ORGANOMETALLICS

Mechanism of Isomerization and Methyl Migration in Heterobimetallic Rhenium–Iridium Complexes: Experimental and DFT Study

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Supporting Information

ABSTRACT: Investigation of the mechanism of conversion of the bimetallic complex [PNP(H)Ir- μ (CH₂)- μ (O)-Re(O)₂][PF₆] (1) to its structural isomer [PNP(Me)(CH₃CN)Ir-ReO₃][PF₆] (2) by detailed kinetics and DFT computational studies is reported. The reaction proceeds by intramolecular rearrangement of 1 to [PNP(Me)Ir-ReO₃][PF₆] (S) via a methyl-bridged [PNP(H)Ir- μ (CH₃)-Re(O)₃]-[PF₆] (P) intermediate followed by CH₃CN coordination. The rate-determining step is the transformation of 1 to P displaying ΔG^{\pm} of 21.8 kcal/mol. Experimental kinetic results include zero-order dependence on acetonitrile, positive ΔS^{\pm} , and deuteration of the bridging methylidene group in the reaction of 1 with CD₃OD. All of these results support the proposed mechanism.



■ INTRODUCTION

Heterobimetallic complexes featuring two metals with vastly different properties and reactivity are of notable interest because of their connection to heterogeneous catalysts that use an early transition metal oxide support and a late noble metal catalyst.^{1–3} In the case of homogeneous systems, heterobimetallic complexes of early and late metals are important because they can carry out chemistry that neither metal by itself can do and in enabling multielectron redox processes. Thomas and Lu have independently reported on a number of heterobimetallic complexes and small-molecule activation.^{4–9}

With increasing R&D in biofuels and biorenewables,¹⁰ our group and others have developed deoxydehydration (DODH) reactions of polyols to alkenes using early transition metal catalysts such as rhenium, molybdenum, and vanadium.¹¹⁻¹⁸ The prevalence of fracking in the U.S. in the past couple of years has revolutionized the availability of natural gas and light hydrocarbons (LHC).¹⁹ As a result, we have become interested in coupling renewable feedstock such as polyols with LHC, where the biomass-derived molecules act as oxidants of LHC, creating value from both feedstocks. This synergy is illustrated in Scheme 1 for the reaction of pentane with glycerol. The thermodynamics are quite favorable, 51% conversion at 200 °C and 40 bar pressure,²⁰ conditions that are akin to DODH reaction conditions. Inspired by the work of Goldman and Brookhart on the use of iridium pincer complexes in alkane dehydrogenation, 2^{1-23} we set out to investigate the properties and reactivity of heterobimetallic Re-Ir organometallic Scheme 1. Proposed Conversion of Light Hydrocarbons (LHC), Illustrated Here with Pentane (C5), with Biomass-Derived Glycerol Using an Ir-Re Heterobimetallic Catalytic System



systems. These could be viable catalysts for the oxidative coupling of LHC with biomass-derived polyols (Scheme 1). Ir would serve as an alkane dehydrogenation catalyst affording alkene and iridium hydride. Re would promote DODH of polyols. Hydride transfer or spillover from iridium to oxorhenium would result in catalyst regeneration and production of water as a byproduct. Therefore, understanding the fundamental chemistry and behavior of heterobimetallic complexes that feature iridium hydride or alkyl and oxorhenium is paramount in this endeavor.

Received: January 8, 2016 Published: February 3, 2016 We have recently reported the synthesis and preliminary reaction chemistry 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 2).²⁴



Herein, we expand the fundamental understanding of these complexes by reporting detailed kinetics, thermodynamics, and density functional theory (DFT) calculations, to elucidate the mechanism of isomerization of 1 to 2. This work also demonstrates overall a migration of a hydride to a methylidene and α -elimination in a bimetallic complex system.

RESULTS AND DISCUSSION

NMR Kinetics and Thermodynamics for the Interconversion of Complexes 1 and 2. In noncoordinating solvent, CD_2Cl_2 , complex 1 is present exclusively as evident by NMR. However, upon addition of CD_3CN , a coordinating solvent, a mixture of 1 and 2 is observed. The isomerization reaction is reversible; removal of CD_3CN and addition of CD_2Cl_2 reverts to complex 1 as the sole species in solution.

The equilibrium reaction between 1 and 2 (Scheme 2) was monitored by ¹H NMR. Under excess acetonitrile and limiting Re–Ir, the rate of reaction follows a pseudo-first-order rate equation, and the observed rate constants k_{Ψ} display zero-order dependence on [CH₃CN] (Figure 1).



Figure 1. Dependence of the rate of conversion between 1 and 2 on $[\mathrm{CH_3CN}].$

The dependence of the equilibrium constant (*K*) on temperature was investigated by ¹H NMR over the range 271–285 K, and the data were fitted to the van't Hoff relationship (eq 2).

$$\ln K = -\Delta H^0 / RT + \Delta S^0 / R \tag{2}$$

The thermodynamic parameters $\Delta H^0 = -5.6 \pm 0.3 \text{ kcal mol}^{-1}$ and $\Delta S^0 = -23 \pm 1 \text{ cal mol}^{-1} \text{ K}^{-1}$ were obtained (Figure 2).



Figure 2. van't Hoff plot for the isomerization of 1 to 2.

Activation parameters (ΔH^{\ddagger} and ΔS^{\ddagger}) were obtained in accordance with the Eyring relationship (eq 3) by following the kinetics of isomerization at different temperatures 271–285 K (Figure 3).

$$\ln(k_{\psi}/T) = -\Delta H^{\mp}/RT + \ln(k_{\rm B}/h) + \Delta S^{\mp}/R \tag{3}$$



Figure 3. Eyring plot for the isomerization of 1 to 2.

The enthalpy and entropy of activation were $\Delta H^{\ddagger} = 22 \pm 2$ kcal mol⁻¹ and $\Delta S^{\ddagger} = 5.3 \pm 0.3$ cal mol⁻¹ K⁻¹, respectively. The positive value of ΔS^{\ddagger} indicated a nonassociative pathway for the isomerization of **1** to **2**.

Reaction of Complex 1 with CD₃OD. Reaction of 1 with a mixture of CD₂Cl₂ and CD₃OD at 60 °C for 30 min resulted in the deuteration of Ir–H as well as the bridging CH₂. While deuteration of Ir–H is expected,^{25–27} deuteration of the bridging methylidene group (CH₂) was intriguing. It should be noted that complex 2 was not observed in the ¹H NMR or ³¹P{¹H} NMR spectrum when 1 was dissolved in CD₃OD. Following the reaction by ¹H{³¹P} NMR and ³¹P{¹H} NMR detected multiple intermediates (Supporting Information). We propose the following mechanism (Scheme 3): Reaction of 1 with CD₃OD results initially in Ir–H/Ir–D exchange. Dynamic equilibrium between 1 (Ir–D) and S results in deuteration of bridging CH₂. This leads to the consideration of S as a viable intermediate in the isomerization of 1 to 2, as 2 differs from S only by coordination of CH₃CN in its structure.

Intermetallic van der Waals Interaction in Complex 2. Complex 2 exhibited intermetallic van der Waals interaction between the hydrogen atoms of its phosphine-bound *tert*-butyl groups and the rhenium metal center (Scheme 4) at 220 K by



Scheme 4. Structural Representation of Intermetallic van der Waals Interactions in Complexes 2 and 3



¹H{³¹P} NMR. One single broad peak observed for the four *tert*-butyl groups bonded to the P atom at 298 K was split into a 3:9:9:3 (buried under *tert*-butyl groups):3:3:3:3 ratio with one set of protons (corresponding to two methyl groups) shifted upfield to ~0.5 ppm (Figure 4). The upfielded methyl groups



Figure 4. ¹H{³¹P} NMR (expanded region) of **2** at 220 K (top) in comparison with 298 K (bottom) showing the van der Waals force of attraction between the rhenium metal center and the *tert*-butyl groups attached to the P atom of ligand a = tert-Bu of **2**, b = Ir-Me of **2**, c = tert-Bu of **1**, i = impurity.

must have originated from the interaction of the *tert*-butyl hydrogens with the rhenium metal center. Analogous observation with the complex [PNP(Me)(CN^tBu)Ir-ReO₃]-[PF₆] (3) (a derivative of complex 2, which did not exhibit the structural isomerism similar to 2) (Supporting Information) ensured the noninterference of this property with the structural isomerism of 1 to 2. The intermetallic van der Waals interaction was supported by the short bond distance (3.02 Å) observed between the hydrogen atom belonging to one of the methyl groups of *tert*-butyl attached to the P atom and the rhenium metal center in the X-ray structure of 3,²⁴ which is lower than the sum of van der Waals radii of Re and H (3.31

Article

Å). From DFT simulations, the presence of van der Waals interactions is also verified by the short distances (3.11 Å in **2** and 3.04 Å in **3**) between Re and hydrogen atoms belonging to one of the *tert*-butyl methyl groups. While the γ -C–H interaction between the phosphine-bound alkyl groups and the metal center is known,^{28,29} the intermetallic interaction in this case was unique and can be potentially useful for future C–H activation studies employing these heterobimetallic complexes.

Experimental Findings Directing DFT Elucidation of the Isomerization Mechanism. The experimental studies on the isomerization of complex 1 to 2 described above provided the following insights on the mechanism:

- (i) Zero-order dependence on acetonitrile means the ratedetermining step depends on the Ir-Re bimetallic complex only and the mechanism is not associative.
- (ii) The positive value of ΔS^{\ddagger} indicates a nonassociative pathway.³⁰
- (iii) Deuteration of the bridging methylidene group (CH_2) in complex 1 from the reaction with CD_3OD supports S as a possible intermediate in the isomerization of 1 to 2.
- (iv) The van der Waals interactions observed for 2 are consistent with formation of intermediate S prior to the ligand (acetonitrile) on iridium, as this facilitates the transfer of the bridged methyl group in P to the iridium center in S.

On the basis of the above results three pathways were explored by DFT calculations (Scheme 5). The reaction





proceeds initially via intramolecular rearrangement of 1 to S via potentially three different intermediates, P, Q, and R, based on the interaction between Re and Ir. Coordination of CH_3CN to iridium completes the reaction to give complex 2.

Choice of Functionals for DFT Calculations. We used two functionals, B3LYP^{31,32} and wb97XD,^{33,34} coupled with three different basis sets: LanL2DZ,³⁵ which includes double- ζ with the Los Alamos effective core, was applied for Ir and Re, the D95(d)³⁶ basis set was applied for C, N, and O, and 6-311G³⁷ basis set was used for hydrogen atoms. Table 1 compares the bond lengths and bond angles of the optimized structure of complex 1 obtained from DFT with the values obtained from single-crystal X-ray diffraction data.²⁴ Both levels of theory have a good agreement with experimental values. For example, calculated Ir–Re distances are 2.74 and 2.71 Å compared to experimental distance of 2.64 Å; calculated Re– O_{bridge} bond distances are 1.80 and 1.79 Å compared to the

ċ	listance (Å) or angle (deg)	B3LYP/LanL2Z/D95(d)6-311G	wb97xd LanL2DZ/D95(d)6-311G	X-ray ²⁴
	Ir-Re	2.74	2.71	2.64
	Ir-O	2.29	2.26	2.22
	Re–O ₁	1.80	1.79	1.81
	Re-O ₂	1.70	1.69	1.71
	Re-O ₃	1.70	1.69	1.70
	N ₁ IrRe	143.0	143.3	145.3
	$N_1 Ir C_1$	169.9	169.2	166.4

Table 1. Comparison of Bond Distances and Angles Obtained by DFT Using Two Different Functionals Coupled to the Same Basis Sets with X-ray Structure Data for Complex 1

Table 2. Standard Enthalpy and Entropy Obtained for the Isomerization of Complex 1 to 2 with Two Functionals, B3LYP and wb97XD

	exptl	B3LYP/LanL2DZ/D95(d)6-311G	wb97Xd/LanL2DZ/D95(d)6-311G
$\Delta H^0/\text{kcal mol}^{-1}$	-5.6	-6.5	-13.9
$\Delta S^{2}/cal mol = K^{2}$	-23	-22	-37.8

experimental distance of 1.81 Å. Regarding bond angles, the calculated values of \angle NIrRe are 143.0° and 143.3° compared to 145.5° (experimental) and for \angle NIrC_{bridge} 169.9° and 169.2° compared to 166.4° (experimental).

Table 2 compares the thermodynamics of complexes 1 and 2 from the two levels of theory used here with experimental data. B3LYP-calculated values for $\Delta H^0 = -6.5$ kcal/mol and $\Delta S^0 =$ -22 cal/(mol K) are in good agreement with experimental values of -5.6 ± 0.3 kcal/mol and -23 ± 1 cal/(mol K), respectively. However, the wb97XD functional overestimated the value of ΔH^0 (-13.9 kcal/mol) as well as ΔS^0 (-37.8 cal/ (mol K)). The difference in results between the two functionals is due to the thermodynamics of complex 2. With the wb97XD functional, complex 2 is lower in energy than with the B3LYP functional, leading to the difference for the standard enthalpy and entropy. However, the wb97XD functional takes account of empirical dispersion necessary for bimetallic systems with the proximity of large ligands to metal atoms, which is absent in the B3LYP functional. So we investigated the reaction mechanism using both B3LYP and wb97XD functionals and compared their results.

Kinetic Study with the B3LYP Functional. Figure 5 describes the structures of complexes 1 and 2, intermediates P, Q, and S, and transition states TS1–TS5, and Figure 6 represents the potential energy surface (PES) of pathways A1 and A2 obtained with the B3LYP functional. All the transition states (TS) have been confirmed by one and only one negative frequency (imaginary frequency). An intrinsic reaction coordinate study connecting each TS to its reactant and product has been done to confirm them. Complex 1 is considered as the zero energy ground level.

Pathway A. In pathway A1 transition states TS1–TS3 and intermediates **P** and **S** have been defined. TS1 (Figure 5) corresponds to the moving of H of Ir toward the bridging CH₂ methylidene. The Ir---H bond increases from 1.58 Å to 1.71 Å and the C---H bond decreases from 2.50 Å to 1.29 Å with the breaking of the Ir–H bond and formation of a new C–H bond. Also TS1 corresponds to the breaking of the Ir–O_{bridge} bond as it reforms a multiple bond with Re (Re=O₃). This TS is the most energetically demanding step of pathway A1, with an activation energy ΔG^{\ddagger} equal to 21.8 kcal/mol.

The step from complex 1 to intermediate P is endergonic as P is present at 14.7 kcal/mol above complex 1. In intermediate P, the CH_3 is bonded to Ir and Re and is found at 2.17 Å from



Figure 5. Structures of complexes 1 and 2, intermediates P, Q, and S, and transition states TS1–TS5. Carbons are in gray, iridium in light blue, rhenium in green, phosphorus in yellow, nitrogen in dark blue, and hydrogen in white. *tert*-Butyl groups attached to phosphorus atoms are omited for clarity.

Ir and 2.34 Å from Re. By scanning the increase of the Re–CH₃ distance, TS2 was found. Elongation of the Re–CH₃ bond resulted in its breaking and allowing the CH₃ group to move toward Ir, thereby justifying the position of TS2 between **P** and **S**. It is found 19.5 kcal/mol above complex **1**. In intermediate **S** the methyl group from MTO has been completely transferred to Ir with the formation of the Ir–Re metal–metal bond. Complex **S** is found –1.9 kcal/mol from complex **1**.

After finding the transition states for the intramolecular rearrangement, CH_3CN addition to intermediate **S** was investigated. A scan for the decrease of the Ir---N \equiv C-CH₃



Figure 6. Potential energy surface diagram for comparison of pathways A1 and A2 using the B3LYP functional.

bond was performed starting with positioning the acetonitrile molecule 3.5 Å from the Ir center of intermediate **S**. The TS found (TS3) is characterized by an Ir---NCCH₃ distance equal to 2.84 Å. TS3 is 9.9 kcal/mol from complex **1**. Overall for pathway A1, the kinetically relevant step with $\Delta G^{\ddagger} = 21.8$ kcal/mol is in agreement with what other authors have found for analogous chemistries.^{38–40}

In pathway A2, transition states TS4 and TS5 and intermediate **Q** in addition to TS3 and **S** discussed earlier have been defined. The first step corresponds to the transformation of complex **1** to **Q**. TS4 corresponds to the movement of the H atom attached to Ir toward CH₂ until reaching an Ir–H bond distance of 1.71 Å. This resulted in a decrease of the C–H bond distance and an increase of the Ir– Re distance to 1.31 and 2.78 Å, respectively, and the formed HCH angle is equal to 98.4°. TS4 has a free energy of 20.4 kcal/mol. In intermediate **Q**, the Re–CH₃ and the Ir---CH₃ bond distances are 2.11 and 3.26 Å, respectively, and the bridging oxygen is positioned between Ir and Re with a distance of 2.03 and 1.81 Å, respectively. **Q** is +3.1 kcal/mol higher than complex **1**.

The second step of this pathway involves the transformation of complex \mathbf{Q} to complex \mathbf{S} . This step is characterized by the moving of CH₃ from Re to Ir, the breaking of the Ir–O bond, and the formation of the Ir–Re bond. The corresponding TS (TS5) has CH₃ positioned 2.23 Å from Ir and 2.50 Å from Re with an \angle IrCRe of 67.7°. The elongation corresponding to the moving of CH₃ back to Ir is found at -299.0 cm⁻¹. ΔG^{\ddagger} for this methyl transfer step is 33.7 kcal/mol. Conversion of intermediate S to complex 2 is the same as described earlier in pathway A1.

In pathway A3, optimization of \mathbf{R} leads to structure \mathbf{Q} , thereby eliminating A3 from further consideration.

To summarize, pathways A3 was eliminated due to the nonexistence of intermediate **R**. On comparing pathways A1 and A2, (i) both pathways display similar energy requirements observed for the first (TS1 and TS4) and final (TS3) transition states. (ii) Intermediate **Q** is more stabilized from a thermodynamic point of view in comparison with intermediate **P**. (iii) However, the high energy barrier found for TS5 of pathway A2, which is considered the rate-determining step (30.6 kcal/mol), is more than the value observed for pathway A1 (21.8 kcal/mol), thereby disfavoring pathway A2. By this process of elimination, pathway A1 stands as the most favorable for isomerization of complex **1** to **2**.

Using this functional, although we had a good agreement of the thermodynamic and kinetic data between the experimental and the theory, the pitfall is that complex 2 is higher in energy than the intermediate S, which suggests that the reaction should stop with intermediate S and not necessarily proceed to complex 2. This is in contrast with the absence of NMR signals for S in CD_2Cl_2 . So the same study using the wb97XD functional was repeated.

Comparison of B3LYP and wb97XD Functionals. Investigation using the wb97XD functional followed similar trends to B3LYP. Pathway A3 was eliminated for the same reason as mentioned using the B3LYP model. The PES diagram comparing pathways A1 and A2 using the wb97XD functional was given in Figure 7. Table 3 compares the energetics of models derived by using functionals wb97XD and B3LYP.



Figure 7. Potential energy surface diagram for comparison of pathways A1 and A2 with the wb97XD functional.

Table 3. Comparison of Energies of Complexes 1 and 2, Intermediates P, Q, and S, and Transition States TS1–TS5 Proposed during the Isomerization of 1 to 2 Computed Using the B3LYP and wb97XD Functionals for Pathways A1 and A2

	B3LYP, kcal/mol	wb97XD, kcal/mol
1	0	0
2	2.9	-2.6
Р	14.7	7.9
Q	3.1	9.3
S	-1.9	-0.3
TS1	21.8	24.2
TS2	19.5	26.2
TS3	9.5	10
TS4	20.5	22.1
TS5	33.7	40.2

The preferred pathway using the wb97XD functional is A1, analogous to the B3LYP functional. The ΔG^{\ddagger} value of 24.2 kcal/mol observed in pathway A1 with the wb97XD functional is in good agreement with the B3LYP functional (21.8 kcal/mol) and comparable with the experimental value of 22 \pm 2 kcal/mol.

In contrast to B3LYP, with the wb97XD functional complex **2** is lower in energy than **S**, consistent with the NMR observation of **2** at the end of the reaction, and justified the use of the wb97XD functional.

Organometallics

CONCLUSIONS

Here we used the combination of experimental kinetics, thermodynamics, and DFT studies to investigate the structural isomerization of 1 to 2. We used two functionals, B3LYP and wb97XD, for the DFT studies. In both cases, the preferred pathway is A1, which involves two intermediates forming via intramolecular reactions of 1. The first intermediate P features a methyl bridging a metal-metal bonded Re-Ir. The second intermediate S has the methyl group fully migrated to Ir. The rate-determining step is formation of P. Acetonitrile coordination to S affords complex 2 in a rapid step. Experimental kinetics is consistent with this mechanism, as the dependence on acetonitrile is zero-order and the activation entropy is small and positive. Further support for this mechanism was provided by the observed deuteration of both bridging CH₂ protons and the Ir-H in 1 from its reaction with CD₃OD. Complexes 2 and 3 exhibited a unique intermetallic van der Waals interaction between the bulky tert-butyl substituents of the pincer ligand and rhenium at temperatures 220 and 203 K, respectively, opening up the plausibility of C-H activation studies with these complexes in the future.

EXPERIMENTAL SECTION

Computational Details. All the calculations have been carried out with the Gaussian 09^{41} code with the B3LYP^{32,42} functional and wb97XD^{33,34} and three different basis sets: LanL2DZ,³⁵ which includes double- ζ with the Los Alamos effective core applied for Ir and Re, the $D95(d)^{36}$ basis set, applied for C, N, and O, and the 6-311G³⁷ basis set for hydrogen atoms. The Wb97xd functional uses a version of the empirical dispersion model with values of S6 and SR6 of 1.0 and 1.1, respectively. This functional uses a similar damping function to that used by the GD3 model, with D6 and IA6 having fixed values of 6.0 and 12, respectively. Structure 1 is taken from singlecrystal X-ray diffraction results, and structure 2 is taken by replacing the tert-butylisocyanide with CH₃CN in [PNP(Me)(CN^tBu)Ir-ReO₃]- $[PF_6]$ (3).²⁴ The other structures have been built using Gauss View software. All structures have $C_{2\nu}$ symmetry. Standard ambient temperature and pressure (298.15 K at 1 atm) were used in all the simulations that run on the gas phase model. Frequency calculations at the same level of theory were carried out to verify all stationary points as minima with one and only one negative (imaginary) frequency. The intrinsic reaction coordinate route toward the corresponding minima has confirmed the different transition states found. The PF₆ anion was not included in the calculations. A molecule of CH₃CN has been included in the outer sphere for the simulations except for complex 2.

Kinetic Studies. All reactions were performed in a nitrogen-filled glovebox or using standard Schlenk techniques under argon. Solvents were degassed and purified with a solvent purification system (Pure Process Technology, Inc.) prior to use. CD₂Cl₂ and CD₃CN were dried over CaH₂, distilled under argon, and stored over molecular sieves. All other chemicals were purchased from Aldrich and used as received. One-dimensional NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer equipped with a 5 mm broadband (BBO) probe. Bruker TopSpin software (version 1.3) was used for data acquisition, and MestReNova (version 8) was used for processing of NMR spectra. All spectra obtained were referenced to residual solvent peaks accordingly. Complexes 1 and 3 were synthesized following a reported literature method.²⁴ Isomerism of 1 to 2 was monitored by ¹H NMR with the observation of 1 in CD_2Cl_2 followed by the addition of CD₃CN. A CD₂Cl₂:CD₃CN ratio of 2:3 with a total volume of 0.7 mL and overall concentration of 5.8×10^{-3} M were used. The temperature range used in the van't Hoff plot as well as the Eyring equation was 271-285 K for the isomerism of 1 to 2.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00010.

Experimental details and DFT details (PDF) Crystallographic data (XYZ)

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Author Contributions

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The authors declare no competing financial interest.

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