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C−H bond activation of benzene and thiophene by photochemically generated rhenocene cation

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Abstract. A cationic rhenocene-acetonitrile adduct $[Cp_2Re(NCMe)](BF_4)$(**1**) reacted with an excess of benzene, thiophene, 2-methylthiophene, and pyrrole under UV irradiation to afford the C−H bond activation products $[Cp_2Re(H)R]BF_4$ (R = phenyl, 2-thienyl, 2-(5-methylthienyl), 2-pyrrolyl) in high yields. In cases of thiophene derivatives and pyrrole, α-C−H bonds are selectively activated. A plausible mechanism involves the photodissociation of acetonitrile from **1** to generate a coordinatively unsaturated rhenocene cation $[Cp_2Re]^+$. When 2,5-dimethylthiophene and dibenzothiophene, having no α-C−H bonds, were used as substrates, products of the activation of other C−H bonds were formed first, but they isomerized to thermodynamically more stable η^1-S-coordinated complexes in refluxing acetone. On the other hand, irradiation of the η^1-S-coordinated complexes reproduced the original C−H bond activation products. Because of the cationic character, $[Cp_2Re(H)R]BF_4$ were readily deprotonated by triethylamine to give neutral rhenocene derivatives Cp_2ReR. When R is thienyl or 2-(5-methylthienyl), treatment of Cp_2ReR with $HBF_4 \cdot Et_2O$ and MeI resulted in protonation and methylation to give $[Cp_2Re(H)R]BF_4$ and $[Cp_2Re(Me)R]I$. Thermolysis of $[Cp_2Re(Me)R]I$ in the presence of PPh_3 unexpectedly resulted in migration of R to the Cp ring to give $[(2\text{-thienyl } C_5H_4)CpRe(PPh_3)]I$.

1. INTRODUCTION

It is well known that photochemically or thermally generated tungstenocene Cp_2W activates the C−H bond of various substrates (Scheme 1) [1, 2].

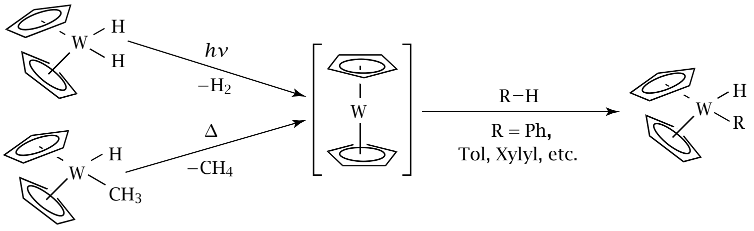
Recently we synthesized a cationic rhenocene acetonitrile complex $[Cp_2Re(NCMe)](BF_4)$ (**1**) by photolysis of the cationic rhenocene dihydride complex $[Cp_2ReH_2]BF_4$ (**2**) in acetonitrile. We found that **1** was a convenient precursor for photochemically generating the rhenocene cation $[Cp_2Re]^+$ (**A**) a species isoelectronic and isostructural to Cp_2W, and the photolysis of **1** in the presence of benzene or thiophene afforded the C−H bond activation products **3** and **4a** in high yields [3] (Scheme 2).

We report here the results of the expansion of this research toward the activation of various thiophene derivatives as well as pyrrole.

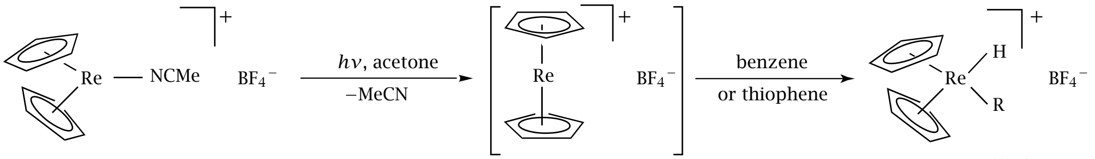
2. RESULTS AND DISCUSSION

2.1. Photoreaction of 1 with 2-methylthiophene. Photolysis of **1** in the presence of 2-methylthiophene afforded **4b** in 70% yield (Scheme 3). In this reaction, the α-C−H bond on 2-methylthiophene was selectively activated and no products through oxidative addition of the β-C−H bond or the C−H bond of the methyl group was observed.

2.2. Photoreaction of 1 with 2,5-dimethylthiophene and dibenzothiophene. When thiophene derivatives having no α-C−H bonds are used as substrates, other C−H bonds are activated. Thus, the photolysis of **1** in the presence of 2,5-dimethylthiophene gave a mixture of **5a** and **5b**, for which the C−H bond at a β-position and that of a methyl group of 2,5-dimethylthiophene were activated, respectively. Similarly, the photolysis of



Scheme 1



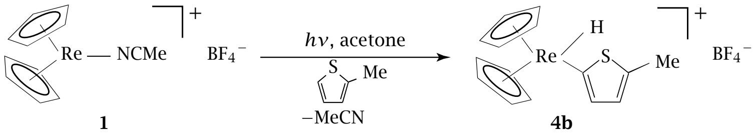
1

A

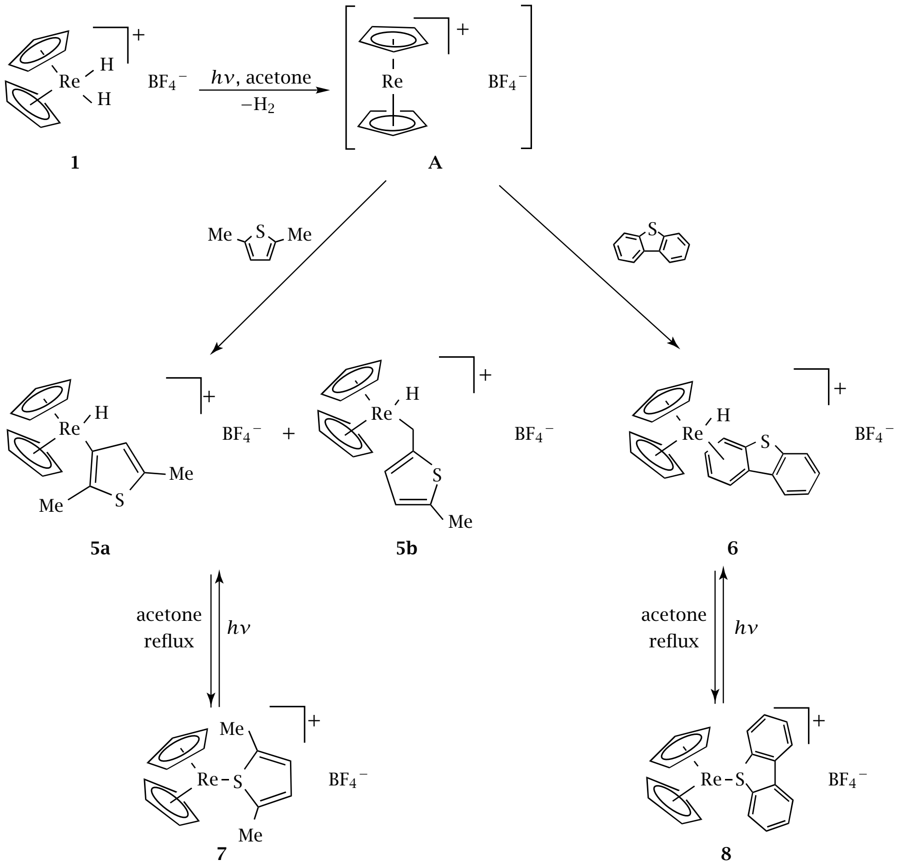
3: R = Ph 88%
4a: R = 2-thienyl 80%

Scheme 2

1 in the presence of dibenzothiophene yielded a mixture of **6** where the C−H bonds of the fused benzene rings were activated. Interestingly, these C−H bond activation products **5** and **6** thermally isomerized in refluxing acetone into the η^1-S-coordinated complexes **7** and **8**, respectively. Moreover, photoirradiation of **7** and **8** reproduced the original C−H bond activation products (Scheme 4).



Scheme 3

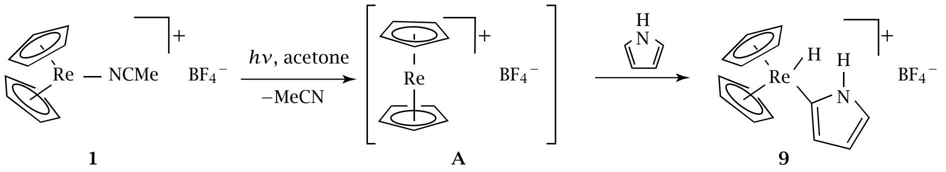


Scheme 4

These results show that the η^1-S-coordinated complexes **7** and **8** are thermodynamically more stable than the C−H bond activation products **5** and **6**, and the barrier of the isomerization between them are relatively low. On irradiation, perhaps the excited **7** and **8** liberate the thiophene derivatives to generate **A**, and then **A** activates the C−H bond of the thiophene derivatives to give **5** and **6**. The η^1-S-coordinated complexes are considered to be the intermediates for C−S bond activation [4, 5], but from **7** and **8**, formation of the C−S bond activation products was not observed.

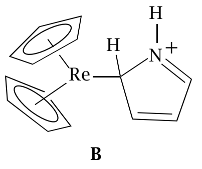
In the cases of α-C−H bond activation products **4a** and **4b**, the isomerization to η^1-S-coordinated complexes is also possible. However, this isomerization was not observed in refluxing acetone either because **4a** and **4b** are more thermodynamically stable than those of the corresponding η^1-S-coordinated complexes or because the isomerization is too slow to occur.

2.3. Photoreaction of 1 with pyrrole. Photolysis of **1** in the presence of pyrrole afforded the α-C−H bond activation product **9** in 87% yield (Scheme 5). The corresponding photoreaction of tungstenocene in the presence of pyrrole was reported to give only the N−H bond activation product $Cp_2W(H)(NC_4H_4)$ [6]. Although there is a reaction of pyrrole with a triosmium complex which gives a mixture of products through both the C−H and N−H bond activation of pyrrole [7, 8], to our knowledge, the reaction in Scheme 5 is the first example of selective C−H bond activation of pyrrole by a mononuclear complex.


Re — NCMe
BF4⁻
hν, acetone
−MeCN
Re
BF4⁻
H
N
Re
H
H
N
BF4⁻
1
A
9

Scheme 5

Since the steric requirements of **A** and Cp_2W seem to be almost the same, the difference of the activated bond may be explained by the electronic difference between them: In the reaction of cationic complex **1** with pyrrole, the σ complex **B** (Shceme 6) can be significantly stabilized by distribution of the positive charge on the nitrogen atom, which makes the C−H bond activation more favorable than the oxidative addition of the N−H bond.

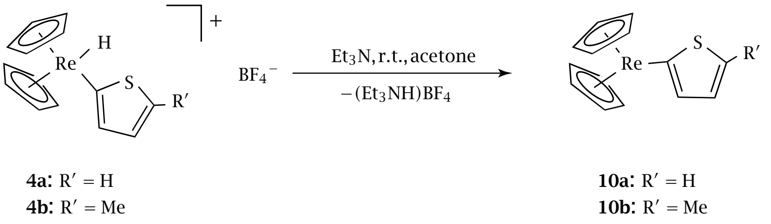


Scheme 6

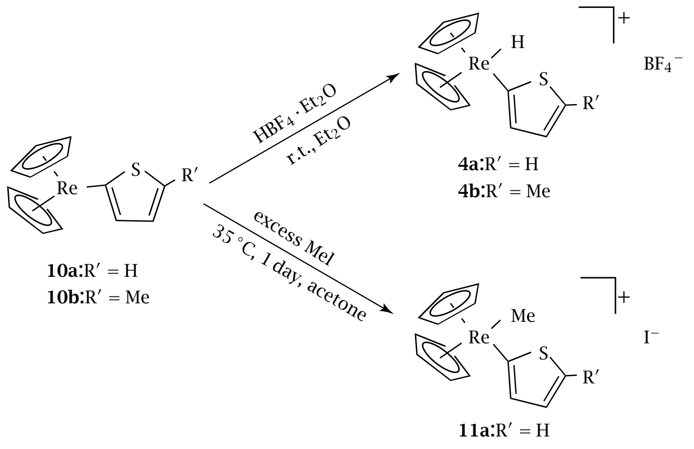
2.4. Deprotonation of $[Cp_2ReH(2\text{-}C_4H_2R'S)]BF_4$ ***(4a:*** R′ = H***, 4b:*** R′ = Me***) with base.*** Because of the cationic character, **4a** and **4b** were readily deprotonated by triethylamine to give neutral thienyl- and methylthienylrhenocenes **10a** and **10b** in 56–64% yields (Scheme 7). A similar behavior has not been observed for the isoelectronic $Cp_2W(H)R$.

2.5. Protonation and methylation of 10 with HBF_4 ***and*** MeI***.*** Neutral rhenocene derivatives are reported to be readily protonated by Brønsted acids [3, 9, 10, 11] and electrophilically methylated by MeI [12, 13]. For **10a**, **b**, $HBF_4 \cdot Et_2O$ and MeI reacted with them under mild conditions to produce **4a**, **b** in 49–87% and **11a**, **b** in 59–89% yields, respectively (Scheme 8).

A bulkier electrophile EtI did not react with **10a**, **b** probably because an ethyl group is too large to be introduced. The large steric repulsion between the alkyl and thienyl ligands is clearly seen in the molecular structure of **11a** shown in Figure 1, where the interatomic distance between C1 and C2 (2.89(1) Å) is extremely short. The above-mentioned results demonstrate that


Re
H
S
R′
BF4⁻
Et3N, r.t., acetone
−(Et3NH)BF4
Re
S
R′
4a: R′ = H
4b: R′ = Me
10a: R′ = H
10b: R′ = Me

Scheme 7


Re
S
R′
10a:R′ = H
10b:R′ = Me
HBF4 · Et2O
r.t., Et2O
excess MeI
35 °C, 1 day, acetone
Re
H
S
R′
BF4⁻
4a:R′ = H
4b:R′ = Me
Re
Me
S
R′
I⁻
11a:R′ = H
11b:R′ = Me

Scheme 8

the hydrido ligand formed by oxidative addition of the α-C−H bond of thiophene derivatives to $[Cp_2Re]^+$ can be easily replaced to a methyl group under mild conditions.

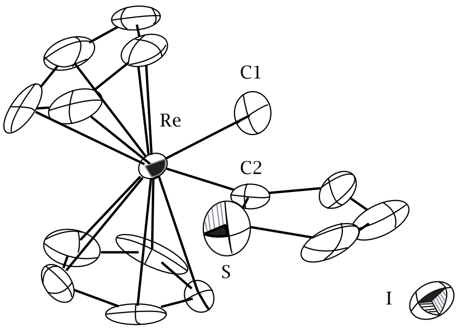
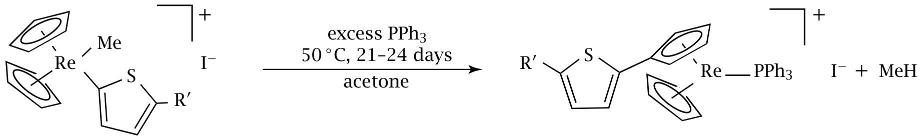


Figure 1. *ORTEP view of **11a**.*

2.6. Migration of a thienyl group in cationic methyl(thienyl)rhenocene derivatives. Thermolysis of **11a**, **b** in the presence of PPh_3 aiming the reductive elimination of 2-methylthiophene derivatives resulted in unexpected migration of a thienyl group to give **12a**, **b** (Scheme 9). Formation of methane was confirmed by ^1H NMR spectroscopy. The reaction was clean and no reductive elimination product was observed.



11a: R′ = H
11b: R′ = Me

12a: R′ = H
12b: R′ = Me

Scheme 9

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