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Uptake of One and Two Molecules of 1,3-Butadiene by Platinum Bis(dithiolene): A Theoretical Study

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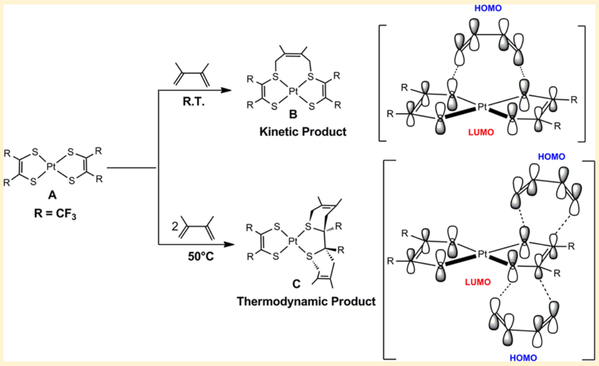
Supporting Information

ABSTRACT: Platinum bis(dithiolene) complexes have reactivity toward alkenes like nickel bis(dithiolene) complexes. We examined the uptake of 1,3-butadiene by platinum bis(dithiolene) [$Pt(tfd)_2$] (tfd = $S_2C_2(CF_3)_2$) via a density functional theory study; both 1,2- and 1,4-additions of 1,3-butadiene to the ligands of $Pt(tfd)_2$ to form both interligand and intraligand adducts were studied. For single 1,3-butadiene addition, direct 1,4-addition on interligand S−S, 1,2-addition on intraligand S−S, and 1,4-addition on intraligand S−C are all feasible at room temperature and are controlled by the symmetry of the highest occupied molecular orbital of 1,3-butadiene and the lowest unoccupied molecular orbital of $Pt(tfd)_2$. However, the formation of the interligand S−S adduct through 1,4-addition of one molecule of *cis*-1,3-butadiene is the most favorable route, with a reaction barrier of 9.3 kcal/mol. The other two addition processes cannot compete with this one due to both higher reaction barriers and unstable adducts. Other possible pathways, such as formation of *cis*-interligand S−S adduct from 1,2-addition of one molecule of 1,3-butadiene via a twisted *trans*-interligand S−S adduct, have higher barriers. Our calculated results show that 1,4-addition of a single molecule of 1,3-butadiene on the interligand S−S gives the kinetically stable product by a one-step pathway. But of at least equal importance is the apofacial 1,4-addition of two molecules of 1,3-butadiene on the intraligand S−C of the same ligand on $Pt(tfd)_2$, which yields the thermodynamically stable product, obtained via a short lifetime intermediate, the 1:1 intraligand S−C adduct, being formed through several pathways. The calculated results in this study well explain the experimental observation that 1:1 interligand S−S adduct was formed in a short time, and the intraligand S−C adduct from two molecules of *cis*-1,3-butadiene was accumulated in 20 h at 50° and characterized by X-ray crystallography.



INTRODUCTION

Interest in metal dithiolene complexes has increased dramatically since the initial synthesis of the nickel bis(dithiolene), $Ni(S_2C_2Ph_2)_2$, by Schrauzer and Mayweg.[1] The structural,[2] spectroscopic,[3] optical,[4] magnetic,[5] and electrochemical properties[6] of many related complexes have been described. Meanwhile, additional studies of ligand-based reactions between metal dithiolene complexes and alkenes, which are a result of the noninnocent character of the ligand in these complexes,[7,8] followed early reports of these reactions by Schrauzer,[9] Wing,[10] and their co-workers. Wang and Stiefel studied olefin purification by nickel bis(dithiolene) complexes $Ni(S_2C_2(R)_2)_2$ (R = CF_3, CN),[11] which encouraged additional studies of various reactions of metal bis(dithiolene)[12] or tri(dithiolene)[13] complexes with various alkenes.[9e,12b,13b] This work also stimulated theoretical studies to investigate the electronic structure and reaction mechanism for reactions of metal bis(dithiolene) with simple alkenes.[14] It has been confirmed that the formation of addition products from pure nickel bis(dithiolene) and alkenes is frontier-molecule-orbital- or symmetry-controlled[14e,f] and results in the allowed *cis*-intraligand addition as this route has a lower energy barrier even though a two-step pathway via a twisted intermediate makes the symmetry-forbidden process of *cis*-interligand addition formally allowed.[14a] Theoretical studies have shown that the commonly observed *cis*-interligand product only occurs readily because of the presence of the nickel bis(dithiolene) anion, which forms a dimetal complex with the neutral that promotes the *cis*-interligand addition.[14e,f]

However, the studies of the mechanism for reactions of conjugated alkenes, such as butadienes, with metal bis(dithiolene) or tri(dithiolene) has been limited to nickel bis(dithiolene);[15] in contrast, the studies on the reactivity of larger alkenes toward heavier metal dithiolenes has been widely studied experimentally.[7a,c,d,9c,10c] The reaction of $Pt(tfd)_2$ with 2,3-dimethyl-1,3-butadiene is shown in Scheme 1. A 1:1 interligand S−S kinetic adduct **B** was formed facilely within 10 min at room temperature, while the intraligand S−C adduct **C** uptaking two molecules of 2,3-dimethyl-1,3-butadiene was observed in very small amounts at the same conditions. However,

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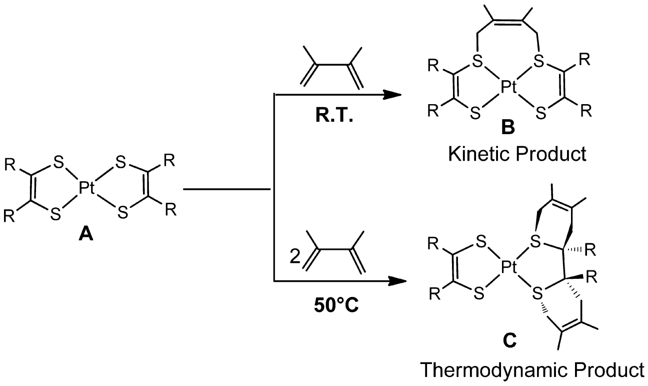
Scheme 1



the product shifts to the thermodynamic intraligand S−C adduct **C** after 20 h at 50°.[12d] These experimentally observed results are easily related to molecular orbital interactions between these two reactants. There are three types of symmetry allowed molecular orbital interactions between the HOMO (highest occupied molecule orbital) of 2,3-dimethyl-1,3-butadiene and LUMO (lowest unoccupied molecule orbital) of Pt(tfd)$_2$, as shown in Scheme 2, but only two of the three possible adducts were observed in the experiment; one is kinetically formed from the 1,4-addition of one molecule of 2,3-dimethyl-1,3-butadiene onto interligand S−S, and the other is thermodynamically formed from 1,4-addition of two molecules of 2,3-dimethyl-1,3-butadiene on intraligand S−C.

Here, we use density functional theory (DFT) calculations to investigate the possible pathways leading to different addition products in the proposed reaction mechanisms as well as to understand the adduct selectivity that appears in the experiment. These theoretical calculations were carried out for the intermediates and transition states of the reactions of Pt(tfd)$_2$ (**1**) with 1,3-butadiene, which is used as the model of 2,3-dimethyl-1,3-butadiene to reduce the computational cost.

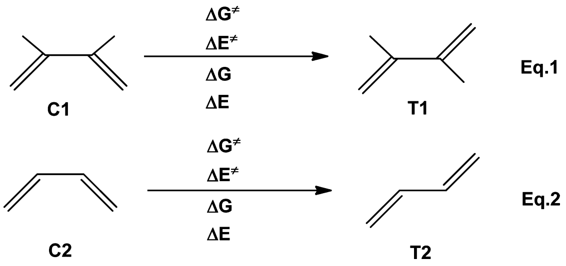
COMPUTATIONAL DETAILS

A benchmark study shows that the barriers for the reaction of M(S$_2$C$_2$H$_2$)$_2$ with ethylene are very dependent on the density functional[14d] and that the ω-B97XD[16] functional produced results similar to those of more accurate coupled cluster calculations and in agreement with the experimental results.[14e,f] In this paper, our calculations were performed using Gaussian 09[17] with the ω-B97XD functional. The effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used in describing Pt;[18] polarization functions were also added for Pt (f = 0.993),[19] whereas the 6-311+G** basis set was used for all other atoms.[20] This basis set is somewhat larger for the main-group atoms than it is for the transition metals because the overall reactions all involve making and breaking bonds on main-group atoms. The geometric structures of all species were optimized in the gas phase. Calculating the harmonic vibrational frequencies and noting the number of imaginary frequencies confirmed the nature of all intermediates (no imaginary frequency) and transition state structures (only one imaginary frequency). The latter were also confirmed to connect the appropriate intermediates by intrinsic reaction coordinate (IRC) calculations.[21] For several cases the most obvious (direct) reaction path is symmetry-forbidden, involves an avoided crossing, and most likely involves a high-energy transition state. In some cases the barriers can be lowered by a geometric change that makes the reactions symmetry-allowed.[14] However, in other cases the avoided crossing would require multi-configuration wave functions or broken symmetry solutions. As the products formed from these reactions are not experimentally observed we have not attempted these additional calculations. The gas-phase free energies, G, were calculated at T = 298.15 K within the harmonic potential approximation using the optimized structures. The solvation effects, with benzene as solvent, were included by utilizing the SMD (Solvation Model Density) solvent model[22] while retaining the gas-phase optimized geometries. We approximated the solution-phase free energy by adding solvation energies on the gas-phase relative free energies; experience has shown this to be very close to full optimization and frequency calculations in solvent. The solution-phase free energies will be used in the discussions, unless otherwise specified. The three-dimensional molecular structures displayed in this article were drawn by using the JIMP2 molecular visualization and manipulation program.[23]

RESULTS AND DISCUSSION

2,3-dimethyl-1,3-butadiene and 1,3-butadiene have both *trans*- and *cis*-conformers; before looking into the reaction mechanism, we first examined the relative stabilities and isomerization barriers for these conformers (eqs 1 and 2 in Scheme 3) by B3LYP,[24] ω-B97XD,[16] and M06.[25] For 2,3-dimethyl-1,3-butadiene, the s-*trans*-conformer (**T1**) is more stable than the s-*cis*-conformer (**C1**) by about 1.7 kcal/mol in gas-phase free energy, and the conversion barrier from *trans*-conformer to *cis*-conformer is only about 4.0 kcal/mol in gas-phase free energy. For 1,3-butadiene (**T2**), the s-*trans*-conformer is more stable than the s-*cis*-conformer (**C2**) by about 3.2 kcal/mol in gas phase free energy, and the conversion barrier from *trans*-conformer to *cis*-conformer (about 6.4 kcal/mol) is also very small. We further

Scheme 3



Scheme 2

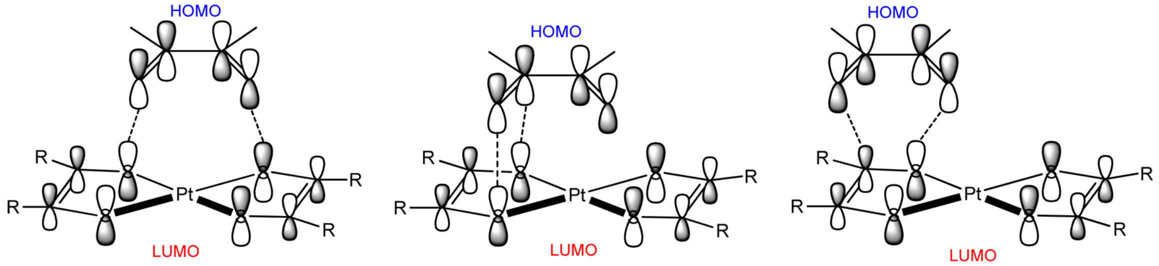


Table 1. Comparison of the Gas-Phase Relative Activation Free Energies ($\Delta G^{\ddagger}$), Gas-Phase Activation Electronic Energies ($\Delta E^{\ddagger}$), Gas-Phase Relative Free Energies (ΔG), and Gas-Phase Electronic Energies (ΔE) Calculated Using B3LYP, ω-B97XD, M06, CCSD, CCSD(T), and MP4 Methods (kcal/mol) for Eqs 1 and 2

	equation 1				equation 2			
method	$\Delta G^{\ddagger}$	$\Delta E^{\ddagger}$	ΔG	ΔE	$\Delta G^{\ddagger}$	$\Delta E^{\ddagger}$	ΔG	ΔE
B3LYP	2.2	2.0	−1.8	−2.4	3.6	3.6	−3.3	−3.6
ω-B97XD	2.2	1.9	−1.4	−1.8	2.7	3.4	−3.2	−2.7
M06	2.6	2.3	−1.9	−2.6	3.4	3.9	−3.2	−3.0
CCSD		1.5		−0.9		2.3		−2.6
CCSD(T)		1.7		−1.0		2.6		−2.6
MP4		1.8		−1.0		2.6		−2.6

calculated the relative stability of the s-*cis*- and s-*trans*-conformers of 2,3-dimethyl-1,3-butadiene and 1,3-butadiene by using CCSD,[26] CCSD(T),[27] and MP4.[28] The calculated results from CCSD, CCSD(T), and MP4 are consistent with the calculated results by B3LYP, ω-B97XD, and M06. All of these calculated results are presented in Table 1. On the basis of these results we concluded that interconversion between the s-*cis*- and s-*trans*-conformers is rapid, and an equilibrium between the conformers exists. As mentioned above, we use the simpler s-*cis*-1,3-butadiene and s-*trans*-1,3-butadiene when modeling the reaction with the metal complex.

The frontier molecular orbitals of complex **1** and *cis*-1,3-butadiene were studied as shown in Figure 1. It can be seen that the energy difference between the LUMO of complex **1** and the HOMO of *cis*-1,3-butadiene is 4.61 eV, which is smaller than that between the HOMO of complex **1** and the LUMO of *cis*-1,3-butadiene by 5.28 eV. At the same time, the molecular orbital interaction between the LUMO of complex **1** and the HOMO of *cis*-1,3-butadiene is symmetry allowed. The three interaction modes between the LUMO of complex **1** and the HOMO of *cis*-1,3-butadiene as shown in Scheme 2 are very important because they are allowed by the principles of molecular orbital interaction.

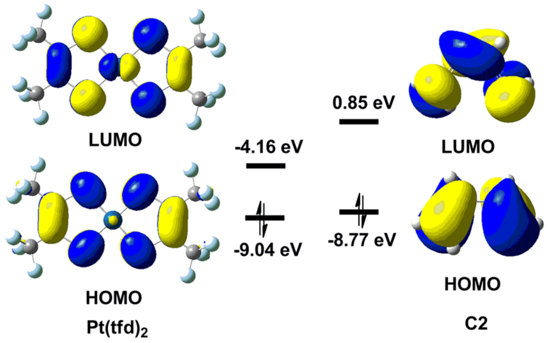


Figure 1. Frontier molecular orbitals of complex **1** and *cis*-1,3-butadiene.

Cis-1,3-butadiene can bind to the platinum bis(dithiolene) complex **1** in a variety of ways as shown in Scheme 4. Three possible addition pathways including the interligand S−S addition, intraligand S−S addition and intraligand S−C addition were studied. The 13 adducts shown in Scheme 4 and later in this article were fully optimized as stable species. The reaction mechanism along these three pathways for forming these adducts and intermediates are described below.

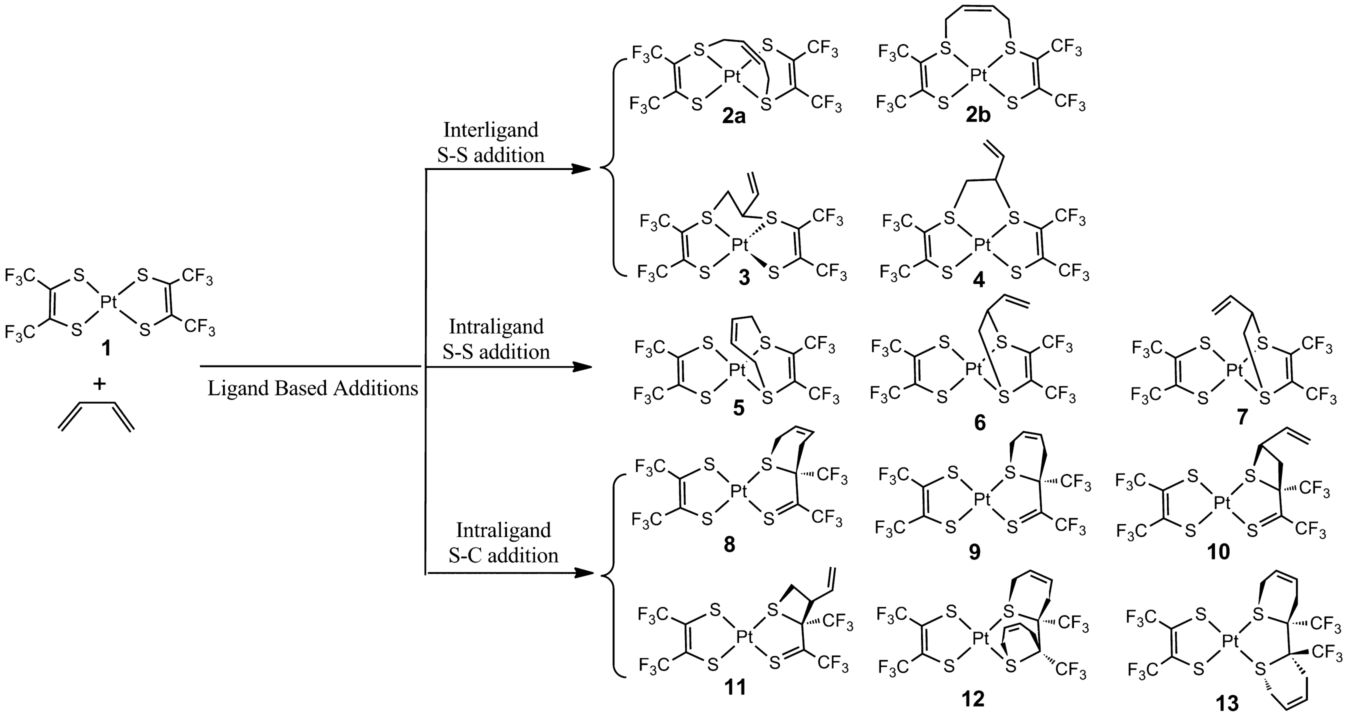
In Figure 2 and the following figures that contain potential energy profiles, the calculated solvation corrected relative free energies (kcal/mol) are presented. The gas phase relative free energies and gas-phase relative electronic energies are presented in Table S1 and Table S2 (Supporting Information). In the gas phase, the relative free energies and relative electronic energies are similar in cases where the number of reactant and product molecules is equal, for example, one-to-one or two-to-two transformations, but differ significantly for one-to-two or two-to-one transformations because of the entropic contribution. In this paper, relative free energies with solvation correction are used in the text to describe and analyze the reaction mechanism unless specified.

Interligand S−S Additions. Figure 2 shows the calculated reaction pathways for the 1,4-addition of *cis*-1,3-butadiene to platinum bis(dithiolene) **1** to give the diagonal *cis*-interligand adduct **2a** and the adjacent *cis*-interligand adduct **2b**. The results show that the formation of diagonal *cis*-interligand adduct **2a** has a higher barrier than the formation of adjacent *cis*-interligand adduct **2b**. **2b** is also more stable than **2a** by 14.4 kcal/mol and more stable than the reactants by 18.4 kcal/mol. The low barrier for the formation of **2b** and significant stability of **2b** are consistent with the experimental observation that the reaction at room temperature gives the product within 10 min. The optimized geometries with selected structural parameters for the species involved in Figure 2 are presented in Figure S1 (Supporting Information), along with experimental structural parameters for **1**. The calculated structural parameters (bond distances) are in good agreement with the experimental ones.

The 1,2-addition of *cis*-1,3-butadiene to interligand sulfurs could occur via a twisted intermediate as previous theoretical studies have shown for the direct interligand addition of nickel bis(dithiolene) with ethylene[11d]. Results for this reaction are shown in Figure 3, where the two-step pathway has a barrier of about 25.8 kcal/mol to give twisted interligand adduct **3**. Adduct **3** then isomerizes to the more stable *cis*-interligand adduct **4** through a barrier of 18.7 kcal/mol. However, the overall barrier for the formation of the *cis*-interligand adduct **4** from 1,2-addition is higher than that of the *cis*-interligand adduct **2b** from 1,4-addition by 16.6 kcal/mol; thus, the formation of **4** via a twisted intermediate **3** cannot compete with the formation of **2b** from **1** and *cis*-1,3-butadiene. At the same time, **2b** is much more stable than **4**. Obviously, molecular orbital symmetry plays a large role in these reaction barriers, i.e. the formation of **2b** is allowed by orbital symmetry, while the direct formation of **4** is forbidden by orbital symmetry; although twisting makes the reaction symmetry allowed, this additional distortion costs energy. The optimized geometries with selected structural parameters (distances in Å) for the species involved in Figure 3 are shown in Figure S2 (Supporting Information).

Intraligand S−S Additions. Although the formation of **4** via **3** from *cis*-1,3-butadiene and **1** cannot compete with the symmetry allowed formation of **2b**, other symmetry allowed processes shown in Scheme 2 may be competitive or even more

Scheme 4



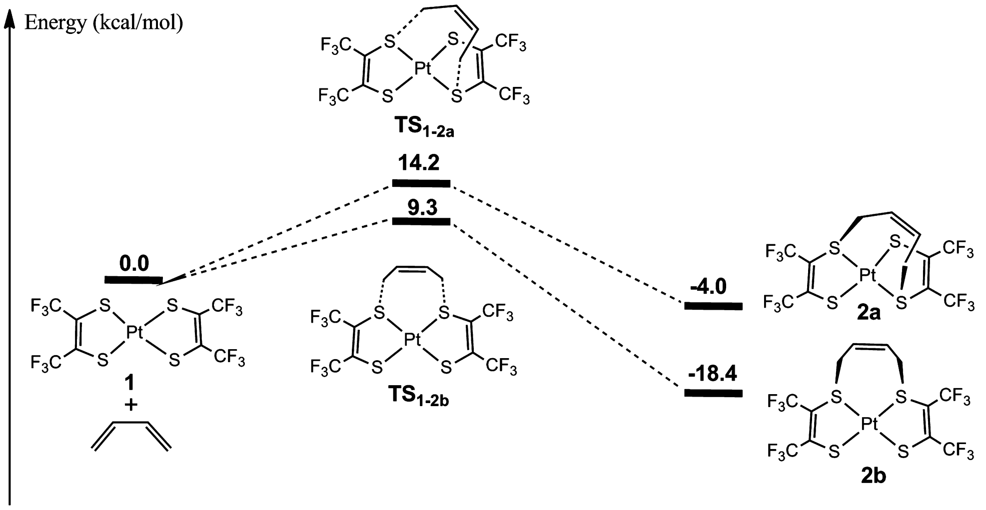


Figure 2. Free energy profiles are shown for the 1,4-addition of *cis*-1,3-butadiene with **1** to form interligand S−S adducts **2a** and **2b**. The solvation-corrected relative free energies are given in kcal/mol.

favorable. Intraligand S- S addition could occur from 1,4-addition of *cis*-1,3-butadiene with **1** to form **5** or from 1,2-addition of *cis*-1,3-butadiene with **1** to form **6** and **7** as shown in Scheme 4. Formation of **5** via 1,4-addition is symmetry forbidden and apparently has a transition state, which was not located. Even if we place the two terminal carbons from butadiene very close to two S atoms, the optimization of transition state led to separation of butadiene from Pt dithiolene. The calculations also show that **5** is an unstable product relative to the reactants. The calculated reaction pathways for the 1,2-addition of *cis*-1,3-butadiene with **1** to form intraligand S−S adducts **6** and **7** are shown in Figure 4. The formation of these two adducts have nearly the same barrier, ~17 kcal/mol. Although these two reactions are symmetry allowed and have relatively low barriers, they cannot compete with the formation of **2b** (Figure 1), whose barrier is lower than that for the formation of **6** and **7** by ~8 kcal/mol. Furthermore, because adducts **6** and **7** are only ~3 kcal/mol more stable than the reactants **1** and *cis*-1,3-butadiene, their formation is reversible at room temperature. Thus, even if some **6** and **7** would be formed together with **2b** at the beginning of the reaction, the reversible reactions would take them back to the reactants, **1** and *cis*-1,3-butadiene, and finally to **2b** since **2b** is more stable than **6** and **7**. These calculations explain the fact that no intraligand S−S adducts or their dissociated products were observed in the experiment,[12d] although dissociated products from the intraligand S−S adduct was observed when nickel bis(dithiolene) reacts with alkenes.[12c] The optimized geometries with selected structural parameters for the species involved in Figure 4 and adduct **5** are shown in Figure S3 (Supporting Information).

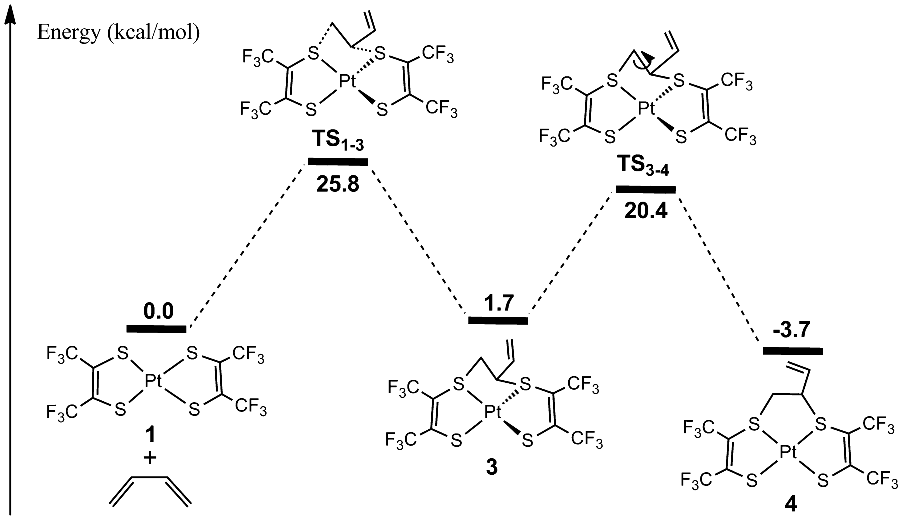


Figure 3. Free energy profiles for the 1,2-addition of *cis*-1,3-butadiene with **1** to form *cis*-interligand S−S adduct **4** via a twisted interligand adduct **3**. The solvation-corrected relative free energies are given in kcal/mol.

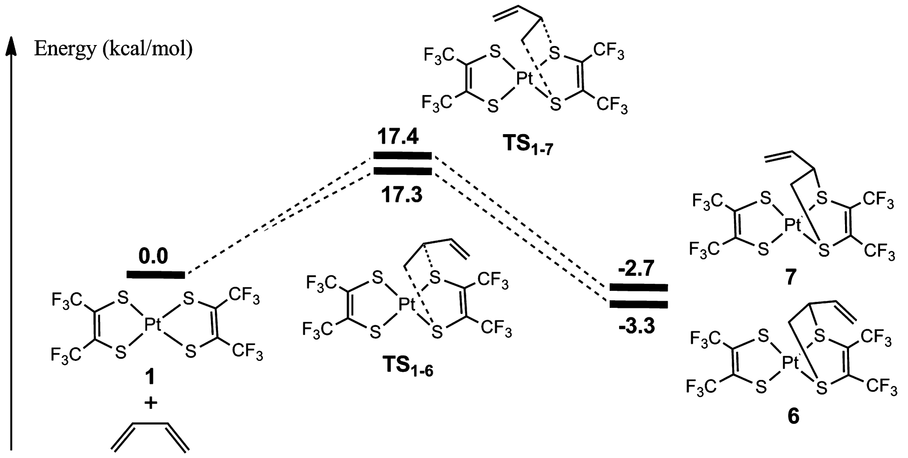


Figure 4. Free energy profiles for the 1,2 addition of *cis*-1,3-butadiene with **1** to form *cis*-intraligand S−S adducts **6** and **7**. The solvation-corrected relative free energies are given in kcal/mol.

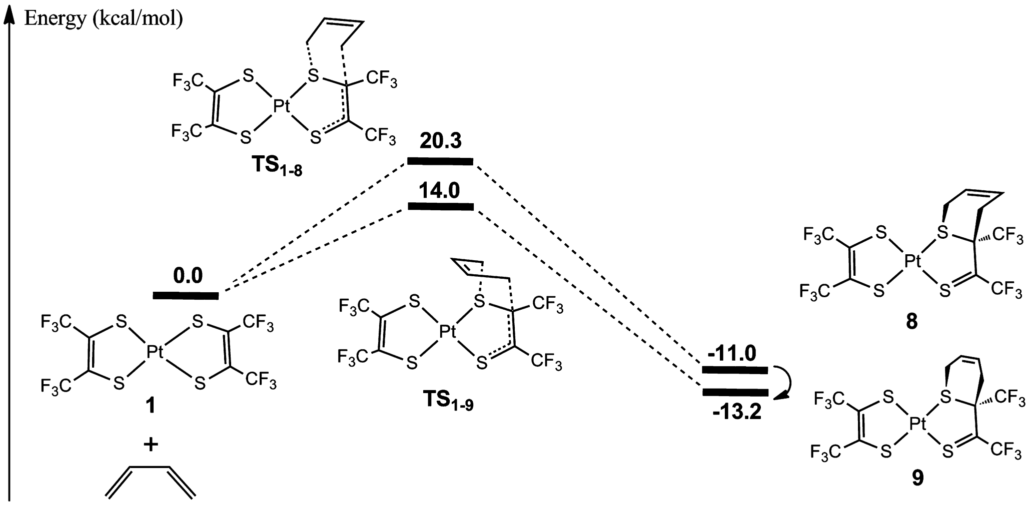


Figure 5. Free energy profiles for the 1,4-addition of *cis*-1,3-butadiene with **1** to form *cis*-intraligand S−C adducts **8** and **9**. The solvation-corrected relative free energies are given in kcal/mol.

Intraligand S−C Additions. Although the formation of intraligand S−C adduct from 1,4-addition of *cis*-1,3-butadiene with **1** is symmetry allowed (Scheme 2), this reaction has been neglected in previous studies since no such adduct was observed

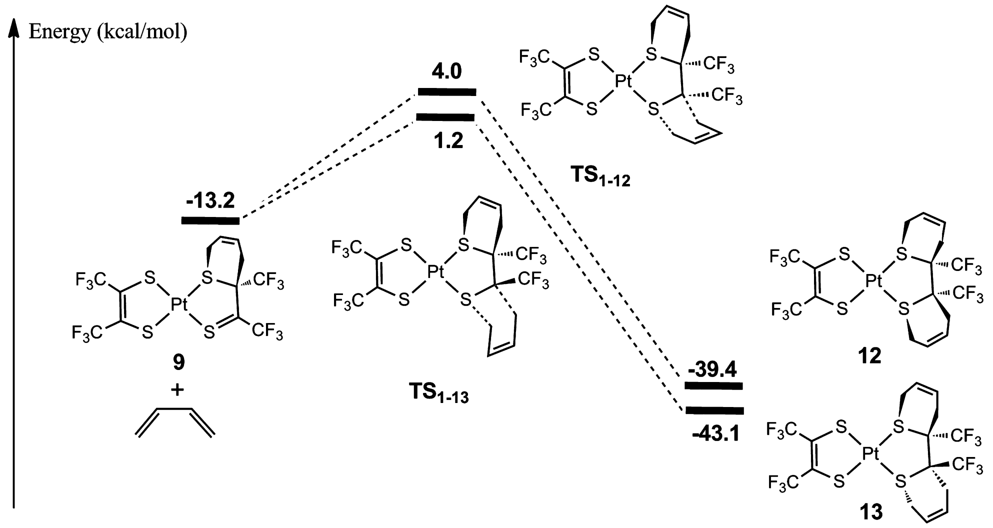


Figure 6. Free energy profiles for the second 1,4-addition of *cis*-1,3-butadiene with **1** to form intraligand S−C adducts **12** and **13**. The solvation-corrected relative free energies are given in kcal/mol.

until the recent report of reaction of $Pt(tfd)_2$ with 2,3-dimethyl-1,3-butadiene.[12d] This unprecedented finding of the very stable intraligand S−C adduct from two molecules of *cis*-1,3-butadiene motivated the study of these processes, in order to shed light on the nature of the reaction of the alkenes with $Pt(tfd)_2$. The calculated reaction pathways for the reaction of one molecule of *cis*-1,3-butadiene with **1** to give the intraligand S−C 1,4-addition adducts **8** and **9** (via a Diels−Alder type) are shown in Figure 5. Adducts **8** and **9** are isomers; **8** forms into a "chair" structure, while **9** forms into a nearly planar structure. The formation of intraligand S−C adducts **8** and **9** are all exothermic and irreversible. On one hand, the formation of **8** has a barrier of 20.3 kcal/mol, which is higher than that for the formation of **9** by 5.7 kcal/mol; On the other hand, **8** and **9** are more stable than reactants by 11.0 and 13.2 kcal/mol, respectively. The higher stability of **9**, by 2.2 kcal/mol, is attributed to the fact that the repulsion between *cis*-1,3-butadiene and the $-CF_3$ group is larger in **8**. This large repulsion promotes the isomerization of **8** to **9** by changing the orientation of the *cis*-1,3-butadiene fragment through a barrierless process. Moreover, **9** is not as stable as **2b** (Figure 2) due to larger ring strain in the former one with a six-membered ring. Although the reactions giving isomers **8** and **9** can occur at room temperature, and **8** can isomerize to **9**, the formation of **9** cannot compete with the formation of **2b** from the initial reactants *cis*-1,3-butadiene and **1**, as the latter one has a barrier of only 9.3 kcal/mol (Figure 2). Again, the transition states for the symmetry forbidden processes leading to the formation of intraligand S−C adducts **10** and **11** (Scheme 4) from 1,2-addition of *cis*-1,3-butadiene with **1** were not located (an avoided crossing). The optimized geometries with selected structural parameters for the species involved in Figure 5 together with adduct **10** and **11** are in Figure S4 (Supporting Information).

Importantly, a trace of an intraligand S−C adduct arising from two molecules of *cis*-1,3-butadiene adding to the same dithiolene was observed at room temperature, but substantial quantities accumulated at 50° in the experiment.[12d] The addition of another molecule of *cis*-1,3-butadiene to **9** was studied and the results are shown in Figure 6. There are two pathways for this second addition; one is from the same face of the previous addition, a suprafacial reaction, while the other is from the opposite face of the previous addition, an apofacial reaction. The suprafacial reaction to yield **12** has a barrier of 17.2 kcal/mol, while apofacial reaction to form **13** has a barrier of 14.4 kcal/mol; both **12** and **13** are very stable. Calculation results suggest that once **9** is formed, the formation of **13** is facile. Although the formation of **9** has higher barrier than the formation of **2b**, the very stable product **13** could drive the reaction toward **13**. However, since it costs about 28 kcal/mol in free energy for the initially formed **2b** to transform back to **1** and *cis*-1,3-butadiene, only a trace of this thermodynamically stable product **13** was observed at room temperature, while 20 h at 50° were needed to make it the major experimentally observed product. The calculations show that the addition of the second *cis*-1,3-butadiene to the other dithiolene ligand leads to compounds that are significantly less stable than **13**. These results are consistent with the frontier molecular orbital study (Figure 7). In Figure 7, the LUMO of **9** is mainly composed of the p orbitals of the unreacted S and C atoms of the dithiolene currently binding diene and the energy difference between the LUMO of **9** and the HOMO of *cis*-1,3-butadiene is 5.93 eV, which is smaller than that between the HOMO of **9** and the LUMO of *cis*-1,3-butadiene by 2.72 eV. The reaction between these S and C atoms of the reacted dithiolene in **9** and terminal C atoms of another *cis*-1,3-butadiene is symmetry allowed. Thus,

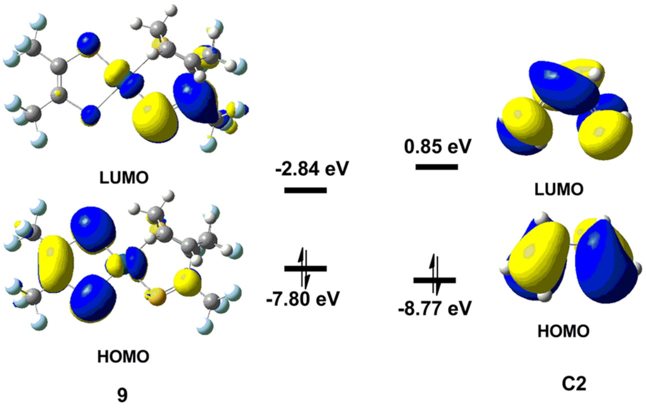


Figure 7. Frontier molecular orbitals for intermediate **9** and *cis*-1,3-butadiene.

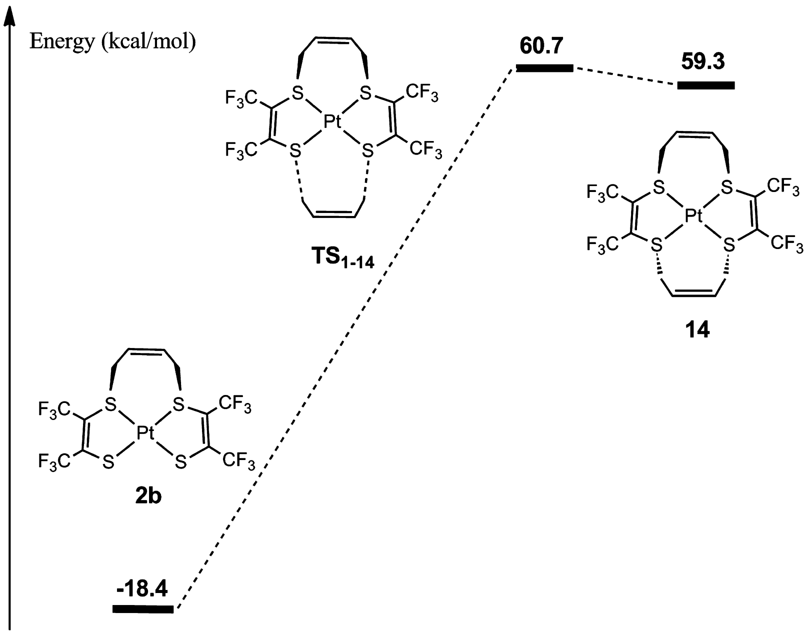


Figure 8. Free energy profiles for the second 1,4-addition of *cis*-1,3-butadiene with **2b** to form interligand S—S adducts **14**. The solvation-corrected relative free energies are given in kcal/mol.

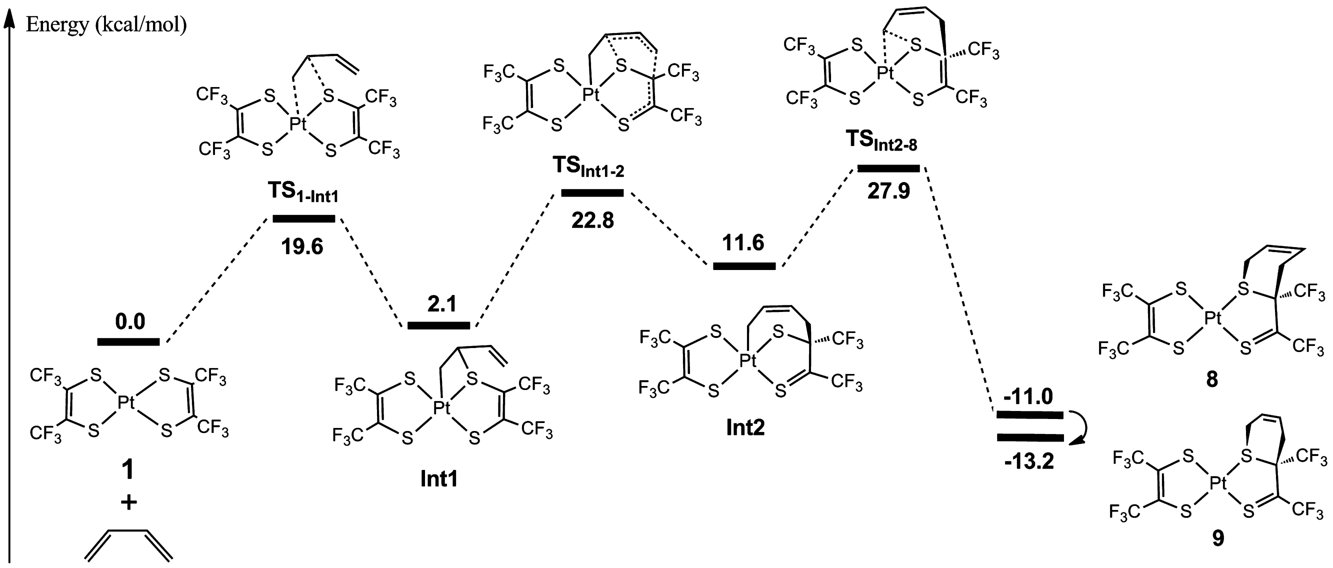


Figure 9. Free energy profiles for an alternative pathway to form **9**. The solvation-corrected relative free energies are given in kcal/mol.

the molecular orbital interactions support the reaction energy study of **9** and *cis*-1,3-butadiene (Figure 6).

The optimized structure of **13** is quite similar to that from the X-ray crystal structure (Supporting Information, Figure S5);[12d] the differences between the calculated and experimental bond distances are 0.06 Å for Pt—S(reacted) and less than 0.02 Å for most others, further confirming that our theoretical method is reliable. The optimized geometries with selected structural parameters for the species involved in Figure 6 are in Figure S5 (Supporting Information).

The energy profiles for the addition of *cis*-1,3-butadiene to the two unreacted S atoms in **2b** are shown in Figure 8. This reaction cannot occur due to the very high reaction barrier of 79.1 kcal/mol and the unstable addition product, which cannot compete with the formation of **13**. The calculated results agree well with the experimental observation that only the thermodynamically stable product **13** was observed. The optimized geometries with selected structural parameters for the species involved in Figure 8 are in Figure S6 (Supporting Information). The calculated relative free energies at 50° for intermediates in Figures 6 and 8 are shown in Tables S1 and S2 in Supporting Information. The relative free energies at 50° are 2—3 kcal/mol higher than those at room temperature.

Alternative Routes to Intermediate 9. As the key intermediate **9** can be transformed to **13** quickly, other possible pathways leading to **9** from the easily obtained stable adducts **Int1** and **6** were explored and are shown in Figures 9 and 10. In Figure 9, **Int1** is formed from the initial reactants, then transformed to **Int2**, followed by an isomerization to **8**, and then **9**. The total barrier for this pathway is 27.9 kcal/mol in free energy in the solution phase, which is similar to the previously discussed total formation barrier of **9** from initially formed **2b**,

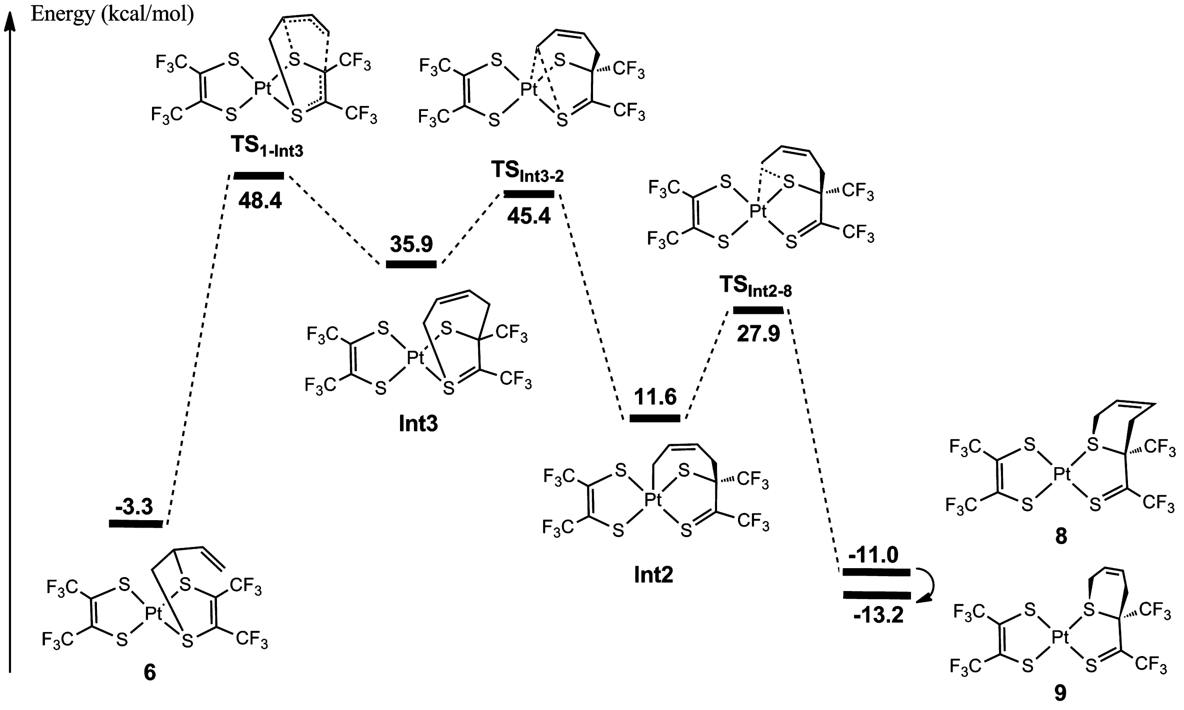


Figure 10. Free energy profiles for the isomerizations from **6** to **9**. The solvation-corrected relative free energies are given in kcal/mol.

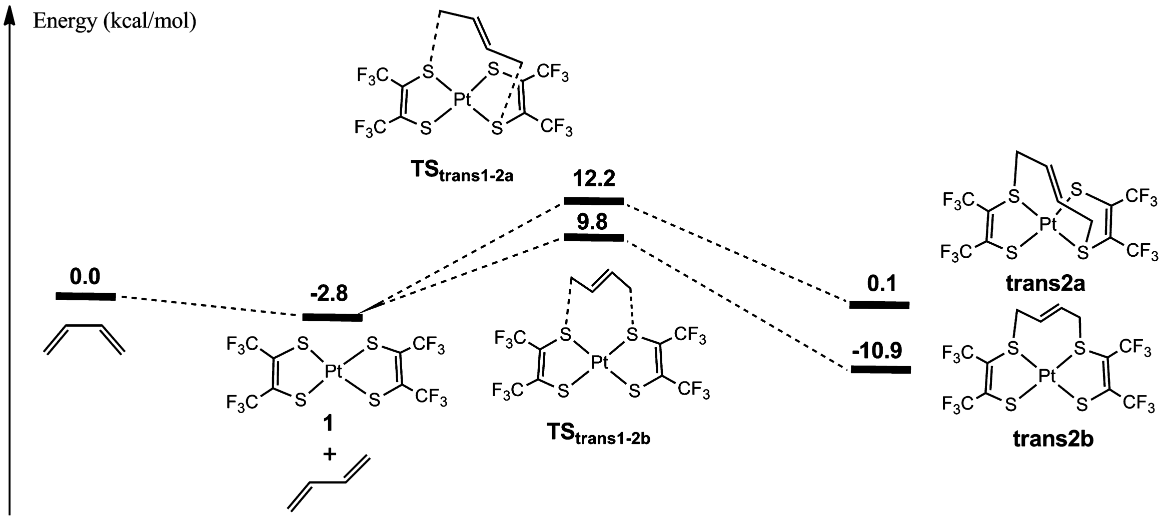


Figure 11. Free energy profiles for the formation of *cis*-interligand S−S adducts **trans2a** and **trans2b** by 1,4-addition. The solvation-corrected relative free energies are given in kcal/mol.

about 28 kcal/mol. Figure 10 gives the energy profile for isomerization processes from **6** to **Int3** and then to **Int2**, **8**, and **9**. This pathway has a very high barrier for the first step, 51.7 kcal/mol; although the following steps have smaller barriers, this pathway cannot compete with the previous pathways for the formation of **9**. The optimized geometries with selected structural parameters for the species involved in Figures 9 and 10 are in Figures S7 and S8 (Supporting Information).

Selected Reactions of *trans*-1,3-Butadiene with Platinum Bis(dithiolene). Figures 11−13 show the reaction pathways of *trans*-1,3-butadiene with **1**, where the activation energies in Figure 11 are a little bit higher than those in Figure 2, but more importantly **trans2a** and **trans2b** are less stable than **2a** and **2b** by 4.1 and 7.5 kcal/mol, respectively. Thus, in agreement with the experimental results, the *cis*-adduct was the only isomer observed. In Figure 12, the total barrier for the formation of **trans4** from *trans*-1,3-butadiene and **1** is higher than that for the formation of **4** in Figure 3 by 2.6 kcal/mol, while adduct **trans4** is more stable than **4** by 1.9 kcal/mol. The formation of **trans6** and **trans7** from *trans*-1,3-butadiene and **1** also have slightly higher barriers (Figure 13) than those for the formation of **6** and **7** in Figure 4. **Trans6** and **trans7** appear slightly more stable than **6** and **7**, but like **6** and **7** the reactions are reversible, and neither **trans6** nor **trans7** can compete with the formation of **2b**. The optimized geometries with selected structural parameters for the species involved in Figures 11−13 are in Figures S9−S11 (Supporting Information).

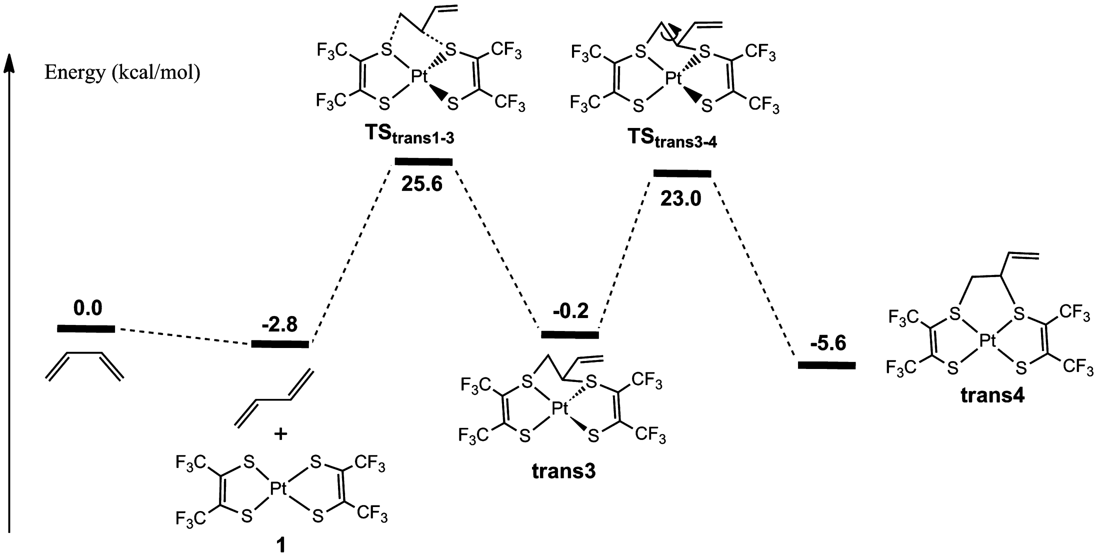


Figure 12. Free energy profiles for the formation of *cis*-interligand S−S adduct **trans4** via a *trans*-interligand adduct **trans3** by 1,2-addition. The solvation-corrected relative free energies are given in kcal/mol.

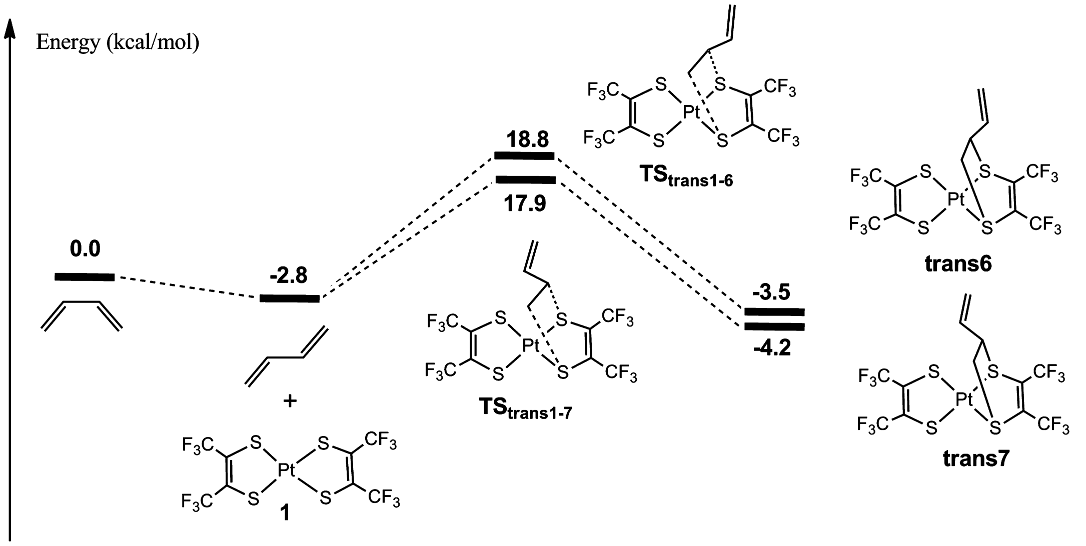


Figure 13. Free energy profiles for the formation of *cis*-intraligand S−S adducts **trans6** and **trans7** by 1,2-addition. The solvation-corrected relative free energies are given in kcal/mol.

■ CONCLUSION

This computational study presented the mechanism for the uptake of one and two molecules of 1,3-butadiene by Pt(tfd)$_2$ (**1**) through unconventional (noninnocent, ligand-based) reactions, in full agreement with the previous experimental report. The calculations clearly predict that the lowest energy path is for the *cis*-1,3-butadiene addition to form the adjacent interligand S−S adduct (**2b**) as observed at room temperature, while increasing the temperature changes the final product to an unprecedented double *cis*-1,3-butadiene intraligand S−C adduct to a single dithiolene, as was observed at 50°. The DFT calculations show that in spite of the lower energy of *trans*-1,3-butadiene, the lower reaction barriers favor reactions with *cis*-1,3-butadiene. Computations show that the intrinsic reactivity of Pt(tfd)$_2$ favors a stable interligand S−S adduct (**2b**) from 1,4 addition of one molecule of *cis*-1,3-butadiene on immediately adjacent S atoms, which is stable and can be formed through a barrier of only 9.3 kcal/mol. Although 1,2 addition of one molecule of *cis*-1,3-butadiene on intraligand S−S and 1,4 addition on intraligand S−C are also symmetry-allowed, the adducts are not as stable as **2b** and the reaction barriers are also higher; thus, these reaction processes cannot compete with the formation of **2b** at room temperature. However, higher temperatures shift the rates toward the addition of another molecule of *cis*-1,3-butadiene to the intraligand S−C adduct (**9**), producing the thermodynamic product, the apofacial S−C adduct (**13**) with two molecules of *cis*-1,3-butadiene. Key intermediate **9**, with one molecule of *cis*-1,3-butadiene added to intraligand S−C bond, is only slightly less stable than the room-temperature product, **2b**, and is formed over a somewhat higher barrier (14.0 kcal/mol); final transformation to **13** only overcomes a barrier of 14.4 kcal/mol. Therefore, the computed overall barriers suggest that the formation of this final apofacial intraligand S−C adduct can occur only slowly at room temperature but much faster at higher temperature and will yield the thermodynamic product exclusively. The calculation results well explain the experimental results that interligand S−S adduct was observed when the reaction started in a short time at room temperature, while apofical intraligand S−C adduct was accumulated as the final product at 50°. Considering recent interest in ligand-based alkene uptake, we think the current examination of $Pt(tfd)_2$ reactivity will be helpful in the future work on olefin absorption, purification, and reactivity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures of optimized compounds/intermediates and transition states, along with tables of Cartesian coordinates and electronic energies for all of the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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