

-Supporting Information-

Regioselective C-H Activation of Cyclometalated *bis*- Tridentate Ruthenium Complexes

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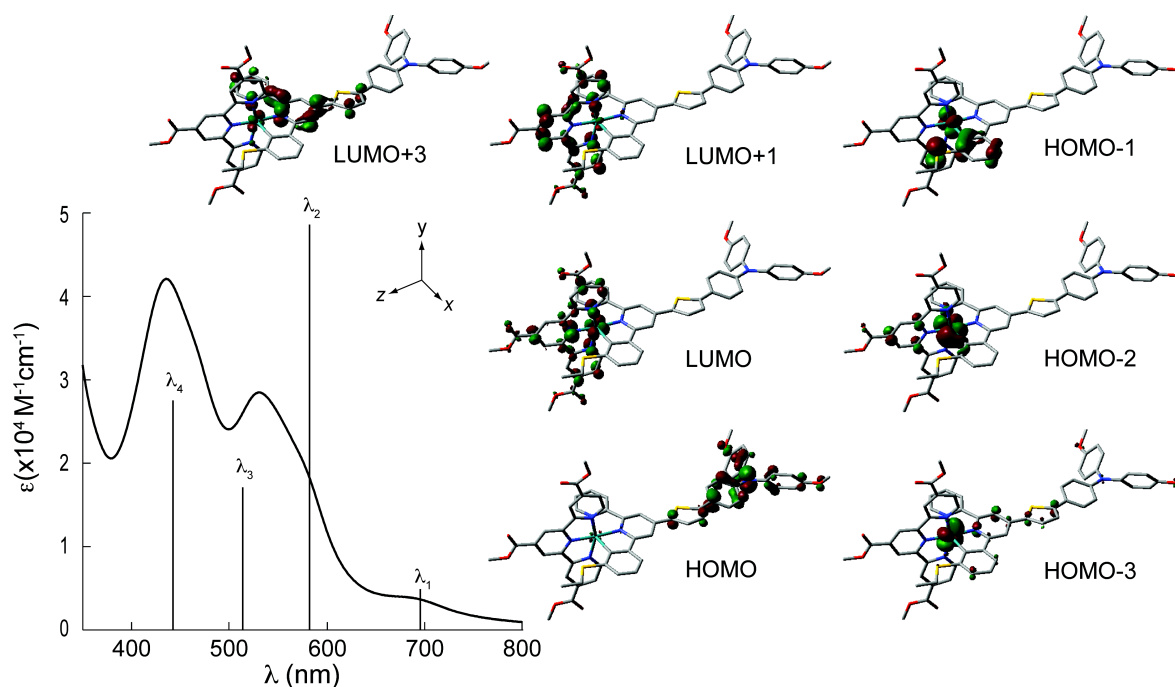


Figure S1. Experimental UV-vis absorption spectrum of **4** overlaid with calculated transitions represented by vertical bars, which represent the highest oscillator strength transition in between 60 calculated transitions (for the four selected ones the discriminative factor for this discussion is a contribution >30%). Details of calculated transitions (theoretical wavelength in nm, oscillator strength, % contribution to the transition): λ_1 , HOMO-1→LUMO (695, 0.0191, 97%); λ_2 , HOMO→LUMO+1 (581, 0.1949, 91%); λ_3 , HOMO-2→LUMO+1 (513, 0.0683, 81%); λ_4 , HOMO→LUMO+3 (442, 0.111, 64%).

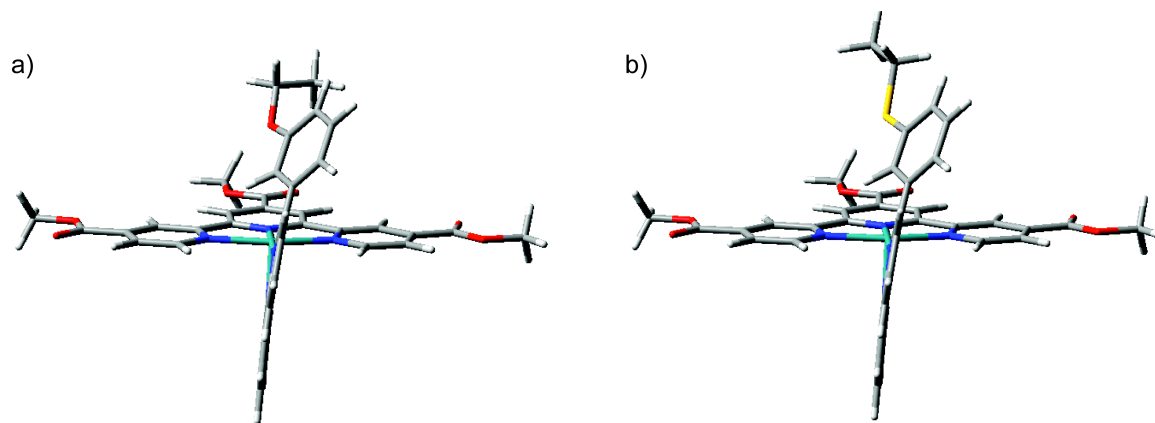
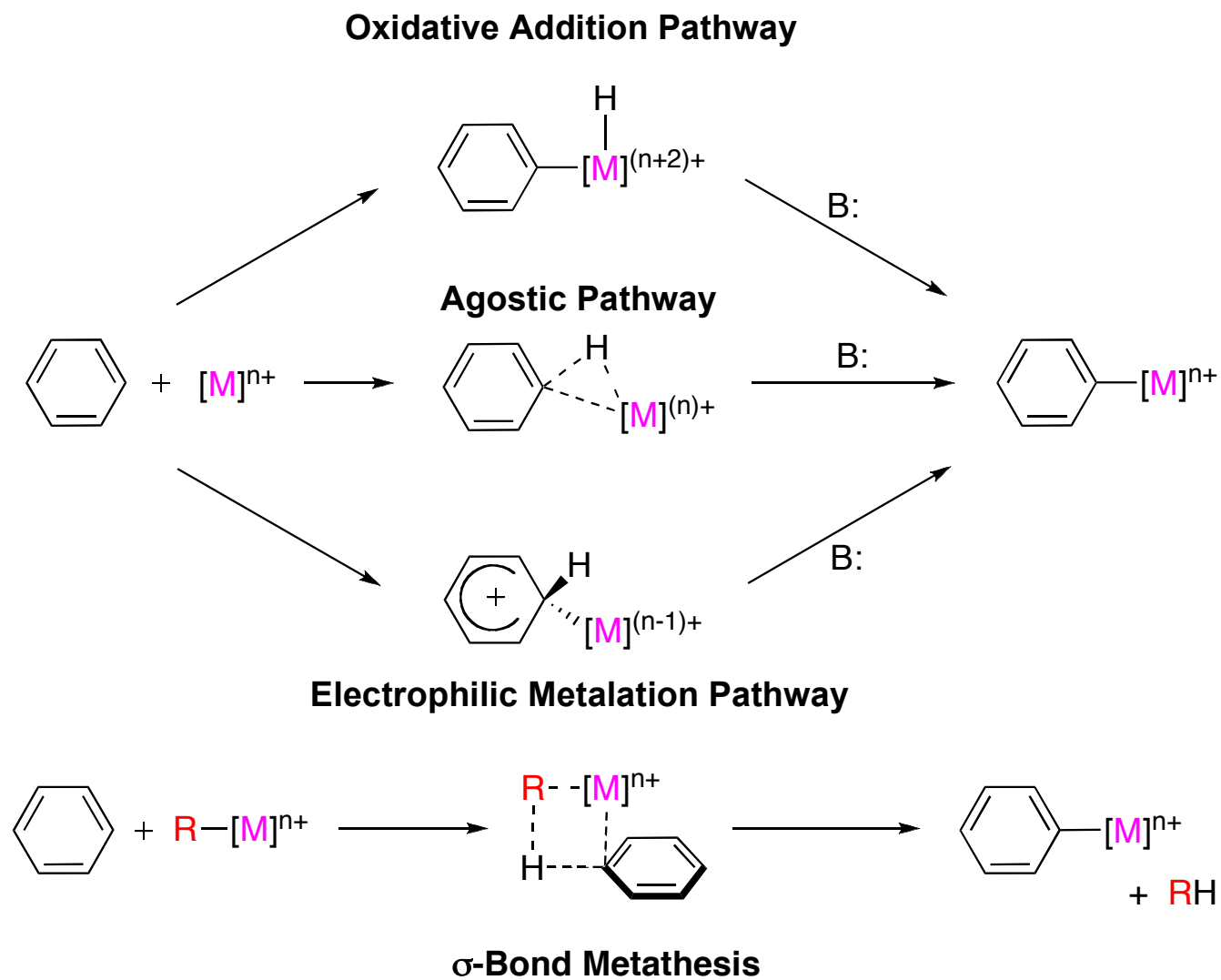


Figure S2. Frequency-optimized transition-state structures for a) –OEt ($\angle\text{MHC} = 100.1^\circ$; $\text{M-C} = 2.642 \text{ \AA}$, $\text{M-O} = 3.890 \text{ \AA}$ and b) –SEt ($\angle\text{MHC} = 103.9^\circ$; $\text{M-C} = 2.642 \text{ \AA}$, $\text{M-S} = 4.126 \text{ \AA}$). Transition states were calculated by DFT using Gaussian 09 by allowing free rotation of the *pro*-cyclometalating ring. The close contact between the Ru and C_{phenyl} atoms is consistent with an electrophilic mechanism, and the large metal-chalcogen distances imply there is no directing effect induced by a Lewis base coordination.

(a)



(b)

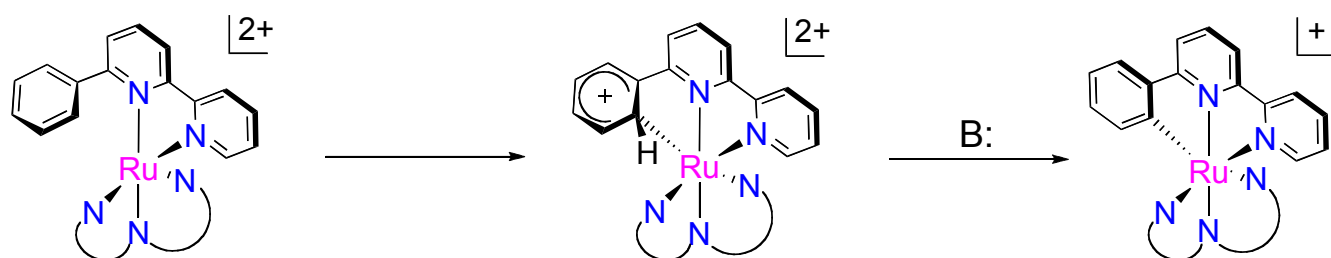


Figure S3. (a) Summary of potential C-H activation pathways. (b) Schematic showing C-H activation process for the relevant molecular fragment of the title complexes.