accessible as reagents in transmetallation reactions.

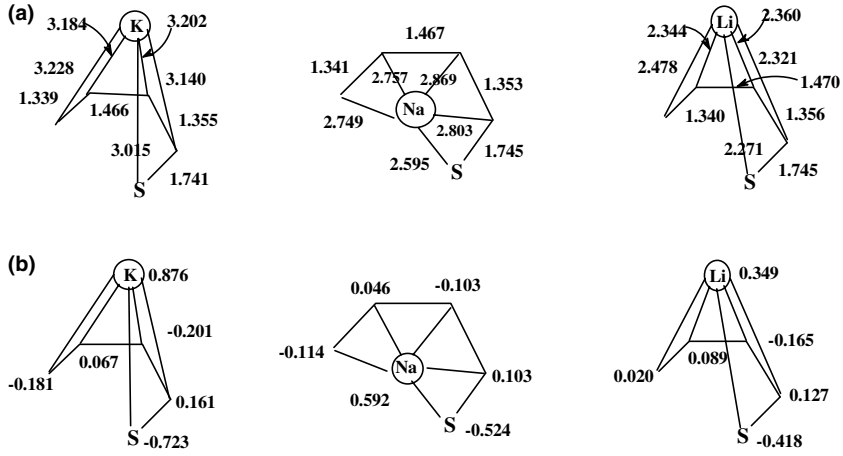
The ^{1}H and ^{13}C NMR data of compounds **1Li**, **1Na** and **1K** are described in Section 4 and they are also consistent with a U conformation, similar to those of **3K**, **3Na** and **3Li**. However, in these thiapentadienyls **1M** (M = K, Na, Li) there is clear evidence, based on the chemical shifts, of the charge delocalization along the acyclic chain (Scheme 6); in contrast with the localized charge detected in the U-shape butadienesulfonyl complexes **3M** (Scheme 1). It is interesting to mention that analogous pentadienyl $(C_5H_7)^-$ anions, depending on the nature of the metallic cation (M^+ = K, Li) can adopt a W (M = Li) or U (M = K) conformation [1b]. The results of monitoring NMR samples of **1Na** and **1K** in DMSO during several months showed a high stability of these species in solution. However, as described above, these thiapentadienyl complexes can not be isolated because they polymerize during the attempt of purification. Contrastingly, there was no evidence of isomerization of **1M** (M = Na, K); while it was evident for the butadienesulfonyl derivatives **3M** and **13M** (M = Li, Na, K). These results are in agreement with the delocalization of the thiapentadienyl and their stabilization through the corresponding cations.

The theoretical calculations yield four lower-energy conformations for the thiapentadienyl anion, with a lower relative energy W-conformer (0.0 kJ/mol) and S-conformer (0.96 kJ/mol), and the higher-energy structures are S-shaped (15.81 kJ/mol) and U-shaped (22.8 kJ/mol). From the analysis of three of them with different conformations, each one with the lowest energy (Scheme 7), it was clear that the calculated bond lengths and charge distributions show that there are no double bonds forming a diene and the charge is distributed along the molecule, although not homogeneously, being strongly located in atoms C5, C3 and essentially in the sulfur atom. Henceforth, it is expected that the interaction between the thiapentadienyl anion and the metal cations, when the complexes are formed, should proceed through the sulfur atom.

The results for the geometry optimization of the metal complexes **1M** beginning alternatively from the S and U shaped anion conformers (vide supra) yield in both cases a U-shaped complex. Whereas, when the W-conformer anion was chosen, the W-shaped metal complex conformer was obtained. Further analysis of the calculated bond lengths and charge distributions of the S and U optimized geometries of complexes **1Li**, **1Na** and **1K** allows to choose the U-geometry as most plausible since in this structure both bond distances and charge distributions (Scheme 8) are in agreement with the experimental observations. In Scheme 8 one can note that the charge transfer from the U-shaped thiapentadienyl ligand towards the cations is larger for the Li-atom and smaller for the K-atom. The charge in complexes **1M** is delocalized across the chain, including the S-atom. Moreover, the calculated metal-carbon and metal-sulfur bond distances indicate that it is plausible to consider that the metal atom is bound to all atoms in the chain and this fact makes the U-conformation as



Scheme 7. Thiapentadienyl anion conformations at the HF/3-21G//3-21G level of theory. (a) Relative energies (kJ/mol) and bond distances in Angstroms. (b) Mulliken charges distributions with all of the hydrogen charges summed to the attached heavy atoms.



Scheme 8. Optimized geometries of **1K**, **1Na** and **1Li** at the HF/6-31+G(d)// HF/6-31+G(d) level of theory. (a) Bond distances in Angstroms. (b) Mulliken charges distributions with all of the hydrogen charges summed to the attached heavy atoms.

the most stable for all the thiapentadienyl complexes. For the U-conformers, the cation size stabilization effect follows the decreasing order of stability: **1K > 1Na > 1Li**.

2.1.4. Potassium and sodium 2,5-dimethyl-thiapentadienyls

The 2,5-dimethylthiophene was partially reduced with sodium as described for thiophene in the literature [12] affording a mixture of 2,5-dimethyl-2,5-dihydrothiophene (**8**) and 2,5-dimethyl-2,3-dihydrothiophene (**8′**). Compounds **8** and **8′** were treated with different bases and solvents, such as NaH, KH, *t*-BuOK, DMSO and THF. The syn-2,5-dimethylthiapentadienyls **10M** (M = Na, K) were obtained along with the anti-isomers **11M** (M = Na, K) as described in Scheme 6. The most effective procedure consists in the reaction of the mixture of **8** and **8′** with NaH in DMSO, heated at 65 °C for 9 h. Compounds **10Na** and **11Na** were obtained in a 1.5:1 ratio, along with **8′**. The last one can be removed under vacuum. Heating longer times or higher temperature affords decomposition products of compounds **10** and **11**, before reaction of **8′** can occur.

Attempts to react the **8** and **8′** with *t*-BuOK or NaH in THF did not succeed. The low reactivity observed with KH in DMSO is attributed to the steric effect of the methyl groups in the dihydrothiophenes **8** and **8′**. Contrastingly, the formation of the methylsulfinyl carbanion, even with an excess of KH in the DMSO, was not reactive enough in front of **8** and **8′** (giving **10K** in 7% and **11K** in 3%) compared to the reaction of **7** (Scheme 2, vide supra). While the C–S bond for unmethylated-dihydrothiophenes is easier to cleavage with KH than NaH; the opposite trend is observed for the 2,5-dimethyl-dihydrothiophenes. All these features can be explained by assuming that because of the higher steric hinderance, the acidic proton is not able to be removed by the *t*-BuOK or the methylsulfinylcarbanion. Meanwhile, the small NaH can react directly with compound **8**, because it does not react efficiently with DMSO in order to give the corresponding methylsulfinyl carbanion.

The ^{1}H and ^{13}C NMR spectroscopy of compounds **10K**, **10Na** and **11K**, **11Na** is described in Section 4. The mixture of isomers **10Na** and **11Na** shows $J_{4,5} = 15.4$ Hz and $J_{4,5} = 11.0$ Hz indicating that the Me5 substituent at C5 is adopting a *syn* and *anti* orientation, respectively (Scheme 6). The $J_{3,4} = 10.3$ Hz confirms the U conformation as observed for **3M**, **9M** and **1M** (M = K, Na, Li).

2.1.5. Potassium and sodium sulfinylpentadienyls

Treatment of **5** and **5′** in acetone with H_2O_2 as described in the literature [13] gives compounds **6** and **6′** which react with KH in DMSO giving, after 30 min, compound **2K** as a major compound, along with unreacted compound **6′** and traces of disproportionation products **3K** and **1K**. After 2.5 h there is a 1:1:1 ratio of **2K**, **3K** and **1K**; after 22 h **6′** has been completely consumed, and **3K** and **1K** remained in solution, without evidence of **2K**. A similar reaction with NaH in DMSO shows evidence of **2Na** which immediately transforms into **3Na** and **1Na**. Compound **6′** is consumed after 22 h. The analogous reaction of **6** and **6′** with Et_3BHLi in THF shows ^{1}H NMR evidence of **3Li** and **1Li**, along with other products which were not identified, which suggests that **2Li** must be formed, but it is rapidly transformed. (Scheme 9).

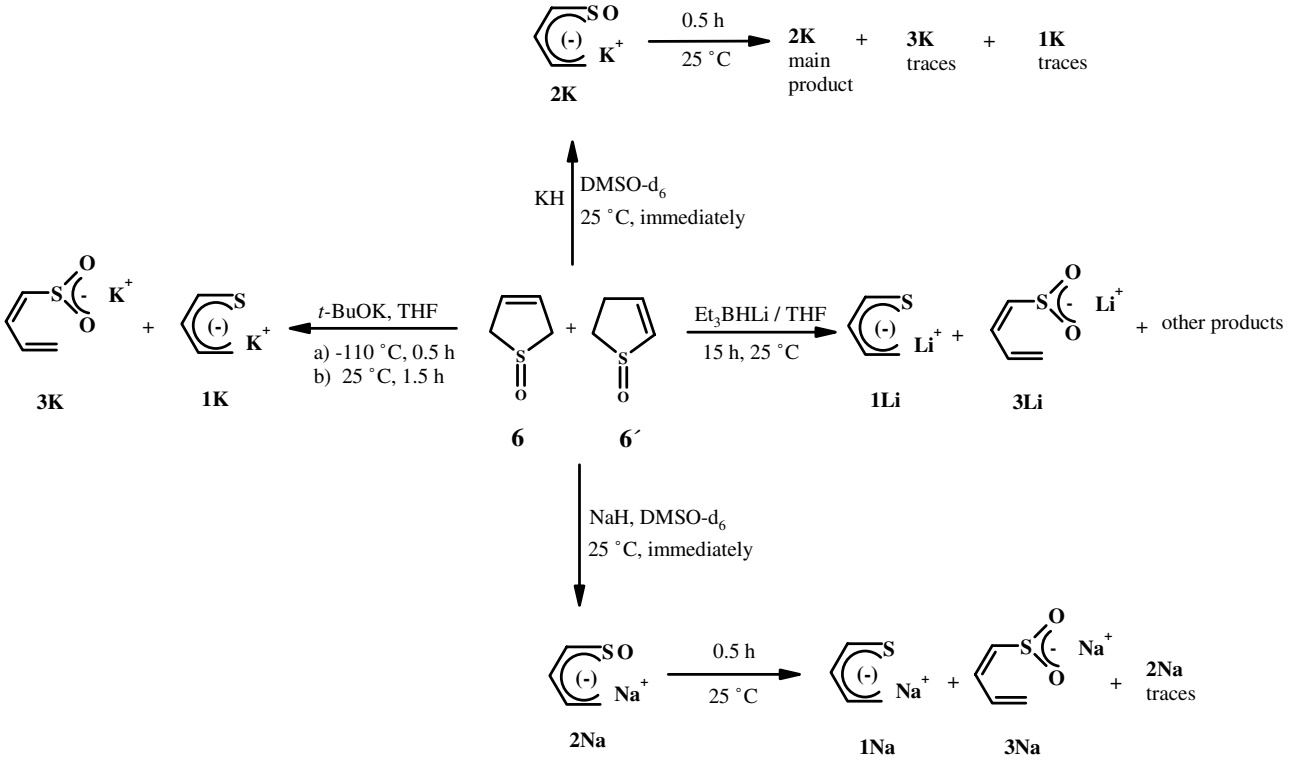
From these results it is clear that the size of the cation is important in the stabilization of the sulfinylpentadienyls **2M** (M = K, Na, Li). Compounds **2M** can easily disproportionate to the corresponding thiapentadienyl (**1**) and butadienesulfonyls (**3**) complexes, as described in Scheme 10. The stability decreases in the following order: **2K** > **2Na** > **2Li**.

Compound **2K** reacts with $[(COD)IrCl]_2$ in THF affording a binuclear compound $[(COD)Ir(1,4,5\text{-}\eta\text{-}CH_2CHCHCHSO)]_2$. The crystal structure gives clear evidence of the stabilization of the sulfinyl ligand in this complex [25].

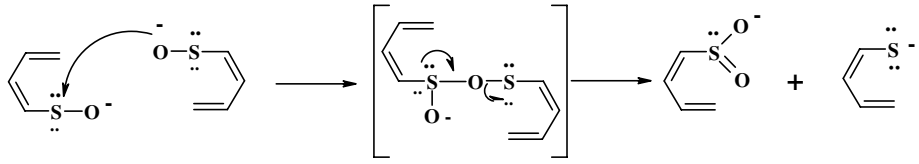
The ^{1}H and ^{13}C NMR spectroscopy of compounds **2K**, **2Na** is described in Section 4. Similar trends in chemical shifts and coupling constants suggest the U conformation and the total delocalization of charge on these sulfinyl complexes, as observed for thiapentadienyl compounds **1M** (M = K, Na).

The theoretical conformational analysis for the sulfinylpentadienyl anion yielded eight lower-energy conformers, from which were selected the lowest three, with geometries: S (0.00 kJ/mol), W (12.19 kJ/mol) and U conformers (24.20 kJ/mol). The structure of these conformers, as well as their relative energies, bond lengths and charge distributions is displayed in Scheme 11. From these results, it is possible to conclude that the sulfinylpentadienyl anion is a delocalized system where the charge is distributed along the chain, including the sulfur and oxygen atoms.

Henceforth, the performance of the geometry optimizations of the corresponding **2M** (M = Li, Na, K) complexes formed from S and W anion conformers of the



Scheme 9. Synthesis of metal sulfinylpentadienyl compounds **2Na** and **2K**.



Scheme 10. Proposed mechanism for disproportionation of compound **2**.

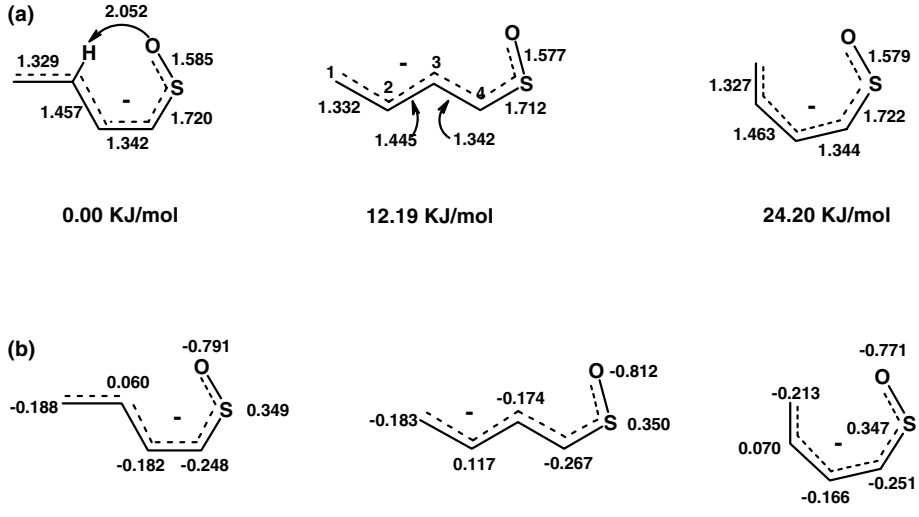
sulfinylpentadienyl anion always give a final S-shaped complex conformer. The bond lengths and charge distributions in the optimized geometries of complexes **2Li**, **2Na** and **2K** are displayed in Scheme 12. In all cases, one can observe an S conformer with the charge distributed along the chain, including the sulfur and oxygen atoms. The computed bond distances for each of the three complexes, between carbons C4–C5 (1.334, 1.335 and 1.336 Å) and C3–C4 (1.345, 1.340 and 1.346 Å) are longer than typical values found for terminal double bonds (1.300 Å) and for internal double bonds (1.318 Å) [26a].

Furthermore, the calculated bond length for S-O in the sulfinylpentadienyl anion (1.577, 1.588 and 1.581 Å), is longer compared with typical experimental S–O bonds (1.445–1.479 Å) [26b]. The observed increment in the computed bond distances for the carbon-carbon double bonds and S–O is consistent with the experimental ^{1}H and ^{13}C NMR chemical shift data, which indicates that the charge is distributed all the chain long. Finally, charge transfer from the sulfinylpentadienyl anion ligand towards the metal cations is larger for Li and lesser for K. The metal-carbon bond lengths for **2M** (M = Li, Na, K), in Scheme 12, show that all distances are shorter than the corresponding values for the van der Waals radius, which suggests an effective interaction of the ligand with the metal. Nevertheless the theoretical study predicts the S-shape as the preferred conformer with the lowest energy; the U-conformer of **2M** (M = Na, K) was found experimentally, at room temperature. As it has been discussed before, **2M** suffers a disproportionation process and it may occur before getting the thermodynamically more stable S-shape, as it has been observed for the butadienesulfonyls **3M**. The decreasing order of stability for **2M** is proportional to the cation size: **1K** > **1Na** > **1Li**.

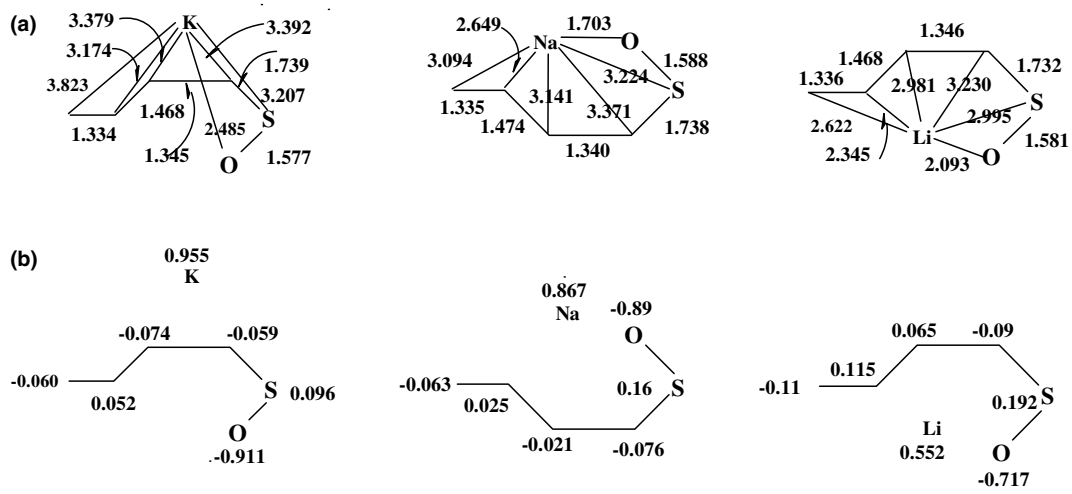
The theoretical study of the stability of the complexes **1M**–**3M** was assessed in two manners:

(a) A frontier orbital [27] (HOMO and LUMO) stability criterion. The energy difference between the HOMO of the donor species (anions) and the LUMO of the acceptor species (cations) is a quantitative indication of the formation reaction of the complexes from the cation and anion fragments. A relatively smaller HOMO–LUMO energy difference corresponds to a more favorable interaction between the heteropentadienyl and the cation. These energy differences are graphically displayed in Scheme 13. One can note that the reactivity of anions with cations Li^{+}, Na^{+}, K^{+} follows the increasing trend $Li^{+} < Na^{+} < K^{+}$. Therefore, the stability of complexes decreases in each series as: **3Li** < **3Na** < **3K**; **2Li** < **2Na** < **2K**; **1Li** < **1Na** < **1K**.

The stability trends may be explained from the fact that interactions between anions **1M**, **2M** and **3M** and



Scheme 11. Sulfinylpentadienyl anion conformations at the HF/3-21G//3-21G level of theory. (a) Relative energies (kJ/mol) and bond distances in Angstroms. (b) Mulliken charges distributions with all of the hydrogen charges summed to the attached heavy atoms.



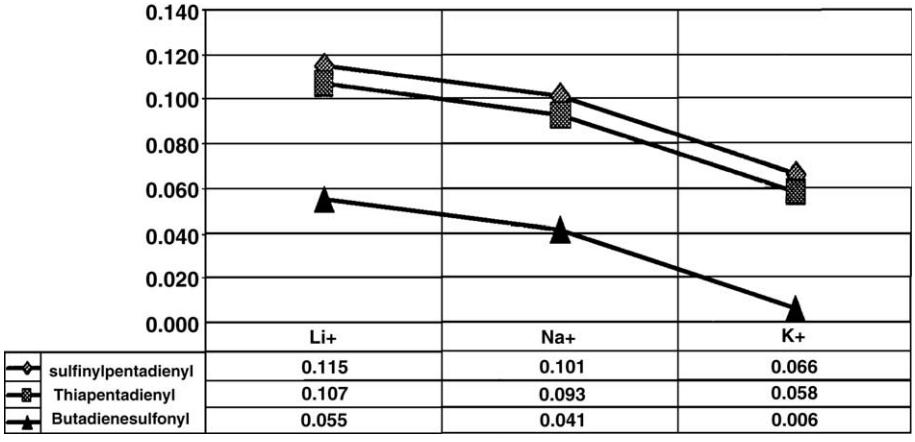
Scheme 12. Optimized geometries of **2K**, **2Na**, **2Li** at the HF/6-31+G(d)// HF/6-31+G(d) level of theory. (a) Bond distances in Angstroms. (b) Mulliken charges distributions with all of the hydrogen charges summed to the attached heavy atoms.

cations M = Li^+, Na^+ and K^+ may be determined by the overlap between the HOMO of anions and the LUMO of cations. Thus, an increase in the drive for complex formation and further stabilization occurs with overlap maximization. Since Li^+ is smaller, this overlap between its LUMO (with the lesser spatial extent) and the anions HOMO will cause very little effective overlap as compared with other cations, such as Na^+ and K^+ LUMO's, and therefore Li^+ is less able to stabilize the complex, which agrees with the observed experimental trends. Perhaps the charge/radius ratio is important, and the spatial extent of the cation, such as that a large one might help stabilize greater degrees of delocalization by being able to be closer to all three potentially charged positions [28].

(b) Second stability criterion relies on the global hardness concept: The electronic chemical hardness (η) [29] and the maximum hardness principle (MHP) [30–32].

The computed chemical hardness was obtained for all anions, cations and the corresponding complexes **1M**, **2M** and **3M** (M = Li, Na and K) from the equation $\eta = \varepsilon_L - \varepsilon_H$, where ε_L and ε_H are the LUMO and HOMO orbital energies. From the individual molecular hardness, hardness differences ($\delta\eta$) have been computed for the reactions: anion + cation → complex. The results of series of compounds, **1M**, **2M** and **3M** (M = Li, Na and K) are in Table 1. From the table values one can observe that the larger reactions $\Delta\eta$ correspond to the most favorable reaction in each series, and the relative stability of complexes in each series, according to the $\Delta\eta$ stability criterion, follows the increasing trends: **3Li < 3Na < 3K**; **2Li < 2Na < 2K**; **1Li < 1Na < 1K**.

In all cases the potassium complexes are always the most stable, whereas sodium and lithium complexes are predicted to be less stable or favorable in a clear relation to the cation size.



Scheme 13. Differences of heteropentadienyl anions' HOMO and the cations' LUMO energies in hartrees at the HF/6-31+G(d)// HF/6-31+G(d) level of theory.

Table 1
Calculated reaction's hardness differences ($\Delta\eta$) for the reaction *heteropentadienyl + cation → heteropentadienyl complex* at the HF/6-31+G(d)//HF/6-31+G(d) level of theory

	1Li	1Na	1K	2Li	2Na	2K	3Li	3Na	3K
Reaction's hardness $\Delta\eta$ (hartrees)	−2.581	−1.636	−1.056	−2.592	−1.650	−1.060	−2.557	−1. 612	−1.030

3. Conclusions

The activation of C–S bond in dihydrothiophenes allows the formation of the corresponding acyclic compounds **1**, **2**, and **3** by different and easy synthetic procedure.The 2,5-dihydrothiophenes reacts always faster than the corresponding 2,3-dihydrothiophenes. NaH and KH react differently during the deprotonation process of dihydrothiophenes. There is a competition between the DMSO and dihydrothiophenes reacting with the NaH; while for KH the reaction with DMSO is favored, giving the corresponding methylsulfinyl carbanion which efficiently deprotonates the dihydrothiophenes without substituents. The effect of methyl substituents in the dihydrothiophenes is significant, modifying considerably the choice of the base.

The influence of the reaction conditions, type of solvent and base is important in order to promote the activation of the C–S bond of the dihydrothiophenes and to stabilize the heteropentadienyl and butadienesulfonyl salts. The different heteroatoms in the chain influence the nature of the corresponding anions. While species with S and SO functional groups have a delocalized charge along the chain, anions with the SO_2 group have a localized diene structure along with an anionic delocalized sulfonyl group. The U conformation is preferred for all derivatives. Nevertheless compounds **3M** (M = K, Na, Li) can suffer a rearrangement, in presence of traces of base, to the most stable S conformation.

The theoretical conformational analysis of the thiapentadienyl, sulfinylpentadienyl and butadienesulfonyl anions yielded the lower energy conformers W, S and S, respectively. The metal complexes **1M**, **2M** and **3M** (M = Li, Na and K) were optimized resulting the most stable conformers, the U, S and S, respectively. The efficient charge transfer obtained for the ligand → lithium cation complex is in agreement with the fact that Li^+ is a harder Lewis acid than K^+, and the thiapentadienyl, sulfinylpentadienyl and butadienesulfonyl anions are good electron donors, which behave comparatively as Lewis bases. These complexes follow the hard and soft acid and base principle of Pearson. The stability trends obtained from the electronic calculations show that the charge transfer interactions between thiapentadienyl, sulfinylpentadienyl and butadienesulfonyl anions with Li^+, Na^+ and K^+ cations involve an effective overlap of the HOMO (anions) with the LUMO (cations) and thus, a better overlap may induce stronger bond formation and higher complex stability. Since the Li cation is the smallest, the spatial extent of its LUMO is the lesser and therefore its overlap is the least effective to stabilize the formed complex. Due to the relative larger spatial extension of LUMO in Na^+ and K^+ cations, their overlap with the HOMO (anions) increases. In general there is good agreement between the theoretical calculated lower-energy conformers, charge distributions, bond lengths and relative complex stabilities with the experimental results.

4. Experimental

4.1. General remarks

All experiments were carried out under nitrogen or argon atmosphere using Standard Schlenk and glovebox techniques. Solvents were distilled from Na/benzophenone (THF) or Na (diethyl ether) under nitrogen before use. Deuterated solvents were degassed and DMSO-d_6 was dried with Na before use.

Na_2S(anh), *cis*-1,4-dichloro-2-butene, thiophene, 2,5-dimethylthiophene, 2,5-dihydrothiophene-1,1-dioxide, 2,4-dimethyl-3-sulfolene, *n*-BuLi (1.6 M in hexane), Et_3BHLi (1 M in THF), LiH, NaH, KH, *t*-BuOK were purchased from Aldrich and used as received, except KH which was separated from the mineral oil by filtration, washed with hexane and dried under vacuum. The mixture of dihydrothiophenes **5** and **5′** (DHTs) was obtained as described in the literature [12]. NMR spectra were recorded with Jeol GSX-270, Eclipse-400 and Bruker 300 spectrometers in $CDCl_3$, CD_3OD, CD_3CN, THF-d_8, D_2O and DMSO-d_6. ^1H and ^{13}C chemical shifts are reported in ppm with reference to TMS, ^{23}Na and ^7Li chemical shifts refer to NaCl/D_2O 0.1 M and LiCl/D_2O 9.7 mM, respectively. IR spectra were recorded in KBr pellets on a Perkin Elmer Spectrum GX spectrophotometer. Elemental analyses were performed at the Chemistry Department of Cinvestav with a Thermo-Finnigan Flash 112 and Desert Analytics, Tucson, AZ, USA. Activation of the C–S bond was carried out in the ultrasound equipment Brandson Ultrasonics Corporation, model 1510R-DTH.

4.2. Synthesis of potassium thiapentadienyl (*1K*)

A mixture of xylenes with 2,5-dihydrothiophene (**5**) (21.3%) and 2,3-dihydrothiophene (**5′**) (10.63%) (0.24 ml, 0.89 mmol of total DHTs, wt/^1H NMR) was

added dropwise to a cold solution (−35 °C) of 1 ml of DMSO-d_6 in the presence of KH (107 mg, 2.65 mmol) under ultrasonic treatment. The reaction mixture was allowed to warm at room temperature and stay in the ultrasound for 1 h, giving an amber solution. At this time, the ^{1}H NMR showed a total conversion of the 2,5-dihydrothiophene into **1K** and, it was after 9 h when the 2,3-dihydrothiophene was totally transformed in **1K** as well; while the xylenes remained intact. Compound **1K** is very stable in solution of DMSO; however, attempts to isolate this complex as a solid were unsuccessful, showing the presence of polymeric species in the NMR spectrum. The ^{1}H NMR of **1K** in DMSO-d_6 gave broad signals, while a mixture of DMSO-d_6 and C_6D_6 allowed to determine the corresponding coupling constants (DMSO-d_6/C_6D_6): δ = 4.66 (d, J = 17.4 Hz, 1H, H^5), 4.48 (d, J = 10.3 Hz, 1H, $H^{5'}$), 7.21 (m, 1H, H^4), 5.82 (dd, J = 10.2, 9.2 Hz, 1H, H^3), 7.09 (d, J = 9.2, 1H, H^2).^{13}C {^{1}H} NMR (DMSO-d_6/C_6D_6): δ = 105.0 (C^5), 136.8 (C^4), 122.9 (C^3), 151.7 (C^2). ^{1}H NMR (DMSO-d_6): δ = 4.70 (1H, H^5), 4.40 (1H, $H^{5'}$), 7.10 (1H, H^4), 5.70 (1H, H^3), 7.00 (1H, H^2). ^{13}C {^{1}H} NMR (DMSO-d_6): δ = 105.1 (C^5), 137.7 (C^4), 122.8 (C^3), 151.5 (C^2).

4.3. Synthesis of sodium thiapentadienyl (*1Na*)

To a solution of 2,5-dihydrothiophene (**5**) (21.3%) and 2,3-dihydrothiophene (**5′**) (10.63%) in xylenes (0.12 ml, 0.45 mmol of total DHTs, wt/^{1}H NMR) in DMSO-d_6 (0.8 ml) was added NaH (13 mg, 0.54 mmol) and the mixture was under ultrasound at ~25–35 °C for 8 h, giving a dark amber solution. The ^{1}H NMR showed the total conversion of 2,5-dihydrothiophene and 2,3-dihydrothiophene in **1Na**, and xylenes which remained intact and were removed under vacuum.

An NMR experiment in which compound **1** (38 mg, 0.45 mmol) in DMSO-d_6 (0.5 ml) was treated with NaH (13 mg, 0.54 mmol). After 8 h under ultrasound, compound **1Na** was formed as the main product. The identification of traces of a second compound was unsuccessful. **1Na** is very stable in DMSO solution; however, all attempts to isolate as a solid gave polymeric insoluble species. ^{1}H NMR (DMSO-d_6): δ = 4.63 (d, J = 17.5 Hz, 1H, H^5), 4.42 (d, J = 10.5 Hz, 1H, $H^{5'}$), 7.07 (m, 1H, H^4), 5.72 (dd, J = 10.0, 8.9 Hz, 1H, H^3), 6.95 (d, J = 8.9, 1H, H^2).^{13}C {^{1}H} NMR (DMSO-d_6): δ = 105.3 (C^5), 136.8 (C^4), 122.9 (C^3), 151.4 (C^2).

4.4. Synthesis of lithium thiapentadienyl (*1Li*)

A 1.6 M solution of *n*-BuLi (0.19 ml, 0.3 mmol) was added dropwise at −35 °C, to a solution of 2,5-dihydrothiophene (**5**) (21.3%) and 2,3-dihydrothiophene (**5′**) (10.6%) in xylenes (82 μL, 0.3 mmol of total DHTs, wt/^{1}H NMR) in THF-d_8 (0.5 ml), under nitrogen. After stirring 5 min the reaction mixture gives a yellow solution which is stable below −35 °C. The ^{1}H NMR showed the total consumption of the 2,3- and 2,5-dihydrothiophenes and formation of **1Li**. ^{1}H NMR (THF-d_8): δ = 4.87 (dd, J = 17.5, 2.7 Hz, 1H, H^5), 4.64 (d, J = 10.4 Hz, 1H, $H^{5'}$), 7.35 (m, 1H, H^4), 5.97 (dd, J = 9.8 Hz, 1H, H^3), (H^2 is overlapped). Compound **1Li** is thermally sensitive and an insoluble white material precipitates in THF-d_8 at room temperature [18]. After 1.5 h at room temperature around 30% of the original **1Li** remained in solution.

4.5. Synthesis of potassium sulfinylpentadienyl (*2K*)

Addition of 0.05 ml of compound **6** (62.5%, 33.7 mmol) and **6′** (37.5%, 20.3 mmol) (0.06 g, 0.54 mmol of total DHTs) to a mixture of 0.6 ml of DMSO-d_6 in the presence of KH (22 mg, 0.54 mmol) gives a brown-yellow solution which after 30 min showed, through the ^{1}H NMR, the presence of **2K** as the main product, and traces of **3K** and **1K**. After 2.5 h **2K**, **3K** and **1K** are in a 1:1:1 ratio along with unreacted compound **6′**. **2K**^{1}H NMR (DMSO-d_6): δ = 4.18 (d, J = 17.2 Hz, 1H, H^5), 4.36 (d, J = 10.3 Hz, 1H, $H^{5'}$), 7.65 (m, 1H, H^4), 5.34 (dd, J = 10.6, 10.6 Hz, 1H, H^3), 6.18 (d, J = 10.6 Hz, 1H, H^2). ^{13}C {^{1}H}NMR (DMSO-d_6): δ = 104.3 (C^5), 137.5 (C^4), 108.5 (C^3), 147.9 (C^2).

4.6. Synthesis of sodium sulfinylpentadienyl (*2Na*)

This complex was prepared as described for **2K**, using NaH (13 mg, 0.54 mmol) and DMSO-d_6 (1 ml). During the first 30 minutes, there is evidence through ^{1}H NMR of **2Na**. ^{1}H NMR (DMSO-d_6): δ = 4.22 (d, J = 17.1 Hz, 1H, H^5), 7. 52 (m, 1H, H^4), 5.35 (dd, J = 10.6, 10.5 Hz, 1H, H^3), 6.26 (d, J = 10.6 Hz, 1H, H^2), ($H^{5'}$ overlapped).

4.7. Synthesis of potassium butadienesulfonyl (*3K*)

A solution of **4** (2.5 g, 21.16 mmol) in 80 ml of THF at room temperature was stirred. Then, a mixture of *t*-BuOK (2 g, 17.82 mmol) in 10 ml of THF was added dropwise. During the addition, a mustard-yellow precipitate was observed. After stirring 1 h at room temperature, the solid went to a pale yellow color. The solution was evaporated under vacuum and the residue was washed five times with THF (20 ml) and dried under vacuum. The yield of the cream solid **3K** was essentially quantitative (99.1%). This compound is soluble in DMSO and H_2O. It does not melt below 250 °C. ^{1}H NMR (DMSO-d_6): δ = 5.14 (d, J = 16.8 Hz, 1H, H^5), 5.08 (d, J = 8.8 Hz, 1H, $H^{5'}$), 6.99 (m, 1H, H^4), 5.97 (dd, J = 10.3, 9.5 Hz, 1H, H^3), 5.75 (d, J = 10.3 Hz,

1H, H^2). (D_2O): δ = 5.43 (d, J = 16.7 Hz, 1H, H^5), 5.36 (d, J = 9.9 Hz, 1H, $H^{5'}$), 7.02 (m, 1H, H^4), 6.44 (dd, J = 10.8, 10.6 Hz, 1H, H^3), 5.94 (d, J = 10.6 Hz, 1H, H^2). ^{13}C {^1H} NMR: (DMSO-d_6): δ = 118.8 (C^5), 133.4 (C^4), 127.2 (C^3), 153.5 (C^2). ^{13}C {^1H} NMR: (D_2O): δ = 123.1 (C^5), 131.2 (C^4), 133.9 (C^3), 144.2 (C^2). IR (KBr): 3401 (m), 1645 (vs), 1581 (m), 1419 (m), 1302 (m), 1209 (m), 1122 (m), 1012 (s), 962 (s), 919 (vs), 778 (m), 643 (m) cm^{-1}. $C_4H_5SO_2K \cdot 0.1H_2O$ (158.04): calc. C 30.40, H 3.31; found C 30.34, H 3.32.

4.8. Synthesis of sodium butadienesulfonyl (*3Na*)

A degassed solution of **4** (1.56 g, 13.2 mmol) was added at room temperature, under argon, to a suspension of NaH (390 mg, 16.1 mmol) in THF (10 ml). The reaction was carried out under ultrasound for 5 h, then 14 h more using an oil bath at 52 °C and finally under reflux (65 °C) for 5.5 h, upon which the mixture turned pale yellow. After cooling to room temperature, the solvent was removed under vacuum and the solid was washed three times with CH_2Cl_2 (10 ml). The yield of the **3Na** was 93.5% (1.73 g, 12.35 mmol). The cream yellow powder does not melt below 250 °C and it is soluble in DMSO and H_2O. ^1H NMR (DMSO-d_6): δ = 5.16 (d, J = 17.2 Hz, 1H, H^5), 5.11 (d, J = 11.0 Hz, 1H, $H^{5'}$), 7.01 (m, 1H, H^4), 6.0 (dd, J = 10.6, 10.2 Hz, 1H, H^3), 5.74 (d, J = 10.2 Hz, 1H, H^2). (D_2O): δ = 5.43 (d, J = 17.9 Hz, 1H, H^5), 5.36 (d, J = 10.1 Hz, 1H, $H^{5'}$), 7.0 (m, 1H, H^4), 6.43 (dd, J = 10.8, 10.3 Hz, 1H, H^3), 5.94 (d, J = 10.3 Hz, 1H, H^2). ^{13}C {^1H} NMR: (DMSO-d_6): δ = 119.0 (C^5), 133.3 (C^4), 127.5 (C^3), 153.1 (C^2). ^{13}C {^1H} NMR: (D_2O): δ = 123.3 (C^5), 131.4 (C^4), 134.0 (C^3), 144.7 (C^2). IR (KBr): 3403 (m), 1621 (m), 1577 (m), 1448 (m), 1142 (m), 1010 (s), 969 (s), 918 (m), 778 (m), 640 (m), 596 (m) cm^{-1}. $C_4H_5SO_2Na \cdot 0.5H_2O$ (149.15): calc. C 32.21, H 3.38; found C 32.26, H 3.89.

4.9. Synthesis of lithium butadienesulfonyl (*3Li*)

A 1.6 M solution of *n*-BuLi (2.65 ml, 4.23 mmol) was added dropwise, at −110 °C (liq N_2/EtOH), to a solution of diisopropylamine (0.6 ml, 4.23 mmol) in THF (5.3 ml), under nitrogen. The freshly prepared LDA was allowed to warm at room temperature and after 20 min the very pale yellow solution was once again cooled to −110 °C. A solution of **4** (0.5 g, 4.23 mmol) in THF (6 ml) was transferred to the LDA solution which turned from yellow to red when the addition has been finished. The reaction mixture was allowed to rise to room temperature, and it was stirred for 1 h. At this time the color of the suspension was yellow. The solid was evaporated under vacuum and the residue was washed three times with THF (10 ml) and washed five times with EtOH (15 ml). Compound **3Li** was partially soluble in EtOH. The soluble fraction was recovered by reducing the volume of EtOH (15 ml), adding Et_2O (80 ml) and cooling down to −5 °C for 24 h. The cream yellow powder was filtered and dried 8 h under vacuum, obtaining 67% yield (0.35 g, 2.82 mmol). The solid is very soluble in DMSO and H_2O and slightly soluble in EtOH, MeOH and insoluble in acetone, THF, Et_2O and hexane. It does not melt below 250 °C. ^1H NMR (D_2O): δ = 5.38 (d, J = 17.5 Hz, 1H, H^5), 5.31(d, J = 9.9 Hz, 1H, $H^{5'}$), 6.96 (m, 1H, H^4), 6.38 (dd, J = 11.0, 11.0 Hz, 1H, H^3), 5.89 (d, J = 11.0 Hz, 1H, H^2). ^{13}C {^1H} NMR (D_2O): δ = 123.1(C^5), 131.2 (C^4), 134.0 (C^3), 144.2 (C^2). ^7Li {^1H} NMR (D_2O): δ = 5.30. IR (KBr): 3410 (m), 1817 (w), 1631 (m), 1580 (m), 1498 (w), 1416 (m), 1324 (w), 1295 (w), 1029 (s), 1008 (s), 902 (vs), 786 (vs), 645 (m), 599 (m) cm^{-1}. $C_4H_5SO_2Li \cdot 0.25H_2O$ (128.594): calc. C 37.36, H 4.30; found C 37.39, H 4.30.

4.10. Synthesis of potassium 3,5-dimethyl-butadienesulfonyl (*9K*)

(a) A solution of *t*-BuOK (190 mg, 1.71 mmol) in THF (20 ml) was slowly added to a cold (−110 °C) THF (10 ml) solution of compound **7** (250 mg, 1.71 mmol). The reaction mixture was allowed to warm at room temperature and stirred 3 h. The white solid from the solution was filtered, washed three times with THF (10 ml) and dried under vacuum. Compound **9K** was obtained in 14.3% yield (45 mg, 0.024 mmol).

(b) A Schlenk tube was charged with KH (20 mg, 0.5 mmol), (previously washed from the mineral oil with hexane, dried under vacuum and kept in a dry box), and compound **7** (62 mg, 0.423 mmol). An exothermic reaction was observed when DMSO-d_6 (0.75 ml) was added with the immediate evolution of dihydrogen gas. After 10 min of stirring there was no insoluble material in the reaction mixture, and 30 min later the pale amber solution was observed through the ^1H NMR showing **9K** as the only product. ^1H NMR (DMSO-d_6): δ = 5.62 (m, 1H, H^5), 1.73(d, J = 5.8 Hz, 3H, Me^5), 6.84 (d, J = 15.0 Hz, 1H, H^4), 1.68 (s, 3H, Me^3), 5.52 (s, 1H, H^2). (D_2O): δ = 6.02 (m, 1H, H^5), 1.77 (d, J = 6.6 Hz, 3H, Me^5), 6.82 (d, J = 15.4 Hz, 1H, H^4), 1.85 (s, 3H, Me^3), 5.71 (s, 1H, H^2). ^{13}C {^1H} NMR (DMSO-d_6): δ = 125.7 (C^5), 18.7 (Me^5), 129.7 (C^4), 130.7 (C^3), 19.6 (Me^2), 150.3 (C^2). IR (KBr): 3300 (m), 2362 (m), 2348 (m), 2169 (m), 1954 (w), 1795 (w), 1643 (vs), 1581 (m), 1500 (w), 1441 (m), 1378 (m), 1254 (m), 1209 (m), 1196 (m), 1002 (s), 958 (s), 853 (m), 806 (vs), 781 (m), 645 (m) cm^{-1}. $C_6H_9SO_2K \cdot 0.75H_2O$ (197.80): calc. C 36.43, H 5.31; found C 36.36, H 5.25.

4.11. Synthesis of sodium 3,5-dimethyl-butadienesulfonyl (**9Na**)

This complex was prepared as described for **9K**, method (b), using compound **7** (160 mg, 1.1 mmol), NaH (31 mg, 1.30 mmol) and DMSO-d_6 (1 ml). After stirring for 1.5 h the ^{1}H NMR gave evidence of a total transformation of **7** to **9Na**. ^{1}H NMR (DMSO-d_6/C_6D_6): δ = 5.60 (m, 1H, H^5), 1.66 (d, J = 5.6 Hz, 3H, Me^5), 7.27 (d, J = 15.4 Hz, 1H, H^4), 1.82 (s, 3H, Me^3), 6.25 (s, 1H, H^2). ^{23}Na NMR (DMSO-d_6): δ = 3.12.

4.12. Synthesis of lithium 3,5-dimethyl-butadienesulfonyl (**9Li**)

A solution of *n*-BuLi (1.6 M in hexane, 1.06 ml, 1.71 mmol) was slowly added to a cold (−35 °C) THF (2 ml) solution of compound **7** (250 mg, 1.71 mmol). The light brown reaction mixture was allowed to warm at room temperature and stirred 1.3 h. The beige solid from the solution was filtered, washed five times with THF (5 ml) and dried under vacuum for 4 h. Compound **9Li** was obtained as a cream solid in 88.4% yield (230 mg, 1.51 mmol). ^{1}H NMR (DMSO-d_6): δ = 5.63 (m, 1H, H^5), 1.73(d, J = 6.4 Hz, 3H, Me^5), 6.84 (d, J = 15.8 Hz, 1H, H^4), 1.69 (s, 3H, Me^3), 5.51 (s, 1H, H^2). (D_2O): δ = 6.04 (m, 1H, H^5), 1.79 (d, J = 6.9 Hz, 3H, Me^5), 6.83 (d, J = 15.3 Hz, 1H, H^4), 1.86 (s, 3H, Me^3), 5.72 (s, 1H, H^2). ^{13}C {^{1}H} NMR (DMSO-d_6): δ = 125.9 (C^5), 18.8 (Me^5), 129.8 (C^4), 130.8 (C^3), 19.7 (Me^2), 150.0 (C^2). ^{13}C {^{1}H} NMR (D_2O): δ = 126.9 (C^5), 17.9 (Me^5), 132.1 (C^4), 140.3 (C^3), 19.0 (Me^2), 139.9 (C^2). ^{7}Li {^{1}H} NMR (DMSO-d_6): δ = 4.30. ^{7}Li {^{1}H} NMR (D_2O): δ = 5.38. IR (KBr): 3036 (m), 2950 (m), 2917 (m), 2854 (m), 2728 (m), 2004 (m), 1925 (m), 1642 (m), 1591 (m), 1443 (vs), 1376 (m), 1333 (w), 1308 (w), 1221 (m), 1176 (m), 1029 (s), 1003 (s), 968 (s), 861 (vs), 816 (vs), 782 (m), 634 (m), 582 (m), 527 (m), 484 (m) cm^{-1}. $C_6H_9SO_2Li$ (152.144): calc. C 47.37, H 5.96; found C 47.64, H 6.20.

4.13. Synthesis of sodium 2,5-dimethyl-thiapentadienyl (**10Na**) and (**11Na**)

An hexane solution (0.51 ml) of compound **8** (12.7%), **8′** (29.4%) and thiophene (16.9%) (202 mg, 1.77 mmol of total DHTs, wt/^{1}H NMR) was added dropwise to a suspension of NaH (130 mg, 5.32 mmol) in DMSO-d_6 (1 ml) at room temperature. Then, the mixture was refluxed at ~65 °C for 6 h and slowly cooled down to 40 °C, evaporation, at this temperature, of the volatiles (0.05 mmHg) afforded the isomers **10Na** and **11Na** in a 1.5:1.0 ratio. **10Na** (DMSO-d_6/C_6D_6): δ = 5.44 (dq, J = 15.4 Hz, 1H, H^5), 1.85 (d, J = 6.4 Hz, 3H, Me^5), 7.35 (m, 1H, H^4), 6.25 (d, J = 10.3 Hz, 1H, H^3), 2.42 (s, 3H, Me^2).^{13}C {^{1}H} NMR (DMSO-d_6/C_6D_6): δ = 115.9 (C^5), 18.3 (Me^5), 135.9 (C^4), 120.4 (C^3), 152.5 (C^2), 35.3 (Me^2). **11Na** ^{1}H NMR (DMSO-d_6/C_6D_6): δ = 5.18 (dq, J = 11.0 Hz, 1H, H^5), 1.83 (d, J = 5.9 Hz, 3H, Me^5), 7.35 (m, 1H, H^4), 6.47 (d, J = 10.6 Hz, 1H, H^3), 2.50 (s, 3H, Me^2). ^{13}C {^{1}H} NMR (DMSO-d_6/C_6D_6): δ = 113.0 (C^5), 13.9 (Me^5), 133.6 (C^4), 116.1 (C^3), 156.2 (C^2), 35.8 (Me^2).

4.14. Synthesis of compounds lithium (*Z*-4-methyl-3-propen-1-sulfonyl) (**14Li**) and (*E*-4-methyl-3-propen-1-sulfonyl) (**15Li**)

A solution of Et_3BHLi (1 M in THF, 2.1 ml, 2.12 mmol) was added dropwise to a frozen THF solution (10 ml) of **4** (250 mg, 2.12 mmol). As the mixture began liquifing, dihydrogen was bubbled for 4 h. After the volume was reduced until ≅ 4 ml, the resulting white precipitate was filtered, washed six times with THF (5 ml) and dried under vacuum. The white solid (30 mg) was a mixture of compounds **3Li**, **14Li** and **15Li** in a 1:6:6 ratios. Isomer **14Li** ^{1}H NMR (D_2O): δ = 2.97(d, J = 7.7 Hz, 2H, $H^{2,2'}$), 5.40 (m, 1H, H^3), 5.67 (m, 1H, H^4), 1.65 (d, J = 6.6 Hz, 3H, Me). ^{13}C {^{1}H} NMR (D_2O): δ = 133.4 (C^4), 120.0 (C^3), 64.5 (C^2), 17.6 (Me). Isomer **15Li** ^{1}H NMR (D_2O): δ = 3.10 (d, J = 7.7 Hz, 2H, $H^{2,2'}$), 5.40 (m, 1H, H^3), 5.80 (m, 1H, H^4), 1.60 (d, J = 6.9 Hz, 3H, Me). ^{13}C {^{1}H} NMR (D_2O): δ = 131.1 (C^4), 119.0 (C^3), 59.4 (C^2), 12.9 (Me). ^{7}Li {^{1}H} NMR (D_2O): δ = 5.28.

4.15. Synthesis of potassium methylsulfinyl

Addition of KH (330 mg, 8.2 mmol) in 2 ml of DMSO (28.2 mmol) gave an immediate exothermic reaction with H_2 evolution. After 1 h there was no evidence of solid KH in the green solution. Immediate reaction of the methylsulfinyl potassium with compound **4** afforded quantitatively compound **3K**.

4.16. Theoretical methodology and calculations

For thiapentadienyl, sulfinylpentadienyl and butadienesulfonyl anions the initial conformational analysis involved a systematic search of the potential energy surface (PES) performed with a Genetic algorithm [33]. At each point in the PES, energies for each structure were determined from calculations at the Hartree–Fock [34] level of theory and with numerical precision given by the use of the split valence basis set 3-21G. This methodology is described by the notation: (HF/3-21G). Calculations and structure and property visualizations were performed with the SPARTAN 5.1.1. software [35].

Thereafter, all metallic complexes were formed from the lower-energy anion conformers previously obtained. The final level of theory/precision for all complexes **1M**, **2M** and **3M** (M = Li, Na, K) was a geometry optimization with no symmetry restrictions at the Hartree–Fock ab initio level with a larger split valence basis set augmented with polarization and diffuse functions 6-31+G(d).

A frequency analysis was performed for all optimized structures to make sure that the obtained geometries corresponded to a minimum in the PES. The final molecular energies, Mulliken charges and wavefunctions were computed in a single point calculation for each species, employing program GAUSSIAN 94 [36]. Then, the final level/precision was HF/6-31+G(d)//HF/6-31+G(d). Results from these calculations were visualized with the aid of the GAUSVIEW 2.0. software [37].

Acknowledgement

We express our thanks to Dr. Armando Ariza Castolo for helping and advice with some of the NMR experiments, and Ma. Luisa Rodriguez Perez and Victor Manuel Gonzalez for running some of the NMR spectra. We also thank Dr. José Román Torres Lubian of CIQA-Saltillo for the GPC data of the polymers produced by thiapentadienyl compounds. P.G.M. thanks IMP and Conacyt for financial support and this research was supported by Conacyt (38507-E), Mexico. M.V. and J.R. gratefully acknowledge support from DGSCA-UNAM for providing an account in a SGI Origin Series 2000 computer.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.12.014.

References

[1] (a) P. Powell, Adv. Organomet. Chem. 26 (1986) 125, and references therein;
(b) H. Yasuda, A. Nakamura, J. Organomet. Chem. 285 (1985) 15, and references therein;
(c) H. Yasuda, M. Yamauchi, Y. Ohnuma, A. Nakamura, Bull. Chem. Soc. Jpn. 54 (1981) 1481;
(d) L.M. Pratt, A. Streitwieser, J. Org. Chem. 65 (2000) 290;
(e) D. Seyferth, J. Pornet, J. Org. Chem. 45 (1980) 1721;
(f) D. Seyferth, J. Pornet, R.M. Weinstein, Organometallics 1 (1982) 1651;
(g) R.D. Ernst, J.W. Freeman, P.N. Swepston, D.R. Wilson, J. Organomet. Chem. 402 (1991) 17;
(h) L. Stahl, H. Ma, R.D. Ernst, I. Hyla-Kryspin, R. Gleiter, M.L. Ziegler, J. Organomet. Chem. 326 (1987) 257;
(i) D.R. Wilson, L. Stahl, R.D. Ernst, in: R.B. King, J.J. Eisch (Eds.), Organometallic Syntheses, vol. 3, Academic Press, New York, 1986, p. 136;
(j) J.R. Bleeke, Y.-F. Xie, W.-J. Peng, M. Chiang, J. Am. Chem. Soc. 111 (1989) 4118;
(k) J.R. Bleeke, Acc. Chem. Res. 24 (1991) 271;
(l) C.W. Shoppee, G.N. Henderson, J. Chem. Soc. Chem. Commun. (1974) 561;
(m) R.B. Bates, R.H. Carnighan, C.E. Staples, J. Am. Chem. Soc. 85 (1963) 3031;
(n) W. Oppolzer, R.L. Snowden, D.P. Simmons, Helv. Chim. Acta 64 (1981) 2002;
(o) H. Yasuda, T. Nishi, K. Lee, A. Nakamura, Organometallics 2 (1983) 21;
(p) H. Yashuda, K. Tatsumi, A. Nakamura, New Aspects of Carbanion Chemistry. Structure of Pentadienyl Anions and Butenediyl Dianions and their Roles in Organic and Inorganic Synthesis, Elsevier Science Publishing Co. Inc., New York, 1987, p. 59.

[2] (a) G.J. Heiszwolf, H. Kloosterziel, Recl. Trav. Chim. Pays-Bas 86 (1967) 807;
(b) J.R. Bleeke, T. Haile, P.R. New, M.Y. Chiang, Organometallics 12 (1993) 517;
(c) M.E. Navarro-Clemente, P. Juarez-Saavedra, M. Cervantes-Vasquez, M.A. Paz-Sandoval, A.M. Arif, R.D. Ernst, Organometallics 21 (2002) 592;
(d) J.R. Bleeke, E. Donnay, N.P. Rath, Organometallics 21 (2002) 4099;
(e) I.I. Rangel Salas, M.A. Paz-Sandoval, H. Nöth, Organometallics 21 (2002) 4696;
(f) R.B. Bates, L.M. Kroposki, D.E. Potter, J. Org. Chem. 37 (1972) 560.

[3] (a) G. Wolf, E.-U. Würtwein, Chem. Ber. 24 (1991) 889;
(b) J.A. Gutiérrez, M.A. Paz-Sandoval, J. Robles, J. Organomet. Chem. 599 (2000) 147;
(c) J.R. Bleeke, S.T. Luaders, K.D. Robinson, Organometallics 13 (1994) 1592;
(d) J.A. Gutierrez, M.E. Navarro Clemente, M.A. Paz-Sandoval, A.M. Arif, R.D. Ernst, Organometallics 18 (1999) 1068.

[4] (a) H. Kloosterziel, J.A. Van Drunen, P. Galama, J. Chem. Soc. Chem. Commun. (1969) 885;
(b) J.R. Bleeke, P.V. Hinkle, N.P. Rath, Organometallics 20 (2001) 1939;
(c) J.R. Bleeke, M.F. Ortwerth, M. Chiang, Organometallics 11 (1992) 2740;
(d) J.R. Bleeke, M.F. Ortwerth, A.M. Rohde, Organometallics 14 (1995) 2813;
(e) J.R. Bleeke, P.V. Hinkle, N.P. Rath, J. Am. Chem. Soc. 121 (1999) 595.

[5] R.L. Crumbie, D.D. Ridley, Aust. J. Chem. 34 (1981) 1017.

[6] (a) J.J. Burger, T.B.R.A. Chen, E.R. De Waard, H.O. Huisman, Tetrahedron 36 (1980) 723;
(b) T.S. Chou, H.-H. Tso, L.-J. Chang, J. Chem. Soc. Perkin Trans. I (1985) 515;
(c) R.C. Krug, J.A. Rigney, G.R. Tichelaar, J. Org. Chem. 27 (1962) 1305.

[7] A.R. Katritzky, M. Piffl, H. Lang, E. Anders, Chem. Rev. 99 (1999) 665, and references therein.

[8] R.H. Everhardous, Rec. Trav. Chim. Pays-Bas 95 (1976) 153.

[9] (a) S. Pagano, A. Mutch, F. Lefebvre, J.-M. Basset, J. Mol. Catal. A: Chem. 133 (1998) 61;
(b) R.H. Grubs, S. Chang, Tetrahedron 54 (1998) 4413;
(c) S.K. Armstrong, B.A. Christie, Tetrahedron Lett. 37 (1996) 9373;
(d) Y.-S. Shon, T.R. Lee, Tetrahedron Lett. 38 (1997) 1283.

[10] (a) J.M. McIntosh, Can. J. Chem. 52 (1974) 1934;
(b) J.M. McIntosh, R.S. Steevensz, Can. J. Chem. 55 (1977) 2442;
(c) J.M. McIntosh, R.A. Sieler, Can. J. Chem. 56 (1978) 226;
(d) J.M. McIntosh, L.Z. Pillon, Can. J. Chem. 62 (1984) 2089.
[11] (a) J.N. Gardener, S. Kaiser, S. Krubiner, H. Lucas, Can. J. Chem. 51 (1973) 1419;
(b) M.G. Pettett, A.B. Holmes, J. Chem. Soc. Perkin trans. I (1985) 1161.
[12] S.F. Birch, D.T. McAllan, J. Chem. Soc. (1951) 2556.
[13] R.C. Krug, D.E. Boswel, J. Heterocycl. Chem. 4 (1967) 309.
[14] R. Glaser, A. Streitwieser, J. Org. Chem. 56 (1991) 6612.
[15] A. Abbotto, A. Streitwieser, P. Schleyer, J. Am. Chem. Soc. 119 (1997) 11255.
[16] R.C. Fort, D.A. Hrovat, W.T. Borden, J. Org. Chem. 58 (1993) 211.
[17] L.M. Pratt, A. Streitwieser, J. Org. Chem. 65 (2000) 290.
[18] (a) S. Kalinowsky, S. Berger, H.-O. Braun, Carbon-13 NMR Spectroscopy, John Wiley & Sons, 1991, p. 134;
(b) S. Kalinowsky, S. Berger, H.-O. Braun, Carbon-13 NMR Spectroscopy, John Wiley & Sons, 1991, p. 185;
(c) S. Kalinowsky, S. Berger, H.-O. Braun, Carbon-13 NMR Spectroscopy, John Wiley & Sons, 1991, p. 187;
(d) S. Kalinowsky, S. Berger, H.-O. Braun, Carbon-13 NMR Spectroscopy, John Wiley & Sons, 1991, p. 417.
[19] H. Günther, NMR Spectroscopy, second ed., J. Wiley & Sons, 1994, p. 124.
[20] D.R. Wilson, R.D. Ernst, T.H. Cymbaluk, Organometallics 2 (1983) 1220.
[21] (a) W. Trakarnpruk, A.M. Arif, R.D. Ernst, Organometallics 13 (1994) 2423;
(b) W. Trakarnpruk, A.M. Arif, R.D. Ernst, Organometallics 11 (1992) 1686.
[22] P. Gamero-Melo, M. Cervantes-Vásquez, A. Ramirez-Monroy, M.E. Sánchez-Castro, M.A. Paz-Sandoval, Organometallics 23 (2004) 3290.
[23] J.R. Torres Lubián, personal communication. The solid sample isolated at room temperature from reaction of 1Li was analyzed by GPC giving molecular weight of 19,496 (UV). Another signal of low molecular weight may suggest the presence of oligomers.
[24] (a) G.A. Russell, S.A. Weiner, J. Org. Chem. 31 (1966) 248;
(b) E.J. Corey, M. Chaykovsky, J. Am. Chem. Soc. 87 (1965) 1345.
[25] P. Gamero-Melo, M.A. Paz-Sandoval, unpublished results.
[26] (a) F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. II (1987) S1–S19;
(b) F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans II (1989) S1–S83.
[27] I. Fleming, Frontier Orbitals and Organic Chemical Reactions, J. Wiley, New York, 1976.
[28] A reviewer has suggest us that charge/radius ratio should be also consider as an important factor.
[29] (a) R.G. Pearson, Chemical Hardness: Applications from Molecules to Solids, Wiley-VCH Verlag GMBH, Weinheim, 1997;
(b) K.D. Sen, D.M.P. Mingos (Eds.), Chemical Hardness: Structure and Bonding, Springer-Verlag, Berlin, 1993;
(c) R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, 1989;
(d) R.G. Pearson, Hard and Soft Acids and Bases, Dowden, Hutchinson and Ross, Stroudsberg, PA, 1973;
(e) R.G. Pearson, J. Chem. Educ. 64 (1987) 561.
[30] R.G. Parr, P.K. Chattaraj, J. Am. Chem. Soc. 113 (1991) 1854.
[31] P.K. Chattaraj, G.H. Liu, R.G. Parr, Chem. Phys. Lett. 237 (1995) 171.
[32] P.K. Chattaraj, Proc. Indian Natl. Sci. Acad. Part A 62 (1996) 1133.
[33] D.E. Goldberg, Genetic Algorithms ins Search, Optimization and Machine Learning, Addison Wesley, Massachusetts, 1989.
[34] W.J. Hehre, L. Radom, P.V.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.
[35] Spartan, version 5.1.1., Wavefunction Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA, USA, 1999.
[36] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, revision E.2, Gaussian, Inc., Pittsburgh, PA, 1995.
[37] GAUSS VIEW 2.0, Gaussian, Inc. Carnegie Office Park, Bldg. 6, Pittsburgh, PA. 15106, USA, 1998.