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Ring flipping in Heterobimetallic Re-Ir Complexes and its effect on structural isomerism: Dynamic NMR and DFT Study

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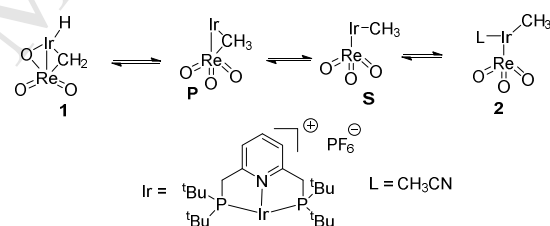
ABSTRACT: Experimental and DFT study on the ring flipping phenomenon from the two fused puckered five-membered rings in complex [PNP(Me)(CH₃CN)Ir-ReO₃][PF₆] (**2**) and its derivative [PNP(Me)(CN^tBu)Ir-ReO₃][PF₆] (**3**) is reported here. Dynamic NMR studies from ³¹P{¹H}NMR on ring flipping revealed that complexes **2** and **3** possess ΔG[‡] value of 11.2 ± 0.3 and 9.2 ± 0.3 kcal/mol at 298 K respectively. Density Functional Theory (DFT) calculations concurred with the Potential Energy (PE) values of 12.36 and 8.09 kcal/mol respectively for the same phenomena. Also, DFT studies revealed that ring flipping and structural isomerism between **2** and its isomer [PNP(H)Ir-μ(CH₂)-μ(O)-Re(O)₂][PF₆] (**1**) possess distinct transition states and can occur concurrently as observed experimentally.

1. Introduction

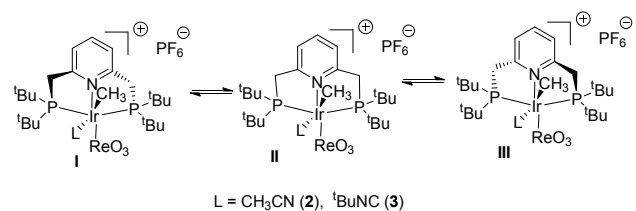
Pincer metal complexes are widely used in catalytic applications.[1-7] One of their characteristics is ring flipping emanating from the two fused and puckered five-membered rings: one pointing up and another down. This characteristic is explored by Variable-temperature Dynamic NMR spectroscopy (DNMR).[8-11] Restricting this motion with structurally rigid chiral pincer molecules having no ring flipping character, was realized in asymmetric catalysis.[9,12-14] Classic examples are the report from Nishiyama and coworkers on effective use of this property for asymmetric aldol-type condensation of isocyanides and aldehydes.[15,16] Crabtree and coworkers controlled this motion via outer sphere anion participation in a Pd(II) CCC pincer carbene complex.[17] On the other hand concurrent occurrence of this ring flipping with a structural isomerism is an unusual phenomenon.

We recently reported the synthesis and mechanistic study of the bimetallic complex [PNP(H)Ir-μ(CH₂)-μ(O)-Re(O)₂][PF₆] (**1**) and the observation of its structural isomer [PNP(Me)(CH₃CN)Ir-ReO₃][PF₆] (**2**) upon switching the solvent from methylene chloride to acetonitrile (Scheme 1).[18] From kinetic studies and Density Functional Theory (DFT) calculations we proposed that the structural isomerism of **1** occurs via methyl bridged complex **P**, with the subsequent formation of **S** and then **2**. [19] Interestingly complex **2** and its isocyanide derivative **3** showed ring flipping phenomena on the NMR time scale (Scheme 2). While structures **I** and **III** represent the two atropisomers, structure **II** is the transition state through which the conversion of **I** to **III** takes place. In this report we investigated this ring flipping by DNMR and DFT cal-

culations with the outlook of influencing the structural isomerism from **1** to **2** in the reverse direction.



Scheme 1 Structural isomerism observed between complex **1** and **2**



Scheme 2. Ring flipping phenomena observed in complex **2** and **3**.

2. Experimental Section

2.1 Computational detail

All the calculations have been carried out with Gaussian 09[20] code with WB97XD[21,22] functional and three different basis set for better description of the different atoms in the molecule: LanL2DZ[23] which include double- ζ with the Los Alamos effective core applied for Ir and Re, D95(d)[24] basis sets was applied for C, N and O and 6-311G[25] basis set for hydrogen atoms. Structure **3** is taken from single-crystal X-ray diffraction results and

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