Preparation and Reactivity of Half-Sandwich Dioxygen Complexes of Ruthenium

Gabriele Albertin,*[†] Stefano Antoniutti,[†] Marco Bortoluzzi,[†] Jesús Castro[‡] and Valentina Ferraro[†]

[†]*Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155, 30172 Venezia Mestre, Italy*

[‡]*Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentais, 36310 Vigo (Galicia), Spain*

Electronic Supporting Information

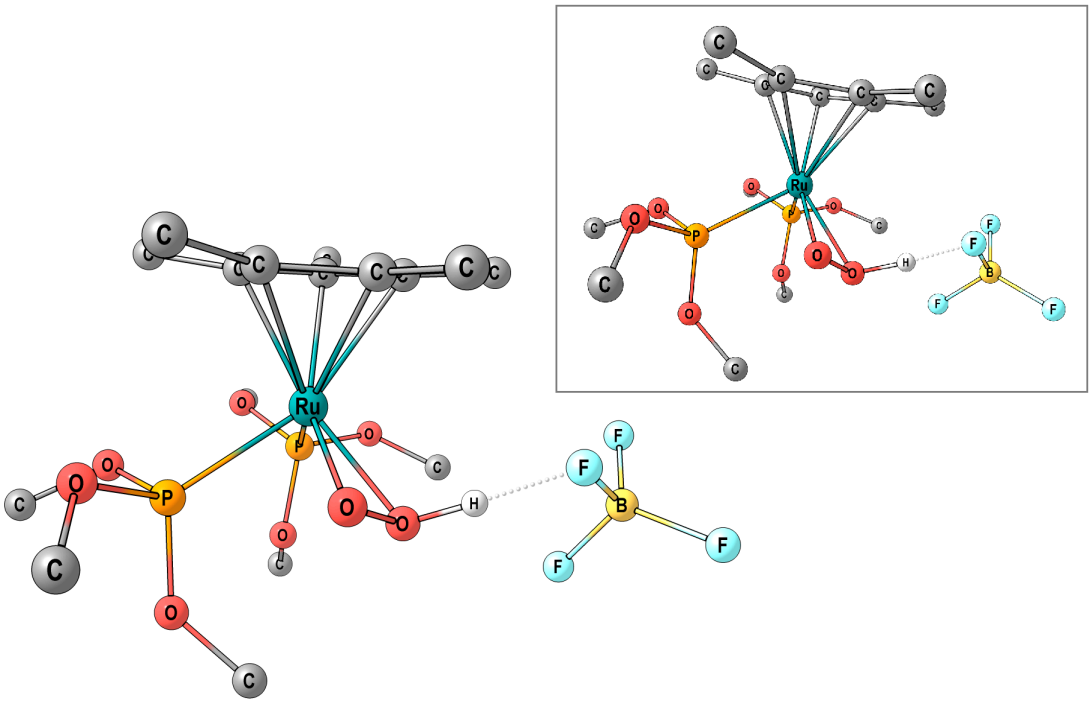

Figure S1. DFT-optimized structure of $[Ru(\eta_5\text{-}C_5Me_5)(\eta^2\text{-}O_2H\text{---}BF_4)\{P(OMe)_3\}_2]^+$ (singlet multiplicity). C-PCM/ωB97X calculation, dichloromethane as continuous medium. Hydrogen atoms of the methyl substituents are omitted for clarity. G = -2431.64183 a.u. Inset: DFT EDF2-optimized geometry of $[Ru(\eta_5\text{-}C_5Me_5)(\eta^2\text{-}O_2H\text{---}BF_4)\{P(OMe)_3\}_2]^+$, G = -2431.48189 a.u.

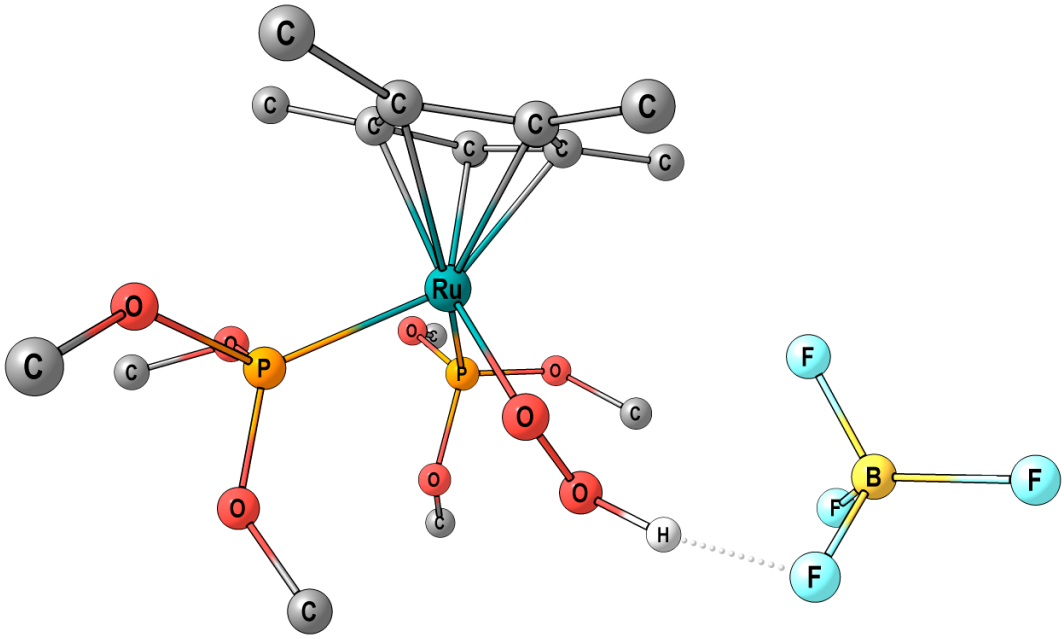

Figure S2. DFT-optimized structure of $[Ru(\eta_5\text{-}C_5Me_5)(\eta^2\text{-}O_2H\text{---}BF_4)\{P(OMe)_3\}_2]^+$ (triplet multiplicity). C-PCM/ωB97X calculation, dichloromethane as continuous medium. Hydrogen atoms of the methyl substituents are omitted for clarity. G = -2431.61654 a.u.

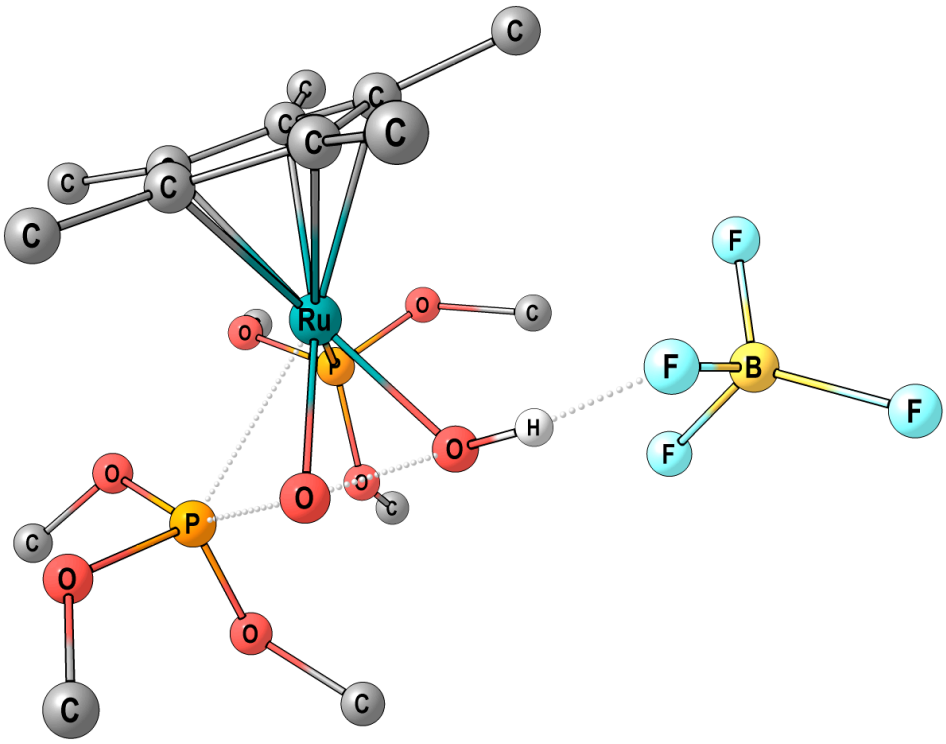

Figure S3. DFT-optimized transition state geometry for O-O dissociation and P-O formation in [Ru(η_5-C_5Me_5)(η^2-O_2H---BF_4){$P(OMe)_3$}$_2$]$^+$. EDF2 calculation. Hydrogen atoms of the methyl substituents are omitted for clarity. G = -2431.41483 a.u.

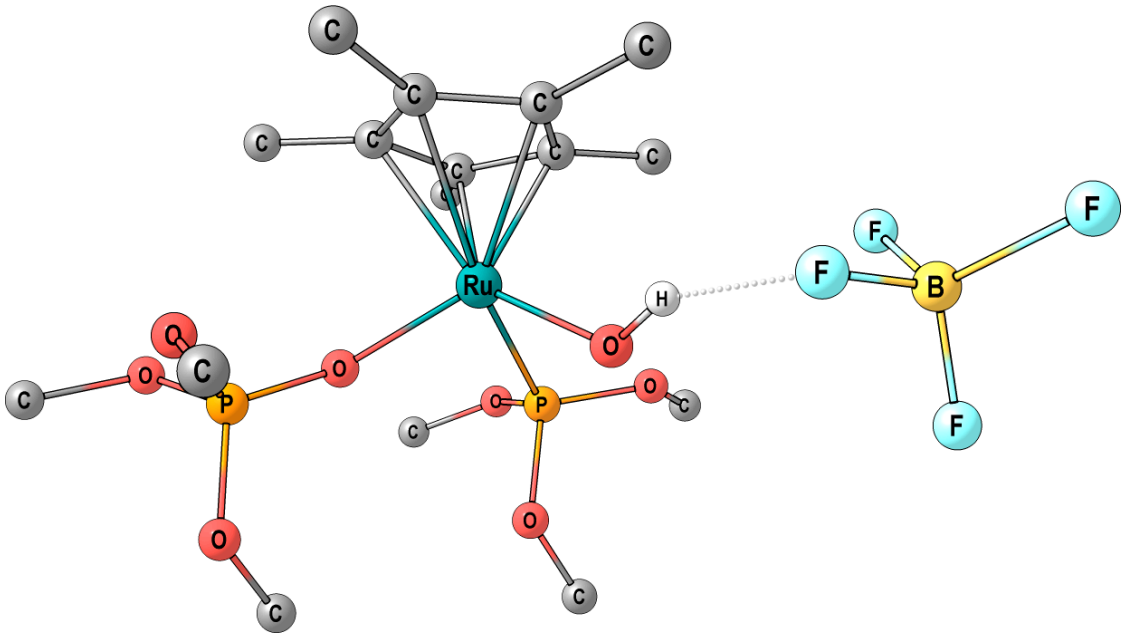

Figure S4. DFT-optimized structure of [Ru(η^5-C_5Me_5)(OH---BF_4){$P(OMe)_3$}{$PO(OMe)_3$}]$^+$. C-PCM/ωB97X calculation, dichloromethane as continuous medium. Hydrogen atoms of the methyl substituents are omitted for clarity. G = -2431.73446 a.u.

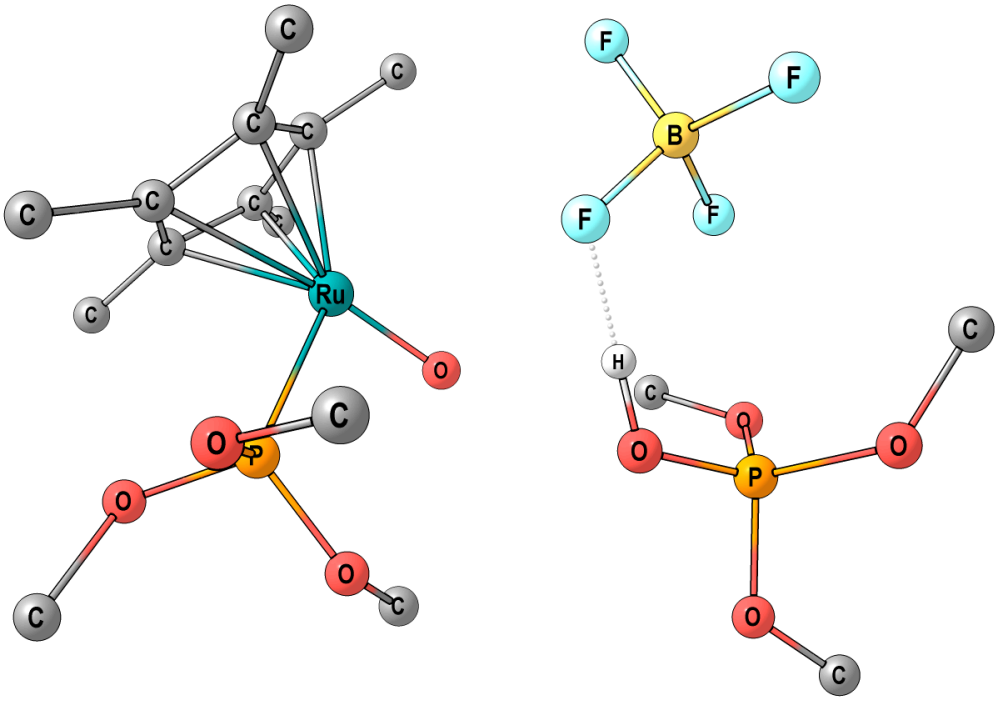

Figure S5. DFT-optimized structure of $[Ru(\eta^5\text{-}C_5Me_5)(O)\{P(OMe)_3\}]^+$ $PO(OMe)_3{\cdot}HBF_4$. C-PCM/ωB97X calculation, dichloromethane as continuous medium. Hydrogen atoms of the methyl substituents are omitted for clarity. G = =-2431.72417 a.u.

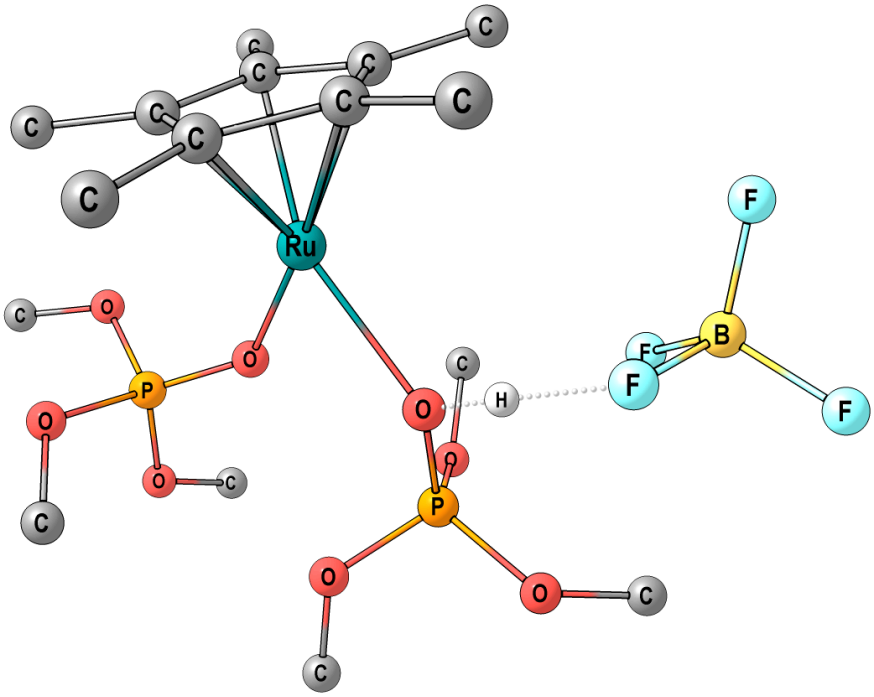

Figure S6. DFT-optimized structure of $[Ru(\eta^5\text{-}C_5Me_5)\{PO(OMe)_3\}\{PO(OMe)_3\text{---}HBF_4\}]^+$. C-PCM/ωB97X calculation, dichloromethane as continuous medium. Hydrogen atoms of the methyl substituents are omitted for clarity. G = =-2431.79171 a.u.