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Computational study of fluxional hydride bridged binuclear transition metal complexes: Effect of secondary bridging ligands

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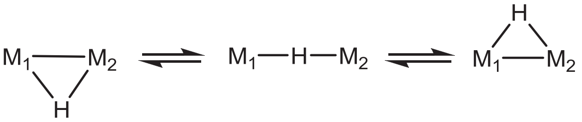
ABSTRACT

The binuclear complex $[Ir_2(CH_3)(CO)_2(dppm)_2]^+$ (dppm = $Ph_2PCH_2PPh_2$) coordinates the olefins of 1,3-butadiene and catalyzes double geminal C–H activation via a proposed fluxional hydride migration. Using DFT computational studies, we examine the fluxional behavior of three model hydride bridged bimetallic systems to elucidate the main factors in this transformation. Our results indicate that the bridging ligand opposite the μ-H controls the barrier to hydride fluxionality and that breaking this bridging interaction is the largest component of the transition state barrier. We found a low barrier, a medium barrier, and a high barrier in systems with no bridging ligand, a partial μ-CO, and μ-CH_2, respectively. The respective systems with their corresponding barriers are: (1) $[RhRe(\mu\text{-}H)(CO)_4(dhpm)_2]^+$, 2.4 kcal/mol, (2) $[IrRu(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(dhpm)_2]^{2+}$, 8.5 kcal/mol, and (3) $[RhOs(\mu\text{-}H)(\mu\text{-}CH_2)(CO)_3PH_3(dhpm)_2]^{2+}$, 26.4 kcal/mol (dhpm = $PH_2CH_2PH_2$). The predicted fluxional hydride migration in the activation of 1,3-butadiene occurs easily and is consistent with these findings.

1. Introduction

Binuclear metal systems offer new transformative powers through the cooperative effects of adjacent metal centers [1]. The Ir–Ir complex $[Ir_2(CH_3)(CO)_2(dppm)_2]^+$ (dppm = $Ph_2PCH_2PPh_2$) (**1**) demonstrates one unique reaction of bimetallic complexes, catalyzing the double geminal C–H activation of 1,3-butadiene [2]. The proposed mechanism has been supported by experimental evidence for complexes **1**, **2**, and **3** with complexes **A** and **B** as presumed intermediates (Scheme 1, note the phenyls of the dppm ligands are omitted). In our computational studies of this double activation we were surprised by the ease of transition between complexes **A** and **B**. The bridging hydride readily migrates back and forth between the metal centers to form a bridging interaction on either side of the complex.

Many different binuclear systems [2–11] display similar (fluxional) hydride migrations in which the μ-H flip-flops between inverted bridging hydride positions on opposite sides of the complex (Eq. (1)). This behavior was first studied in A-frame complexes [3] and occurs at room temperature so the linear M–H–M transition state must occur without an appreciable energy barrier. While bridging hydride ligands have been extensively studied as three-center two-electron interactions (3c–2e) [12–18], their fluxionality has not been described in detail. The review article by Parkin [14] details the difficulty that arises in assessing the nature of the metal–metal bonding in these three-center interactions. In our depiction, Eq. (1), the solid lines are not meant to depict the number of electrons involved in any pairwise interaction. Rather, we are simply depicting the geometry changes in the fluxional rearrangement.



(1)

Most known examples of fluxionality occur in symmetric systems in which the hydride migration is readily reversible and the two structures that are in flux with each other are essentially identical; this does not demonstrate immediate usefulness to inorganic chemists. However, in the Ir–Ir system, the hydride migration between the metals leads to the final product **3** [2]. Our computational work investigates fluxional hydride migrations between the metals of bimetallic complexes to better understand transitions such as those between complexes **A** and **B**.

2. Systems studied

We studied hydride migrations in three model systems within the context of the 1,3-butadiene activation mechanism. First, we examined a Rh–Re system $[RhRe(\mu\text{-}H)(CO)_4(dhpm)_2]^+$ as a representative example of a fluxional hydride migration (Scheme 2) [7]. Second, we created, for comparison, the model analogue $[IrRu(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(dhpm)_2]^{2+}$ by replacing Rh and Re with Ir

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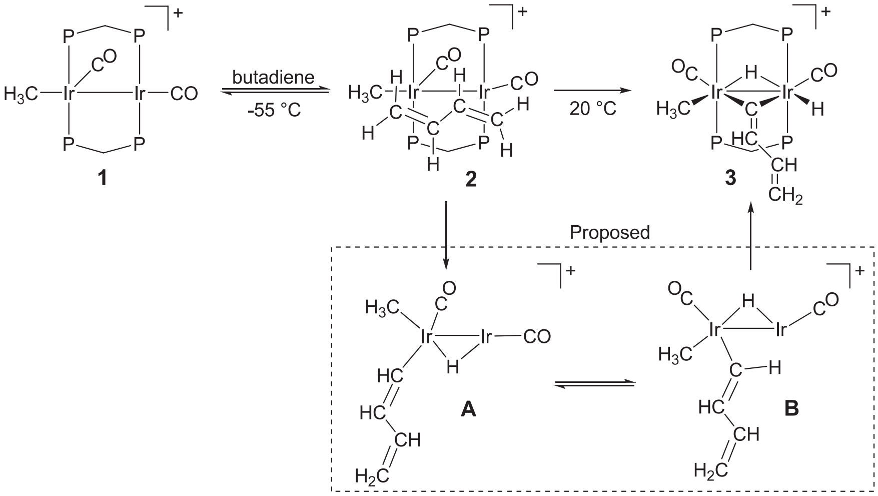
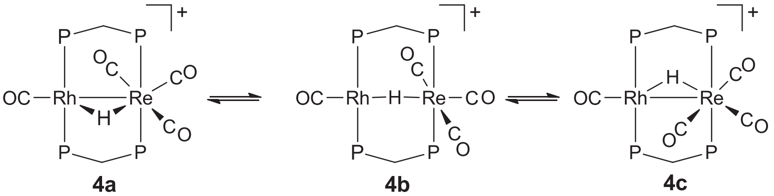
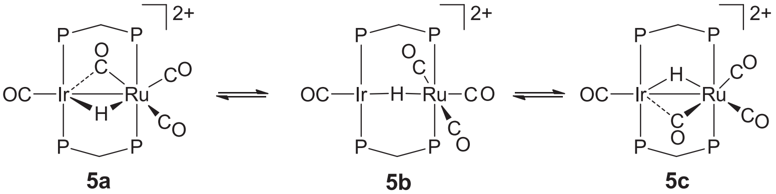


Scheme 1.



Scheme 2.



Scheme 3.

and Ru, respectively, and by changing the charge to maintain an isoelectronic species. When structurally optimized this proposed Ir–Ru system retained a partially bridging CO ligand (Scheme 3).

For a final comparison, we used the system [RhOs(μ-CH_2)$(CO)_3PH_3(dhpm)_2]^+$ (**6**) [19]. This system is not precisely "fluxional" like the other systems. This system has no μ-H ligand and when protonated it forms an agostic CH_3 interaction. However, the chemistry of this protonation reaction could, in theory, proceed via the hydride bridged complex **7a** which reacts to form product **7c** via an analogous "fluxional-like" hydride migration (Scheme 4). Clearly, **7c** cannot readily transform back to **7a** because of the transformation of methylene into a methyl group. Nonetheless, this theoretical mechanism, with the hydrogen atom migrating between the metals, is identical to the other systems. Moreover, our interest is in the barrier to intranuclear migration and how further chemical evolution can occur after an intranuclear migration such as that proposed in Scheme 1.

We do not claim the Rh–Os system is protonated to form **7a**. Protonation chemistry of methylene bridged binuclear systems has already been studied and is not the focus of this work [20,21]. In fact, a hydride bridged species has yet to be experimentally discovered in this system [20] although related binuclear complexes have shown that such structures are possible [22]. Regardless, we computationally examined the outcome as if the transformation did happen by a fluxional-like hydride migration for comparison purposes only. We note that this Rh–Os system is not isoelectronic with the previous systems and we address this later.

3. Computational details

To save on computational resources dppm ligands ($Ph_2PCH_2PPh_2$) were truncated to dhpm ($H_2PCH_2PH_2$). Because we are interested in the chemistry surrounding the metal atoms, this is sufficient. All calculations were performed with the hybrid density functional B3LYP [23,24]. The LANL2DZ basis set [25] was used on the transition metal atoms and cc-pVTZ [26] on all other atoms. The synchronous transit-guided quasi-Newton method was used to determine the transition states between stable structures [27,28]. Intrinsic reaction coordinate (IRC) [29,30] calculations were performed on an as need basis. Vibrational frequency calculations were completed on all structures to verify minima and transition state structures based upon the number of imaginary frequencies. All energies reported include zero point energy