Are Pi-Ligand Exchange Reactions of Thiirenium and Thiiranium Ions Feasible? An Ab Initio Investigation

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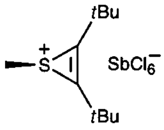
Abstract: Ab initio calculations at the G2 level have been employed to investigate the hitherto unobserved π-ligand exchange reactions of thiirenium and thiiranium ions. Two pathways for exchange and one pathway for insertion are presented. The lower energy exchange pathway has barriers of 19.8–46.6 kJ mol^{-1}. The barriers for the second exchange pathway and for the insertion reaction are considerably larger. The calculations predict that π-ligand exchange is indeed feasible for thiirenium and thiiranium ions, that the exchange reaction is stereospecific with respect to the configuration at sulfur, and that insertion will not compete with exchange despite a high thermodynamic driving force for the former. These conclusions closely parallel those reached in a recent theoretical investigation of the corresponding phosphorus systems for which π-ligand exchange was observed experimentally.

Keywords: ab initio calculations · exchange reactions · insertions · pi interactions · sulfur heterocycles

Introduction

Salts consisting of a nonnucleophilic anion and a thiirenium ion bearing *tert*-butyl or phenyl substituents on the ring carbon atoms (e.g., **1**) have been isolated as well-defined solids at room temperature.[1, 2] The identities of the salts have been verified by NMR spectroscopy[2] and in one case also by X-ray diffraction.[3] Thiirenium salts with less bulky substituents have not been isolated, but have been observed in cold sulfur dioxide by NMR spectroscopy.[2a, 4] Interestingly, salts of 2,3-di- and 2,2,3,3-tetra-alkylthiiranium ions bearing both small and bulky substituents in the ring have been isolated at room temperature, for example **2,** which is stable for several weeks at −10 °C.[5, 6] NMR spectroscopy[5] and X-ray diffraction[6, 7] measurements have again provided unambiguous proof of the identities of such salts. Salts of thiiranium ions that are unsubstituted at carbon or with 2,3-di- or 2,2,3-trimethyl substitution have yet to be isolated, although the existence of the latter two compounds in cold sulfur dioxide has been confirmed by NMR spectroscopy.[5]



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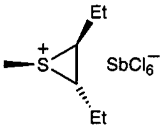

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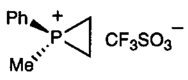
Thiirenium and thiiranium ions are involved in a number of important reactions[1, 8] and theoretical investigations of their chemistry have been reported previously.[9, 10] Much of this work has been focussed on the electrophilic character of the ring carbon atoms, for example S_N2 and Ad_N-*E* ring-opening reactions by nucleophiles.[10]

A novel reaction of the analogous three-membered phosphorus heterocyclic ions was recently reported, wherein the reaction of the phosphiranium salt **3** with dimethylacetylene cleanly gave the phosphirenium salt **4** by displacement of ethylene.[11] It was subsequently found that **4** reacted with a variety of alkynes to give thermodynamic mixtures of phosphirenium salts.[12] The behavior of **3** and **4** towards alkynes is reminiscent of π-ligand exchange in organometallic chemistry, and it is tempting to consider these salts as π-complexes of the six-electron methylphenylphosphenium ion and to refer to the novel reaction as π-ligand exchange. A high-level ab initio investigation indicated that the observed exchange reaction is indeed a very low-energy process.[13]



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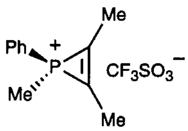

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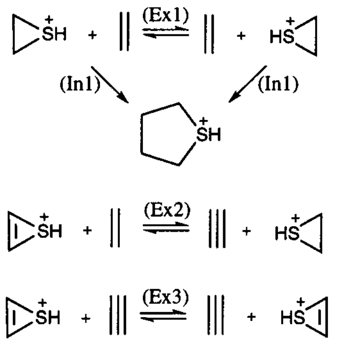
To our knowledge, π-ligand exchange in salts of thiirenium and thiiranium ions has yet to be observed experimentally. In the present work, we have employed ab initio molecular orbital calculations on prototypical systems in order to investigate the feasibility of the π-ligand exchange in thiirenium and thiiranium salts. In addition, we present results for a competing insertion reaction that leads to thermodynamically favorable five-membered heterocyclic cations of sulfur.

Computational Methods

Ab initio molecular orbital calculations[14] were carried out by means of a modified form of G2 theory[15] with the GAUSSIAN 94[16] and MOLPRO 96[17] systems of programs. G2 theory corresponds effectively to energy calculations at the QCISD(T)/6-311 + G(3df,2p) level on MP2(full)/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies (ZPVEs) and a so-called higher level correction. It has been shown to perform well for the calculation of atomization energies, ionization energies, electron affinities, bond energies, proton affinities, acidities, and reaction barriers.[15, 18] In the present work, we have used a slightly modified version of G2 theory in which the ZPVEs were calculated with MP2(full)/6-31G(d) harmonic vibrational frequencies scaled by 0.9646.[19] This makes possible direct comparison with our previous results for the analogous phosphorus systems.[13] The modified version of G2 theory is formally called G2(ZPE = MP2),[20] but we use the G2 label here for the sake of brevity. The transition structures for the reactions reported in the present work have been confirmed in each case by the calculation of vibrational frequencies (one imaginary frequency) and an intrinsic reaction-coordinate analysis. Calculated G2 total energies are presented in Table S1 of the Supporting Information. Relative energies within the text correspond to G2 values at 0 K. GAUSSIAN archive entries for the MP2(full)/6-31G(d) optimized geometries are given in the Supporting Information (Table S2).

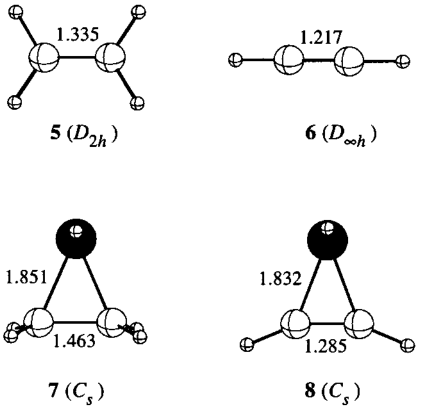
Results and Discussion

A schematic representation of the model exchange (Ex1–Ex3) and insertion (In1) reactions investigated in the present work is displayed in Scheme 1. Two pathways were characterized for the exchange reaction and one pathway was characterized for the insertion reaction. The results for the two exchange pathways, the pathway for insertion, comparisons between them, and comparisons with the corresponding results for the analogous phosphorus systems are discussed separately in the sections that follow.



Scheme 1. Model exchange (Ex1–Ex3) and insertion (In1) reactions.

Figures 1, 2, 4 and 6 depict MP2(full)/6-31G(d) optimized structures, including optimized values of selected geometric parameters, for all species investigated. Complete geometries in the form of GAUSSIAN archive entries are presented in Table S2 of the Supporting Information. Barriers and reaction energies for the reactions in Scheme 1, calculated at the G2 level at 0 K, are given in Table 1. Schematic energy profiles are displayed in Figures 3, 5 and 7.



5 (D_{2h}) **6** ($D_{\infty h}$) **7** (C_s) **8** (C_s)

Figure 1. Selected MP2(full)/6-31G(d) geometrical parameters of reactant molecules involved in the Ex1–Ex3 exchange and In1 insertion reactions. Bond lengths in Å.

Table 1. Calculated barriers and reaction energies for exchange (Ex) and insertion (In) reactions.[a]

	Pathway	Barrier	Reaction energy
Ex1[b]	A	46.6	0.0
	B	240.8	0.0
Ex2[b]	A	19.8	– 53.0
	B1	193.7	– 53.0
	B2	205.5	– 53.0
Ex3[b]	A	42.0	0.0
	B	222.2	0.0
In1[b]		393.0	– 196.6

[a] G2 values in kJ mol^{-1} at 0 K. [b] See Scheme 1.

Exchange reactions—pathway A: In the identity reaction Ex1, the thiiranium ion **7** reacts with ethylene. Pathway A of the Ex1 reaction (Figures 2 and 3) involves the initial formation of a C_s complex (**9**), with a binding energy of 25.6 kJ mol^{-1} relative to the reactants. Product and reactant complexes are connected by the C_{2v} transition structure **TS-Ex1A** at 46.6 kJ mol^{-1}.

The Ex2 reaction proceeds in a manner similar to reaction Ex1. Ethylene and the thiirenium ion (**8**) initially form the C_s complex **14**, with a binding energy of 28.7 kJ mol^{-1} relative to the separate species (Figures 4 and 5). In the reverse reaction, acetylene and thiiranium ion give the C_s complex **17**, with a binding energy of 35.8 kJ mol^{-1} relative to acetylene and thiiranium ion. The C_s transition structure **TS-Ex2A** at 19.8 kJ mol^{-1} directly connects the reactant and product complexes **14** and **17**, and is very similar to **TS-Ex1A**. Reaction Ex2 is predicted to be exothermic by 53.0 kJ mol^{-1} and, in accordance with Hammond's postulate, **TS-Ex2A** resembles more closely the higher energy complex **14**.

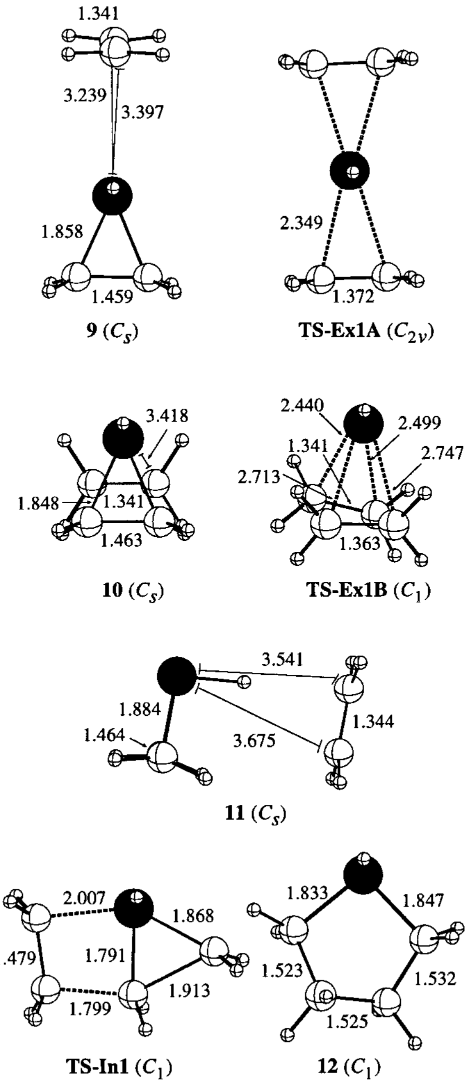


Figure 2. Selected MP2(full)/6-31G(d) geometrical parameters of species involved in the Ex1 and In1 reactions. Bond lengths in Å.

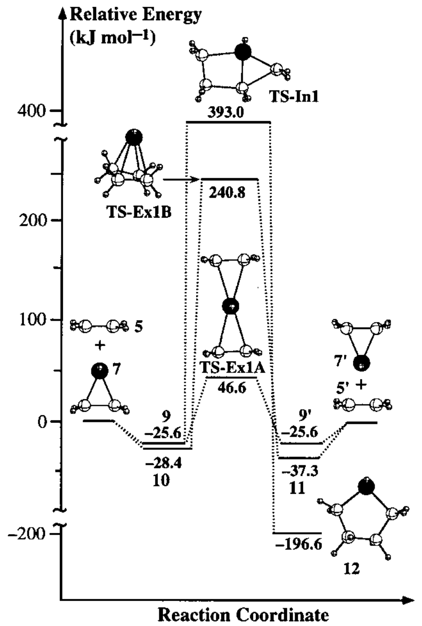


Figure 3. Schematic energy profiles for the Ex1 and In1 reactions.

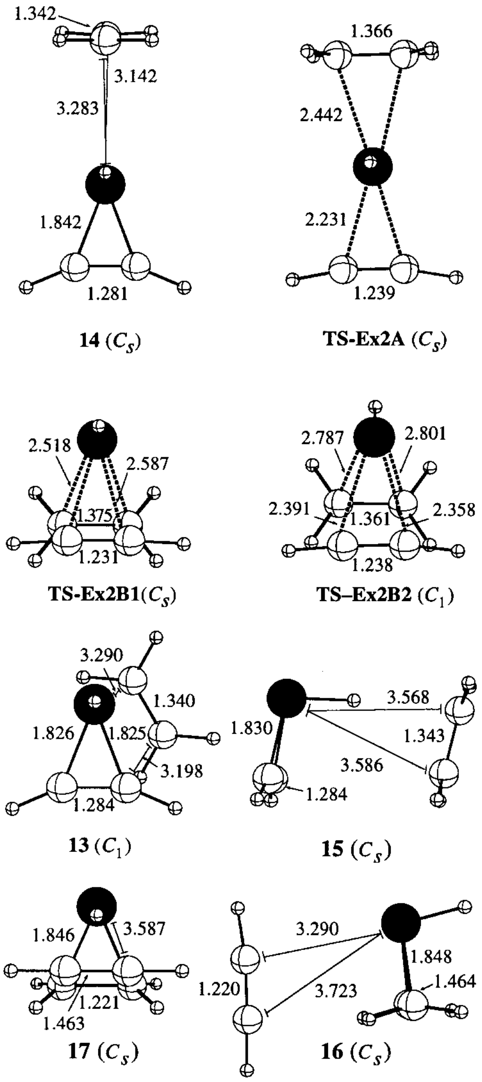


Figure 4. Selected MP2(full)/6-31G(d) geometrical parameters of species involved in the Ex2 exchange reaction. Bond lengths in Å.

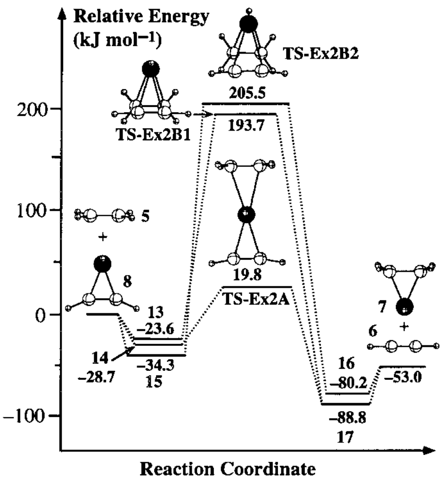
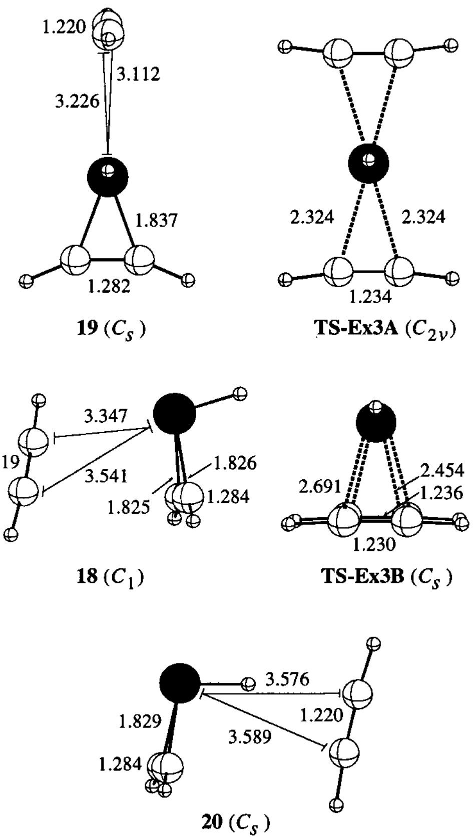


Figure 5. Schematic energy profile for the Ex2 reaction.

The results for the Ex3 reaction (Figures 6 and 7) are very similar to those found for the Ex1 reaction. The initial C_s complex **19** has a binding energy of 26.4 kJ mol^{-1} relative to the reactants. The C_{2v} transition structure **TS-Ex3A** at



19 (C_s) **TS-Ex3A** (C_{2v})

18 (C_1) **TS-Ex3B** (C_s)

20 (C_s)

Figure 6. Selected MP2(full)/6-31G(d) geometrical parameters of species involved in the Ex3 reaction. Bond lengths in Å.

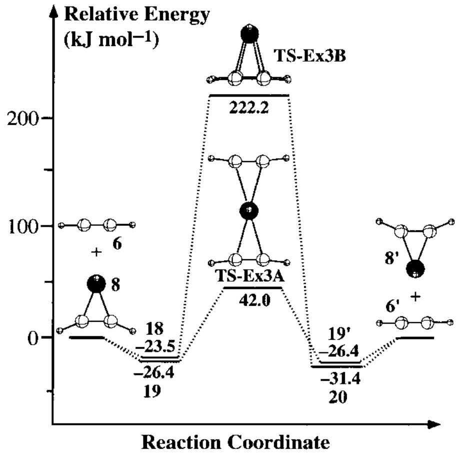


Figure 7. Schematic energy profile for the Ex3 reaction.

42.0 kJ mol^{-1} connects **19** with the product complex **19'**. **TS-Ex3A** is again very similar to the transition structures found in both the Ex1 and the Ex2 reactions.

A characteristic feature of the transition structures for pathway A for all of the exchange reactions is the orientation of the SH$^+$ moiety, which becomes perpendicular to the plane defined by the four carbon atoms. This occurs in concert with the approach of the reactant hydrocarbon and elimination of a hydrocarbon moiety from the original ring.

The Ex1 and Ex3 exchange reactions by pathway A are predicted to proceed with the almost identical barriers of 46.6 kJ mol^{-1} and 42.0 kJ mol^{-1}, respectively, whereas Ex2 is predicted to have a significantly lower barrier, namely, 19.8 kJ mol^{-1}. The lower barrier may be attributed to the significant exothermicity for reaction Ex2.

Exchange reactions—pathway B: In pathway B of the Ex1 reaction, the reactant thiiranium ion (**7**) and ethylene initially form the C_s complex **10**, with a binding energy of 28.4 kJ mol^{-1} relative to the reactants (Figures 2 and 3). The C_s product complex **11** has a binding energy of 37.3 kJ mol^{-1} relative to the reactants and is connected with the reactant complex by the C_1 transition structure **TS-Ex1B** at 240.8 kJ mol^{-1}. There is a symmetry-related pathway that proceeds from reactants to complex **11'**, to **TS-Ex1B'**, and then to **10'** and products. This is omitted from Figure 3 for simplicity.

Because the Ex2 reaction is not an identity reaction, there are two distinct exchange transition structures (Figures 4 and 5) geometrically similar to the one found for the Ex1 reaction. The first transition structure (**TS-Ex2B1**) has C_s symmetry and lies at 193.7 kJ mol^{-1}. It connects the C_1 reactant complex **13** with the C_s product complex **17**. The reactant complex has a binding energy of 23.6 kJ mol^{-1} relative to the reactants, while the product complex has a binding energy of 35.8 kJ mol^{-1} relative to the products. The second transition structure (**TS-Ex2B2**) lies at 205.5 kJ mol^{-1} and is slightly distorted to C_1 symmetry. It connects the C_s reactant complex **15**, which has a binding energy of 34.3 kJ mol^{-1} relative to the reactants, and the C_s product complex **16**, which has a binding energy of 27.2 kJ mol^{-1} relative to the products.

In pathway B of reaction Ex3, the thiirenium ion and acetylene initially combine to give the C_1 complex **18**, which has a binding energy of 23.5 kJ mol^{-1} relative to the reactants (Figures 6 and 7). The C_s product complex **20** has a binding energy of 31.4 kJ mol^{-1} relative to the reactants. The reactant and product complexes are connected by the C_s transition structure **TS-Ex3B** at 222.2 kJ mol^{-1}, which is geometrically similar to the analogous structures found for reactions Ex2 and Ex1. As was the case for the Ex1 reaction, there is a symmetry-related pathway that is omitted from Figure 7.

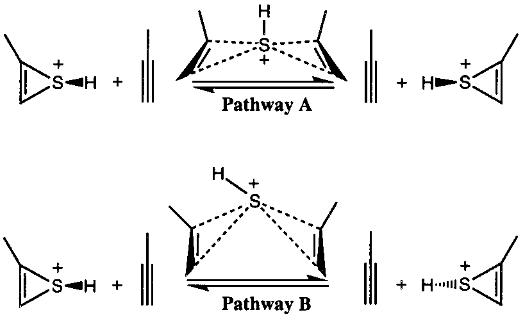
Pathway B becomes energetically less expensive in the order Ex1B > Ex3B > Ex2B2 > Ex2B1. The higher barrier for Ex1 compared with Ex3 may be a reflection of a greater release of strain in the latter, when the C–S bonds of the unsaturated three-membered ring are stretched. The barriers for the Ex2 reaction are the lowest, possibly because of the thermodynamic driving force for this reaction.

Insertion reactions: In our investigation of the reactions of the phosphirenium and phosphiranium ions, we found the formation of the five-membered phosphorus heterocycles by insertion of acetylene or ethylene into the three-membered heterocycles to be highly thermodynamically favorable.[13] However, we also found that the insertion reactions have very high barriers.[13] It is therefore of interest to investigate the barriers for insertion for the analogous sulfur compounds.

Reaction In1 models insertion of ethylene into the thiiranium ion **7**, yielding the C_1 saturated five-membered heterocycle **12** (Figures 2 and 3). The reaction involves the same initial complex as the corresponding exchange reaction that proceeds by pathway A. The C_1 transition structure (**TS-In1**) connecting complex **9** with **12** represents insertion into the C–S bond of the thiiranium ion. It is intriguing that the breaking C–S bond of **7** is shorter in **TS-In1** than in either the reactant **7** or the product **12**. Attempts to find a transition structure for the insertion of ethylene into the stronger C–C bond of the thiiranium ion were unsuccessful.

The barrier for the In1 reaction is found to be 393.0 kJ mol^{-1}, while the reaction exothermicity for the process is large (196.6 kJ mol^{-1}). The differences between the barrier for the insertion reaction In1 and the barriers for the exchange reaction Ex1 by either pathway A or B are substantial (346.4 kJ mol^{-1} and 152.2 kJ mol^{-1}, respectively). Hence we predict that insertion of alkenes into thiiranium salts will not compete with exchange, despite the higher exothermicity of the former process. This was also found to be the case for the phosphorus insertion reaction analogous to In1, and for the other possible phosphorus insertion reactions involving the phosphirenium and phosphiranium ions reacting with acetylene or ethylene. These two sets of results strongly suggest that the insertion reactions that might potentially compete with Ex2 and Ex3 will have very large barriers and hence they were not investigated further.

The exchange reaction: pathway A versus pathway B: The exchange reaction is predicted to be stereospecific[21] with respect to the configuration at sulfur when proceeding by both pathways A and B. However, the stereochemical outcome of exchange by pathway A is the opposite of that from pathway B. This is exemplified by the reactions given in Equation (1), in which methyl substituents are introduced purely as stereochemical markers.

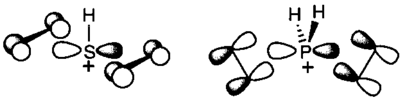


(1)

The difference between the energy barriers for the two pathways is significant, that is, 194.2 kJ mol^{-1} for Ex1, 173.9 kJ mol^{-1} for Ex2 (by B1), 185.7 kJ mol^{-1} for Ex2 (by B2) and 180.2 kJ mol^{-1} for Ex3, with pathway A being favored in each case. We therefore predict that exchange will proceed *only* by pathway A. Hence, only the pathway A type transition structure need be taken into account when predicting the major stereoisomer formed in exchange reactions of thiirenium and thiiranium ions.

Of course, it would require the construction of constrained systems to probe the stereospecificity experimentally. In the unconstrained systems of the reaction given in Equation (1), the possibility of *syn* or *anti* approaches (quite apart from the possibility of inversion at sulfur[22]) would result in reduced stereoselectivity.

Phosphorus versus sulfur: The lower energy exchange pathways (that is, pathway A) of thiirenium and thiiranium ions and of their phosphorus analogues show several similar features: the exchange reactions are predicted in both cases to proceed with only moderate barriers (no higher than 46.6 kJ mol^{-1}), the reactions are predicted in both cases to be stereospecific with respect to the configuration at the heteroatom, and the exchange reactions are predicted in both cases to be highly favored compared with the corresponding insertion reactions. The electronic characteristics of the transition structures are also similar, as depicted in Scheme 2, resembling in both cases the triple-ion configurations ($X^- \cdots CH_3^+ \cdots X^-$) found in the S_N2 transition structure.



Scheme 2. Electronic interactions in exchange transition structures.

Conclusion

The present calculations indicate that the barriers for π-ligand exchange reactions of thiiranium and thiirenium ions with acetylene or ethylene are of similar magnitude to those found for the analogous phosphorus systems. This suggests that π-ligand exchange, already observed in salts of the phosphorus systems, should also be experimentally feasible for thiirenium and thiiranium salts. The exchange reactions, which are predicted to be stereospecific with respect to the configuration at sulfur, are strongly favored over the competing insertion reactions, despite the high thermodynamic preference for insertion.

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