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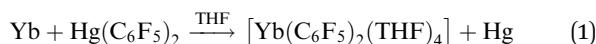
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On the reaction mechanism of redox transmetallation of elemental Yb with $\text{Hg}(\text{C}_6\text{F}_5)_2$ and subsequent reactivity of $\text{Yb}(\text{C}_6\text{F}_5)_2$ with pyrazole: a DFT investigation[†]

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DFT investigations of the redox transmetallation reaction of the diorganomercurial ($\text{Hg}(\text{C}_6\text{F}_5)_2$) with Yb metal, yielding $\text{Yb}(\text{C}_6\text{F}_5)_2$, allowed us to define a very low energy reaction mechanism. This involves formation of a metal–metal bonded, formally $\text{Yb}^{\text{l}}\text{–Hg}^{\text{l}}$, intermediate valence complex, $(\text{C}_6\text{F}_5)\text{Yb}\text{–Hg}(\text{C}_6\text{F}_5)$. The subsequent reactivity of the divalent ytterbium complex with pyrazole was also computationally investigated, indicating that σ -bond metathesis occurs at divalent ytterbium.

The synthesis of compounds with unsupported lanthanoid–metal bonds (main group (MGM) or transition metal (TM)) has been a challenge, perhaps partly because the 4f orbitals are embedded and are shielded by the $5s^25p^6$ orbitals,¹ and partly owing to the intrinsic difficulty of binding together two electropositive elements. Nevertheless recent synthetic ingenuity has enabled a flowering of initially Ln–MGM^{1,2} and then Ln–TM³ bonded compounds with no supporting donor/bridging atoms. An unsupported Ln–M bond was initially proposed⁴ in intermediates, namely $\text{Yb}^{\text{+}}\text{–Hg}^{\text{–}}(\text{C}_6\text{F}_5)_2$ and $\text{C}_6\text{F}_5\text{Yb}\text{–HgC}_6\text{F}_5$, in the first redox-transmetallation synthesis of an organolanthanoid^{4,5} (1, and see structure⁶ of isolated complex $[\text{Yb}(\text{C}_6\text{F}_5)_2(\text{thf})_4]$).



However, no experimental evidence for the Yb–Hg species could be obtained. Structurally uncharacterized bimetallics proposed to be $\text{R}(\text{HgYb})\text{I}$ were later obtained from reaction of RHgI with Yb metal.⁷ Reactions analogous to (1) with a variety of mercurials, e.g. $\text{Hg}(\text{CCPh})_2$, HgPh_2 , HgCp_2 , have made redox transmetallation a fruitful general synthetic route to organolanthanoids, though in

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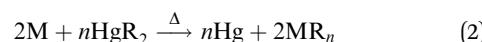
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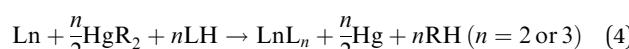
[†] Electronic supplementary information (ESI) available: Details of DFT calculations. See DOI: 10.1039/c5cc05439g

some cases activation of Ln^0 by HgCl_2 , $[\text{YbI}_2(\text{thf})_4]$ or LnI_3 is needed.⁸ Reaction (1) and analogues are lanthanoid examples of a long known synthesis⁹ (2) mainly used to give donor-solvent free main group



organometallics. We now report a study of reaction (1) utilizing DFT calculations, which provide evidence for the formation of an intermediate valence, Yb–Hg bonded species $\text{C}_6\text{F}_5\text{Yb}\text{–HgC}_6\text{F}_5$ in the reaction.

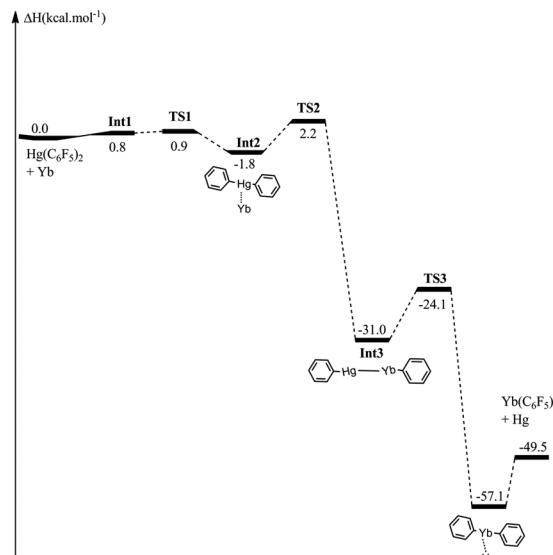
Also studied is the mechanism of the cleavage of $\text{Yb}(\text{C}_6\text{F}_5)_2$ with pyrazole (pzH) (3). Besides being a general model for the protolysis of $\text{Yb}(\text{C}_6\text{F}_5)_2$ with phenols,¹⁰ cyclopentadienes,¹¹ and substituted pyrazoles,¹² reactions (1) and (3) or analogues are considered steps in the synthetically valuable redox transmetallation/protolysis (RTP) reaction (4),¹³ which is an excellent route to both divalent and trivalent cyclopentadienyls,¹³ aryloxides,^{14,10a} pyrazolates,¹² formamidinates¹⁵ etc. Reaction (1) is considered the first step and reaction (3) the final step for $n = 2$, whilst reaction (1) is the first step and reaction (3) an intermediate step for $n = 3$. Thus, the calculations shed light not just specifically on the mechanism of (1) and (3) but also on the general RTP synthesis (4).^{12–15}



Since the last decade, computational methods have proven their ability to describe redox reactions involving f-element complexes as well as the “classical” bond activation.^{16,17} Therefore, DFT calculations (B3PW91/SDD(Yb,Hg)/6-31G(d,p) other atoms) were conducted in order to determine a plausible reaction mechanism for the redox transmetallation reaction $\text{Yb} + \text{Hg}(\text{C}_6\text{F}_5)_2 \rightarrow \text{Hg} + \text{Yb}(\text{C}_6\text{F}_5)_2$ (Scheme 1).

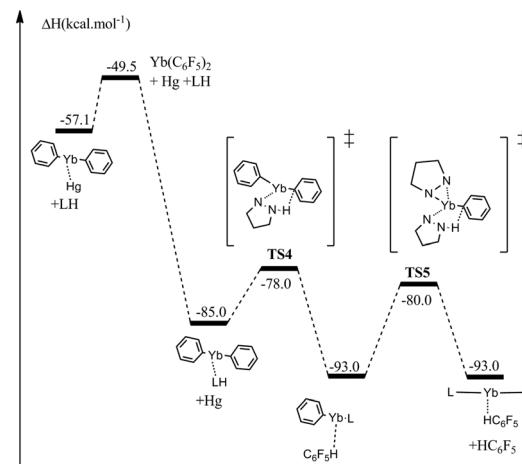
In a first step, the coordination of the ytterbium metal to the mercury center is observed through **TS1** with a marginal activation barrier (0.9 kcal mol^{–1}). This coordination compound (**Int2**) is slightly stabilized (1.8 kcal mol^{–1}) with respect to the separated





Scheme 1 Computed reaction profile (kcal mol⁻¹) for the redox transmetallation reaction. The F atoms are omitted for clarity in the scheme.

reactants. It is noteworthy that in **Int2**, a donor-acceptor interaction between Yb and Hg (donation from the 6s orbital of Yb into the 7p orbital of Hg and a Wiberg bond index of 0.35) is found. Analysis of the NPA charges indicates that the oxidation states of Hg and Yb are both intermediate between 0 and +II (Hg: decrease of the charge from 0.96 to 0.75 and Yb: increase of the charge from 0.0 to 0.24). From **Int2**, the compound undergoes a migratory insertion of Yb into a C₆F₅-Hg bond *via* **TS2**. The barrier to this migration is small (4.0 kcal mol⁻¹), indicating a facile process. Interestingly, at the TS, NBO analysis indicates the formation of a covalent bond between Hg and Yb (Wiberg bond index of 0.82) that concomitantly induces a drastic change of the charges (and therefore of the oxidation states) of the two metals (Hg: decrease of the charge from 0.75 to 0.22 and Yb: increase of the charge from 0.24 to 0.96). **TS2** yields intermediate **Int3** exhibiting an unsupported Yb-Hg interaction (bond found at the second order donor-acceptor NBO and Wiberg bond index of 0.58) with one C₆F₅ ligand having been fully transferred to Yb. Interestingly, in this intermediate, the Hg-Yb bond is strongly polarized toward Hg as reflected by the NBO analysis (donation from the 7s of Hg to an hybrid d/p of Yb) and the NPA charges (Hg: decrease from 0.22 to 0.1 and Yb: increase from 0.96 to 1.25). By comparison, with the other NPA charges, this complex is of intermediate spin.¹⁸ Finally, the second ligand transfer occurs through **TS3** with a low activation barrier (6.9 kcal mol⁻¹) yielding an highly thermodynamically stable Hg adduct to Yb(C₆F₅)₂. NBO analysis of the latter reveals at the second order a donor-acceptor interaction between Hg and Yb (donation from 7s of Hg to a d/p hybrid of Yb) with strength computed to be 7.6 kcal mol⁻¹. Other reaction pathways involving for instance Single Electron Transfer, direct double migration of the C₆F₅ ligand were investigated but either failed to converge (double transfer), were leading to the same profile as the one reported here (Single Electron Transfer) or leads to other energy profiles (ionic



Scheme 2 Computed reaction profile of the reactivity of the divalent ytterbium complex with pyrazole (kcal mol⁻¹). L stands for pyrazolate. The F atoms and pyrazole/pyrazolate double bonds are omitted for clarity in the scheme.

dissociation). There might be other plausible pathways but the one reported here is the lowest energy one that was found.

The subsequent reactivity of the divalent ytterbium complex with a nitrogen acid (pyrazole in this case) has then been investigated using the same theoretical approach (Scheme 2).

The “ligand exchange” between Yb(C₆F₅)₂ and the pyrazole is predicted to be thermodynamically favorable (exothermic by 27.9 kcal mol⁻¹) and can occur *via* a dissociative pathway (energetic cost of only 7.6 kcal mol⁻¹). From the pyrazolate adduct to the divalent ytterbium complex, two consecutive N-H activations can easily occur with moderate activation barriers (7.0 and 13.0 kcal mol⁻¹). These two N-H activations are classical σ -bond metatheses, where N, H and C_{ipso} are almost aligned,¹⁷ and can be viewed as proton transfer between the two ligands. In line with the Hard and Soft Acid-Base (HSAB) principle, the formation of a Yb-N bond is favored over the Yb-C one, explaining the exothermicity of the reaction.

In this study, the redox transmetallation reaction of Hg(C₆F₅)₂ with metallic Yb has been computed at the DFT level. The reaction is found to be kinetically and thermodynamically favourable. The formation of a transient complex bearing a Hg-Yb bond is also predicted, that rapidly evolves to the final divalent ytterbium complex. The latter can then react with a proton donor (pyrazole in this study) through σ -bond metathesis. This reaction is also kinetically and thermodynamically favourable and indicates the propensity of divalent ytterbium to react without change of oxidation state. The challenge now arises for us to isolate an intermediate involving a Yb-Hg bonded species.

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