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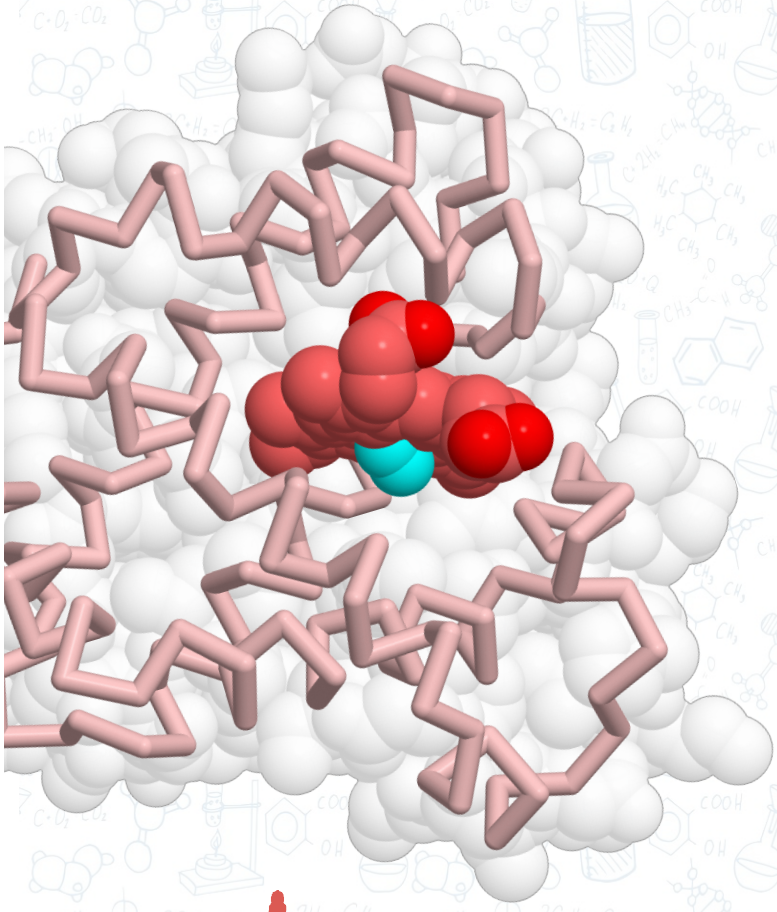

Proceedings

Società Chimica Italiana
Divisione di Chimica Inorganica

ALMA MATER STUDIORUM
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Half-Sandwich Dioxygen Complexes of Ruthenium: Preparation and Reactivity

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Dioxygen complexes $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}O_2)\{P(OR)_3\}L]BPh_4$ (**1–3**) were prepared by reacting chloro-compounds $RuCl(\eta^5\text{-}C_5Me_5)[P(OR)_3]L$ with air (1 atm) in the presence of $NaBPh_4$.

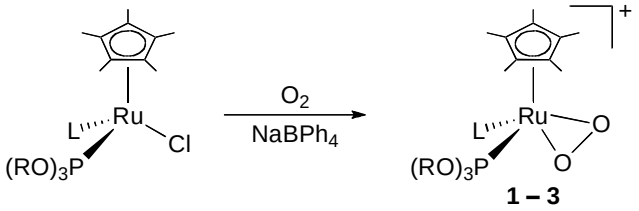

***Figure 1**: R = Me, Et; L = P(OR)3, PPh3*

Protonation of complexes **1–3** with triflic acid yielded phosphate complexes $[Ru(\kappa^1\text{-}OTf)(\eta^5\text{-}C_5Me_5)\{P(O)(OEt)_3\}_2]$ (**4**) and $[Ru(\kappa^1\text{-}OTf)(\eta^5\text{-}C_5Me_5)\{P(O)Ph_3\}\text{-}\{P(O)(OMe)_3\}]$ (**5**).

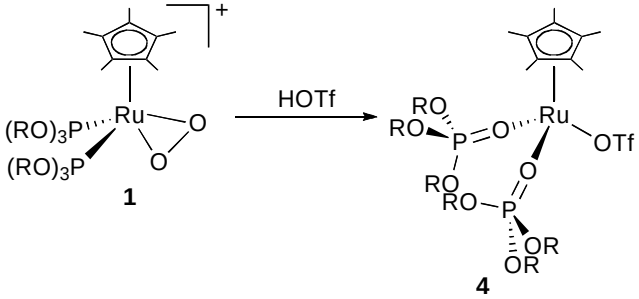

***Figure 2**: R = Me, Et*

A reaction path for the formation of complexes **4** and **5** is proposed by DFT studies. Besides the phosphate complex **4**, protonation of dioxygen complex **1** under a $CH_2{=}CH_2$ atmosphere (1 atm) afforded acetic acid.

All the complexes were characterised spectroscopically (IR and NMR) and by X-ray crystal structure determination of complexes **1**, **2** and **3**.