C–C coupling reaction of pyridine derivatives at the dimethyl rare-earth metal cation [YMe$_2$(THF)$_5$]$^+$: A DFT investigation*

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ARTICLE INFO

ABSTRACT

Applying DFT methods, the reductive elimination reaction of bis(pyridyl) rare-earth metal cation [Ln(η^2-C, N-pyridyl)$_2$(THF)$_3$]$^+$ (Ln = Y, La) was studied. The effect of both electron-donating and electron-withdrawing substituents in the para-position of the pyridine ring was considered. An alternative mechanism for the C–C coupling reaction between pyridine derivatives (pyridine, DMAP and 4-trifluoromethyl-pyridine) and [LnMe$_2$(THF)$_5$]$^+$ (Ln = Y or La) is suggested. The reaction involves a single electron reductive C–C coupling to form of Ln(II) complexes with a bipyridine radical anion.

1. Introduction

In contrast to late transition metals, reductive elimination at d^0 early transition metal centers involving two hydrocarbyl ligands under C–C bond formation is not common. Early transition metal complexes often react with N-heterocycles to lead to ortho-metalated complexes [1–11]. Two examples for reductive coupling of pyridyl functions were reported in the literature: Teuben et al. [2] have shown that thermolysis of Cp$^*_2$Y(η^2-C,N-pyridyl) with excess pyridine led to the formation of 2,2′-bipyridine under H$_2$ elimination. Cummins et al. [12] observed a C–C coupling between two pyridine ligands in the presence of H$_2$ in tantalum(V) chemistry, leading to a bipyridine complex. This reaction clearly involved a twoelectron C–C reductive elimination of the two pyridyl ligands, resulting in a tantalum(III) complex. This reaction was possible, since tantalum(III) is an accessible oxidation state. Recently, Carver and Diaconescu [13] reported a similar observation in scandium (III) chemistry. A C–C coupling between two pyridine ligands was

reported to give a dearomatized bipyridine ligand. These authors also repeated experiments similar to that reported by Teuben et al. and confirmed the formation of bipyridine. Since oxidation state + I is highly unstable for group 3 metals, Carver and Diaconescu proposed that the above reactions occur via the formation a dearomatized bipyridine. Schumann et al. [14] suggested the possible formation of an ytterbium complex, exhibiting a dianionic bipyridine ligand. Moreover, a recent study by Booth et al. [15] have shown that coordination of bipyridine derivatived to Cp$^*_2$Yb was leading to a single electron transfer between divalent ytterbium and the bipyridine ligand to trivalent ytterbium. Here the +II and +III oxidation states of ytterbium are accessible, but the low-lying π^* orbital of the bipyridine ligand appears to be important in the C–C coupling reaction in group 3 complexes. We have studied the reductive and non-reductive type of reactions and proposed an alternative mechanism for C–C coupling reaction between pyridine derivatives (pyridine, DMAP, and 4-trifluoromethyl-pyridine) and [LnMe$_2$(THF)$_5$]$^+$ (Ln = Y or La). The reaction appear to involve a single electron reductive C–C coupling to form a Ln(II) complex with a bipyridine radical anion.

2. Computational details

Based on our previous work, it has been shown that lanthanide center could be treated with f-in-core ECPs [16–21]. Thus, Y and La were treated with a Stuttgart-Dresden pseudo-potential in

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combination with its adapted basis set [22,23]. In both cases, the basis set has been augmented by a set of polarization function f. Carbon, oxygen and hydrogen atoms have been described with a $6-31G(d,p)$ double-ζ basis set [24]. Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91 [25,26]. Geometry optimizations were carried out without any symmetry restrictions, and the nature of the *extrema* (*minima*) was verified with analytical frequency calculations. All these calculations were performed with the Gaussian 03 [27] suite of programs. The electronic density has been analyzed using the Natural Bond Orbital (NBO) technique [28].

3. Results and discussion

Cationic dimethyl complexes $[LnMe_2(THF)_5]^+$ undergo a variety of reactions, such as *ortho* C—H activation of pyridines derivatives [29], benzophenone [30] as well as olefin and 1,3-diene insertions [31]. A previous theoretical/experimental study on C—H activations of pyridine derivatives [29] demonstrated that the reaction is exergonic and the activation barriers were accessible with around $20-25$ kcal mol^{-1}. The cationic complex was thus able to undergo two successive *ortho*-metalation of two pyridine derivatives to form $[Ln(\eta^2\text{-C,N-pyridyl})_2(THF)_3]^+$. A similar intermediate was postulated in the two electrons reductive C—C coupling reported by Cummins et al. [12] Coupling of two anions is not a trivial task, as electron—electron repulsion between the two lone pairs has to be overcome. Moreover, after forming the C—C bond, two electrons remains that have to occupy molecular orbitals. In the case of group 3 or lanthanide complexes where oxidation state + I is not stable, two possibilities are conceivable (Scheme 1).

Either there is a single reduction of the metal center and formation of bipyridine radical anion (Scheme 1, left), or there is no reduction of the metal center (Scheme 1, right). In the former case, triplet spin state will be formed, whereas a singlet spin state is formed in the later case. The two electronic distributions as well as the thermodynamics of the reaction, are defined by the relative energetic positions of the empty orbitals (namely the d on the metal and π^* on the bipyridine ligand). This relative position of the empty orbitals is a parameter that can be adjusted by changing the substituents on the pyridine. A donor substituent such as in the case of DMAP will increase the π^* orbital energy, whereas an electron-withdrawing ligand such as in the case of 4-(trifluoromethyl)pyridine, will decrease the π^* orbital energy. The reference is pyridine. From the experimental point of view, only results with DMAP are well-behaved and no C—C coupling product was isolated. For pyridine, the results are not clear. Side reactions occurred so that C—C coupling products could not be identified. Finally for 4-(trifluoromethyl)pyridine, the C—H bond activation reaction was slower than for pyridine or DMAP, so that no attempts were made to identify C—C coupling products. In the case of DMAP, the mechanism for a non-reductive C—C coupling, leading to a dearomatized bipyridine complex, will be detailed for La (the profile for pyridine is given in Fig. 1). Starting from the bis(*ortho*-metalated) product **1**, the coordination of a pyridine molecule is favorable (roughly 10 kcal mol^{-1} for

DMAP **2a** and up to 23 kcal mol^{-1} for pyridine **2b**). The activation barrier for the non-reductive C—C coupling is predicted to be 23.2 kcal mol^{-1} for DMAP **3a** and 27.4 kcal mol^{-1} for pyridine **3b**, which is in line with kinetically accessible reactions. From the pyridine derivatives adduct **2**, the reaction is endergonic by 10.8 kcal mol^{-1} for DMAP **4a** and 5.4 kcal mol^{-1} for pyridine **4b**. This is in agreement with the lack of C—C coupling reactivity observed with DMAP.

However, from the dearomatized bipyridine product **4**, a ring opening reaction can occur and has to be investigated. The reaction is endergonic by 5.9 kcal mol^{-1} for DMAP **7a** (16.7 kcal mol^{-1} from the bipyridine derivatives adduct) and 14.2 kcal mol^{-1} for pyridine **7b** (19.6 kcal mol^{-1} from the adduct). Thus, this ring opening reaction is predicted to be not favorable. The reaction of non-reductive C—C coupling reaction is unlikely to occur with excess of pyridine derivatives. The non-reductive C—C coupling reaction was computed with only two equivalents of pyridine derivatives (from the mixed pyridyl—methyl complex). The activation barrier for the C—C coupling **5** is predicted to be 2.0 kcal mol^{-1} higher than the one for C—H bond activation by the methyl. The reaction is also predicted to be athermic, whereas C—H bond activation is exergonic by 20 kcal mol^{-1} [29]. Thus, the non-reductive C—C coupling is clearly not a possible reaction path. This is different from the mechanism proposed by Carver and Diaconescu [13]. An alternative reductive reaction mechanism was considered.

The reactions are predicted to be endergonic by more than 10 kcal mol^{-1} for DMAP and athermic for pyridine (Fig. 2). This is in agreement with the lack of reaction for DMAP. The reactions energies are in line with the energetic position of the π^* orbital of the bipyridine ligand formed. In the case of the DMAP, the amido substituent is an electron donor increasing the energetic level of the π^* orbital. This disfavors all complexes where this π^* orbital is occupied. As mentioned earlier, in both cases a singlet and a triplet spin state C—C coupling products have been located on the Potential Energy Surface (PES). The singlet state can be described as a Ln(III) complex of the bipyridyl anion (two electrons located in the π^* orbital), whereas the triplet state is a Ln(II) complex of the bipyridine radical anion (one electron located in the π^* orbital). The singlet state is η^4-coordinated (coordination by two N and the two C to the metal center) and the triplet state is only η^2-coordinated (coordination only by the two N) (Fig. 3). In the case of DMAP, the triplet spin state is found to be lower than the singlet state, as expected (Fig. 2). It is noteworthy that the singlet-triplet gap is larger for La than for Y. This may be due to the fact that the 5d orbitals are higher in energy than the 4d orbitals due to relativistic effects, so that the 5d orbitals are closer in energy to the π^* orbital than the 4d orbitals. For pyridine, the π^* orbital is lower in energy than that of DMAP, so that the singlet—triplet gap is decreased. At this stage, it is hard to predict for pyridine if the triplet state would be lower than the singlet state. The calculations indicate that the singlet state is in fact lower than the triplet state. As expected, the gap is lower for La than for Y.

From the kinetic point of view, the reactions are predicted to proceed with a relatively high activation barrier **10** (around 40 kcal mol^{-1} for DMAP and around 37 kcal mol^{-1} for pyridine). The barriers are high so that the reactions are predicted to be kinetically difficult. Including solvent effects (THF), by means of continuum model (CPCM) [32,33], leads to a decrease of the barrier by 5–6 kcal mol^{-1}, indicating a kinetically accessible reaction for pyridine. Thus, the C—C coupling reaction could occur for pyridine, but it is of interest to test whether the reaction is more favorable with an electron-withdrawing substituent on the pyridine ring. The reaction with 4-(trifluoromethyl)pyridine was investigated (Fig. 4). Contrary to the pyridine and DMAP cases, the C—H bond activation reactions were not discussed in a previous publication for 4-(trifluoromethyl)pyridine and will be described here.
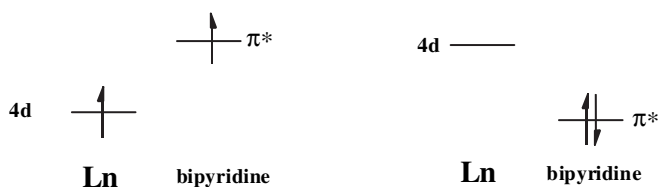
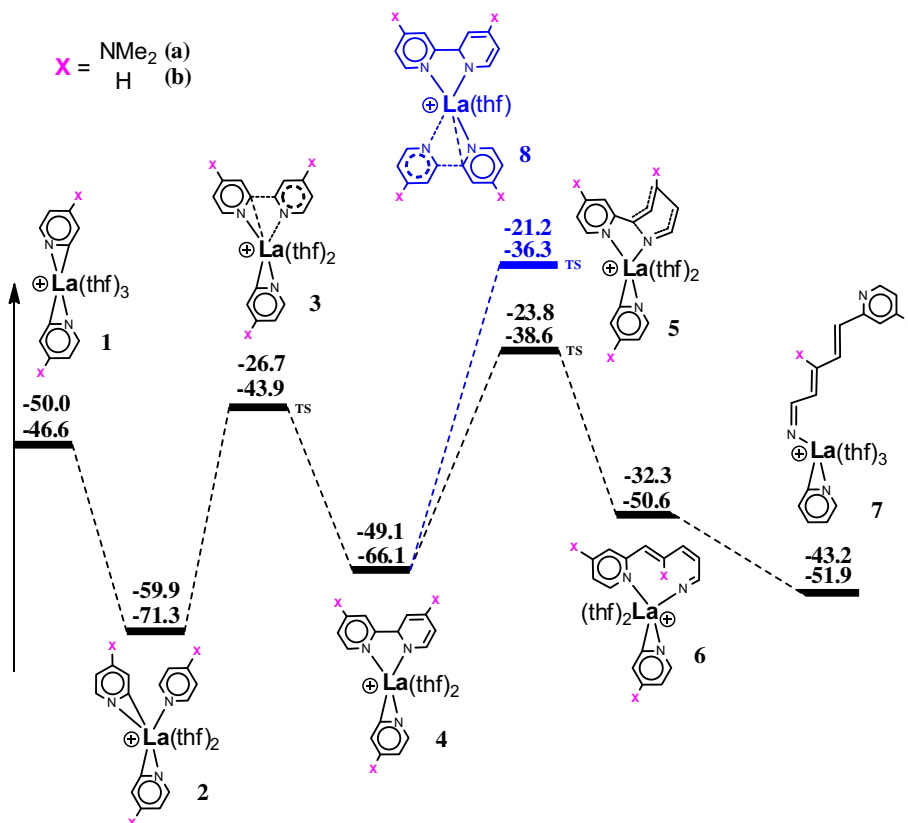**Scheme 1.** Possible distributions of two electrons during the C—C coupling reactions between two anions.

Fig. 1. Gibbs free energy profile (in kcal mol^{-1}) for the non-reductive C−C coupling reaction for pyridine (lower value) and DMAP (upper value). The reference energy is taken from [LnMe$_2$(THF)$_5$]$^+$ + 2 pyridine derivatives [29].

The C−H bond activation of the first molecule of 4-(tri-fluoromethyl)pyridine is predicted to be thermodynamically favorable (Fig. 4), as in pyridine and DMAP cases [29]. From the kinetic point of view, the activation barriers are found to be accessible and rather close to what found for the two other substrates. Thus, the first C−H bond activation is found to be thermodynamically (**16**) and kinetically (**14**) accessible. Similarly to the other substrates, the C−H activation of a second molecule is predicted to be also kinetically (**18**)

and thermodynamically (**20**) favorable. The formation of the bis (*ortho*-metalated) product is predicted to be favorable. As for the two other substrates, the non-reductive C−C coupling is endergonic and only the reductive pathway is reported.

As expected, the reaction is found to be slightly exergonic or endergonic, depending on the spin state of the product (Fig. 4). This is in agreement with a low-lying π^* orbital. A difference between the two metals is also reported. Indeed, for yttrium, the singlet state **22** is the most stable, whereas the triplet state **23** is the most stable for lanthanum. This is related to the difference of energetic positions of the 5d and 4d orbitals. From the kinetic point of view, the calculated barriers to form **21** are high in the gas phase (around 35 kcal mol^{-1} for both metals), which is slightly lower than for
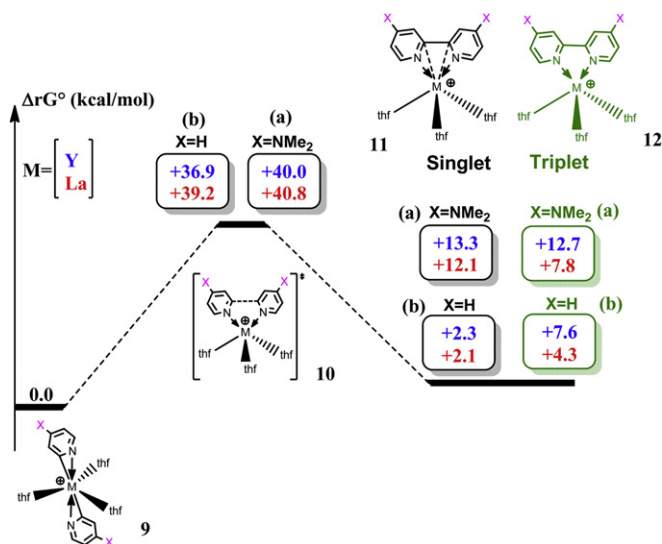

Fig. 2. Free energy profile (in kcal·mol^{-1}) for the C-C coupling reaction for pyridine (X=H) and DMAP (X=NMe$_2$). The red values account for La and in blue for Y.
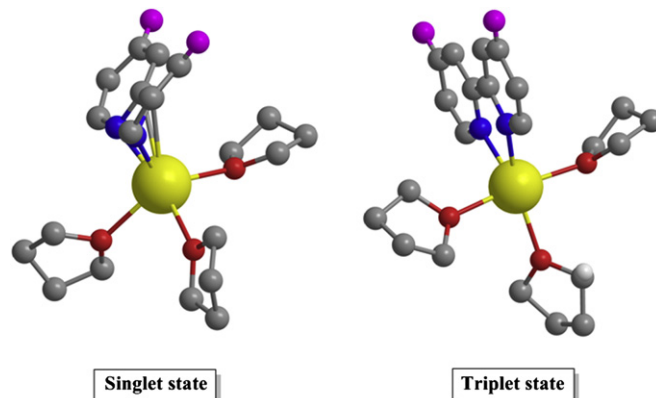

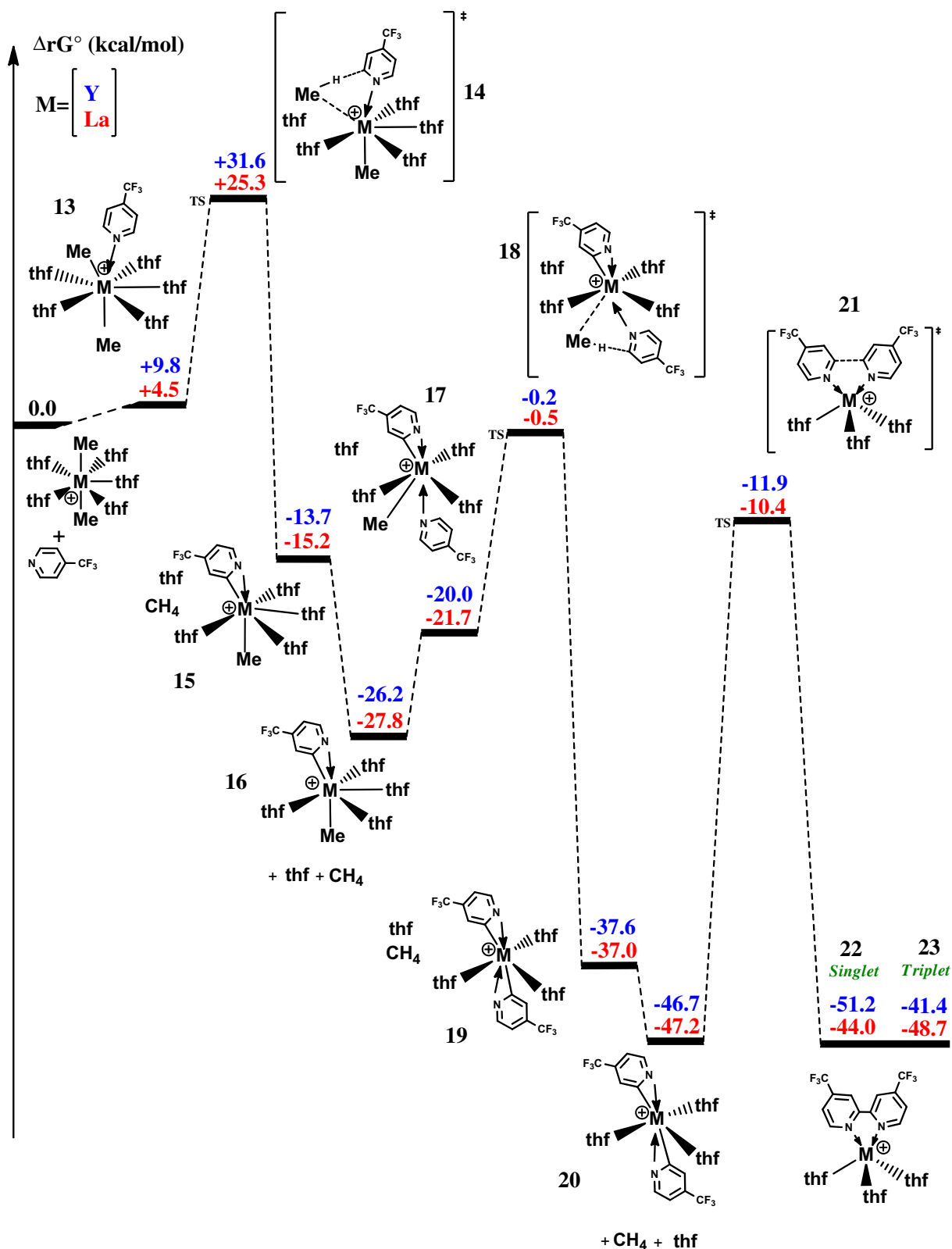**Fig. 3.** Optimized structures of the two possible C−C coupling products.

Fig. 4. Gibbs free energy profile for the reaction of [LnMe$_2$(THF)$_5$]$^+$ with two molecules of 4-(trifluoromethyl)pyridine. Numbers for the reaction with yttrium is in above and lanthanum below.

pyridine. Moreover, solvent effects decrease the barrier by 5−6 kcal mol^{-1}, leading to kinetically accessible reactions.

For lanthanum, a single electron reductive C−C coupling reaction can take place, which is a rather unique type of reactivity. The non-reductive C−C coupling leading to dearomatized bipyridine complexes, as reported by Carver and Diaconescu [13], is not competitive in the case of methyl cations [LnMe$_2$(THF)$_5$]$^+$. The reactivity of such cations with other substrates such as N-

methylimidazole is currently under investigation, to see if reductive coupling is still preferred over the non-reductive pathway.

Acknowledgment

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