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Electron acceptors promote proton-hydride tautomerism in low valent rhenium β -diketiminates

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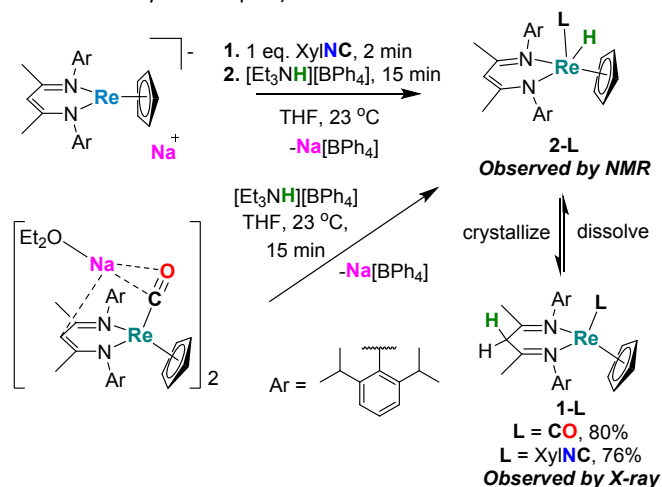
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We report a series of β -diketimate (BDI) complexes in which tautomeric rhenium(III) hydride and rhenium(I) protio-BDI species readily interconvert between the solid and solution states. This phenomenon, which is only operative when an electron-accepting ligand is bound to rhenium, was investigated by a combination of experimental and computational methods.

Dynamic processes involving hydrogen in organometallic systems have been a subject of both fundamental chemical interest and modern clean energy research.^{1–3} Proton-hydride tautomerism, wherein a hydrogen atom migrates between an organic site (where it is formally protic) and a metal site (where it is formally hydridic), has been of particular interest of late,^{4–12} as this conversion is likely to play a key role in a number of valuable transformations such as electrocatalytic hydrogen evolution^{6–8} and cooperative bond activation in homogeneous catalysis.⁹ In many cases, ligand conjugation (typically in cyclopentadienyl ligands or derivatives thereof, which have displayed numerous other modes of non-innocence)^{13–19} allows for a thermodynamically-feasible proton-hydride tautomerization process.⁵ More recently, ion pairing has also been found to have substantial effects on these tautomeric equilibria.¹² Here, we report a neutral rhenium system in which proton-hydride tautomerism can be triggered by the introduction of electron accepting groups (e.g. CO, 2,6-xylylisocyanide, and N₂) into the metal coordination sphere. Intriguingly, we find that the ligand-proton tautomer prevails in the solid state, while the metal hydride tautomer tends to dominate in solution. The role of the electron acceptors in this phenomenon has been established by a combination of experimental and computational methods.

We have previously reported protonation of Na[Re(η^5 -Cp)(BDI)] (BDI = N,N'-bis(2,6-diisopropylphenyl)-3,5-dimethyl- β -diketimate)

at room temperature to yield the rhenium(III) hydride complex Re(H)(η^5 -Cp)(BDI).²⁰ Following our subsequent syntheses of the carbonyl and isocyanide adducts of the anionic rhenium(I) starting material,²¹ we became interested in identifying the products formed following their protonation. We found that the reaction of these anionic rhenium(I) complexes with triethylammonium tetraphenylborate ([Et₃NH][BPh₄]) readily yielded red crystalline products: their X-ray crystal structures show them to be the neutral rhenium(I) complexes **1-CO** and **1-XyINC** (Scheme 1, Figure 1).[‡] Both compounds are unambiguously protonated at the BDI backbone, such that BDI-H (BDI-H = N,N'-bis(2,6-diisopropylphenyl)pentane-2,4-diimine) has lost its conjugation and anionic charge yet remains chelated to the Re center. This mode of BDI ligand non-innocence, wherein the backbone C-H group acts as a basic site, has been well documented in a number of other systems.^{22,23} The IR absorbance spectra of these complexes indicates a substantial decrease in backbonding to the π -acceptors in comparison to that in their anionic precursors, with an IR absorbance peak for **1-CO** at 1774 cm⁻¹ (as compared to 1617 cm⁻¹ in the anionic carbonyl) and a very broad IR absorbance band for **1-XyINC** at 1831 cm⁻¹ (as compared to 1560 cm⁻¹ in the anionic XyINC complex).



Scheme 1. Synthesis of the complexes **1-L** and depiction of their tautomerization to form **2-L** in solution.

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While the crystallographic data for **1-CO** and **1-XylINC** were unambiguous, we found that determining the speciation of these compounds in solution was non-trivial: the ^1H NMR spectra of these compounds in C_6D_6 display no resonances corresponding to the diastereotopic methylene group on the BDI-H ligand. Instead, the spectra of both complexes exhibit a singlet for an anionic, conjugated BDI C-H backbone proton, as well as a second sharp singlet at ca. -5 ppm. We believe this indicates that, upon dissolution, **1-CO** and **1-XylINC** undergo a proton-hydride tautomerization in which a hydrogen exchanges between the BDI backbone and the metal center, leading to our spectroscopic observation of the rhenium(III) hydrides **2-CO** and **2-XylINC** (Scheme 1) rather than the crystallographically characterized products. We attempted to form these putative hydride species by the addition of CO or XylINC to $\text{Re}(\text{H})(\eta^5\text{-Cp})(\text{BDI})$ in C_6D_6 . We found the addition of ca. 1 atm. CO to a solution of $\text{Re}(\text{H})(\eta^5\text{-Cp})(\text{BDI})$ led to rapid darkening and decomposition to a mixture of products, while the addition of 1 equivalent of XylINC to a solution of $\text{Re}(\text{H})(\eta^5\text{-Cp})(\text{BDI})$ rapidly gave **2-XylINC**, with additional equivalents of XylINC leading to no further reaction at room temperature. Thus, we established that the species derived from **1-CO** and **1-XylINC** in solution are indeed likely to be the proposed metal hydrides.

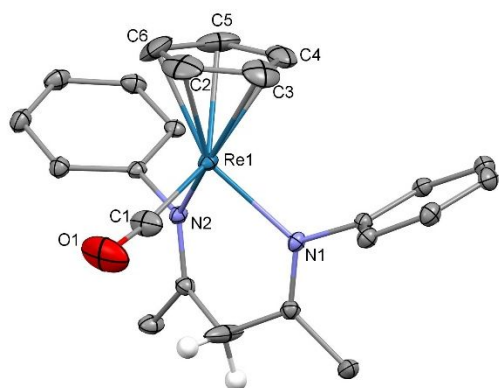
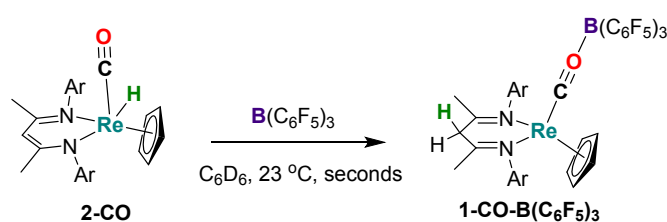


Figure 1. X-ray crystal structure of **1-CO** with 50% probability ellipsoids. H atoms (except for those on the BDI-H methylene carbon) and ^iPr groups are omitted.

Variable-temperature ^1H NMR spectroscopy measurements of **2-CO** and **2-XylINC** (up to 82 $^\circ\text{C}$ in toluene- d_8) showed no changes in speciation, showing that the solution equilibrium between these species and **1-CO** and **1-XylINC** highly favors the metal hydride tautomers. Using triethylammonium- d_1 tetraphenylborate ($[\text{Et}_3\text{ND}][\text{BPh}_4]$) we generated solutions of monodeuterated **2-CO** and **2-XylINC**: we observed by ^2H and ^1H NMR spectroscopy that the deuterium had incorporated mainly into the metal hydride position sites, indicating that the metal behaves as the basic site in solution. Leaving these deuterated samples in solution for 24 hours did not lead to significant change in the distribution of the deuterium label. We also combined isolated, non-deuterated **1-CO** with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$, and found by ^1H NMR spectroscopy that the metal hydride resonance of **2-CO** was not observed, and instead a broad set of doublet resonances attributable to the BDI-H methylene group could be seen (Supporting Information, Figure S10). The two broad doublets in question gave rise to a cross

peak in a subsequent ^1H - ^1H COSY experiment (Supporting Information, Figure S11). Based on the spectroscopic evidence and literature precedent, we concluded the added Lewis acid binds to the metal carbonyl of **1-CO** in solution, forming the species **1-CO-B(C₆F₅)₃** (Scheme 2).^{24,25} We propose the enhanced electron withdrawing ability of the borane-capped carbonyl weakens the metal hydride bond in **2-CO**, leading to a thermodynamic preference for the BDI-H tautomer in solution. These experiments demonstrate that **2-CO** and **2-XylINC** are the more stable tautomers in solution, but this equilibrium can be readily perturbed by the addition of Lewis acids. We hypothesize the repeated isolation of **1-CO** and **1-XylINC** as crystalline products is likely due to crystal packing effects (*i.e.* the relative lattice energies of the series **1-L** are significantly greater than those of the series **2-L**, leading to the selective crystallization of the former as opposed to the latter).



Scheme 2. Formation and structure of **1-CO-B(C₆F₅)₃**.

To complement our experimental observations, we conducted DFT calculations to probe the role of the electron accepting ligands on this proton-hydride tautomerization process (Figure 2 and Supporting Information, Table S3).⁵ Accordingly, in addition to the observed CO and XylINC tautomers, we also conducted calculations on the analogous, though experimentally unobserved N_2 complexes **1-N₂** and **2-N₂**, as well as the known, base-free hydride $\text{Re}(\text{H})(\eta^5\text{-Cp})(\text{BDI})$ with its unobserved rhenium(I) tautomer $\text{Re}(\eta^5\text{-Cp})(\text{BDI-H})$. First, the calculated energy difference between $\text{Re}(\eta^5\text{-Cp})(\text{BDI-H})$ and $\text{Re}(\text{H})(\eta^5\text{-Cp})(\text{BDI})$ in the gas phase was found to be -39.1 kcal/mol, which implies that the former species is much higher in energy and is not likely to be observed. For the series **2-L**, we found that two isomers of these species could be optimized, one with the hydride and electron acceptor (*i.e.* N_2 , CO, or XylINC) in a *cis* orientation, and another with these ligands in a *trans* arrangement on opposite faces of the Re-BDI complex. For **2-CO** and **2-XylINC**, the *cis* isomers were found to be significantly lower in energy than the *trans* isomers; thus the *cis* isomers were believed to be the most relevant to this study. The solution symmetry of **2-CO** and **2-XylINC** as observed in their NMR spectra (C_1) also align with that of the *cis* isomers optimized by DFT, whereas the *trans* isomers would be expected to display a higher solution symmetry (C_2). Interestingly, we found both the *cis* and *trans* isomers of **2-N₂** were both lower in energy than **1-N₂**, with the *cis* isomer being the most stable.

An assessment of the calculated free energies of the series **2-L** relative to those of the series **1-L** as a function of the electron accepting ligand (namely, CO, XylINC, or N_2) shows that the stronger π -acids lead to less preference for the Re hydride tautomer over the protonic BDI-H tautomer. This suggests that

as the strength of the electron acceptor increases, the relative strength of the Re-H bond in **2-L** versus that of the BDI-H C-H bond in **1-L** decreases. This trend is in line with our experimental observation of the complex **1-CO-B(C₆F₅)₃** in solution, which demonstrated that enhancing the strength of the electron acceptor can invert the relative energies of these proton-hydride tautomers.

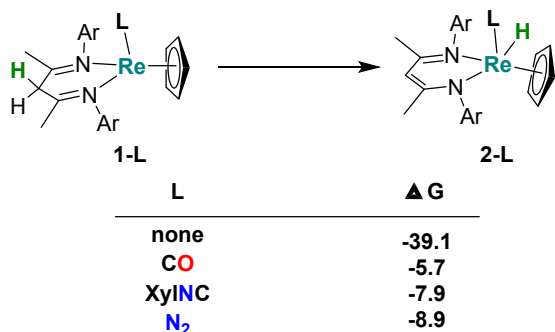


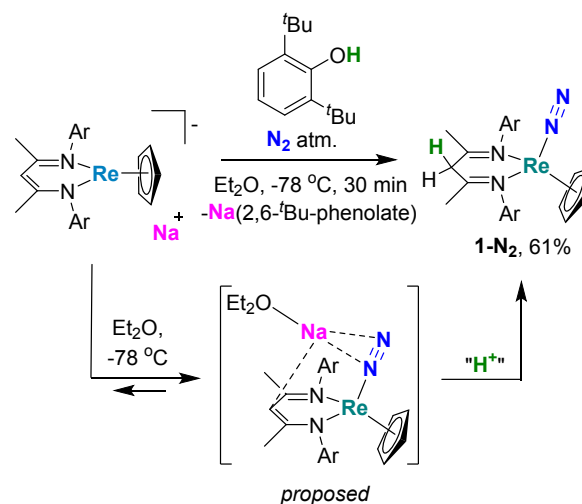
Figure 2. Summary of DFT results for proton-hydride tautomerization calculations as a function of the electron acceptor.

Based on our initial DFT results, we also optimized the structures of the rhenium(II) complexes $\text{Re}(\text{L})(\eta^5\text{-Cp})(\text{BDI})$ ($\text{L} = \text{N}_2$, CO, or XyINC) in order to determine (after applying an appropriate correction, see Supporting Information)^{5,26} the relative Re-H and C-H bond dissociation free energy (BDFE) values for the range of tautomers under study. We found that the calculated BDFEs for the metal hydrides of the **2-L** series fell within the narrow range of 43.5 to 45.3 kcal/mol. The corresponding range of C-H BDFEs in the **1-L** series was found to be 34.5 to 39.7 kcal/mol. We also calculated the Re-H and C-H BDFE values of the acceptor-free complexes $\text{Re}(\text{H})(\eta^5\text{-Cp})(\text{BDI})$ and $\text{Re}(\eta^5\text{-Cp})(\text{BDI-H})$.^{20,27} The Re-H BDFE for the rhenium(III) hydride $\text{Re}(\text{H})(\eta^5\text{-Cp})(\text{BDI})$ was calculated to be ca. 54.4 kcal/mol, which is *higher* than the corresponding values found for the series **2-L** (by 9 to 11 kcal/mol). Meanwhile, the C-H BDFE for the BDI-H ligand in $\text{Re}(\eta^5\text{-Cp})(\text{BDI-H})$ was calculated to be ca. 14.6 kcal/mol, which is substantially *lower* than the corresponding BDFE values found for **1-L** (by 20 to 25 kcal/mol). This suggests that the binding of electron-acceptors to Re in this system not only decreases the strength of the Re-H bonds in the metal hydride tautomers, but more significantly it *increases* the strength of the methylene C-H bonds in the corresponding BDI-H tautomers. Thus, the observation of proton-hydride tautomerization in this system is the result of two contrasting effects on the strengths of these Re-H and ligand C-H bonds.

The calculations also show the impact of this proton-hydride tautomerization on the ligand dissociation energies of CO, XyINC, and N₂ in these systems (Supporting Information, Table S3). In all cases the dissociation energies are much higher in the BDI-H tautomers than they are the metal hydride tautomers, likely owing to the lower valence of the former (formally d^6 vs. d^4) leading to an enhancement of backbonding to the π -acidic ligands. Again, the relative increases in ligand dissociation energy can be correlated to the π -acceptor ability of the ligand: the CO dissociation energy in **1-CO** being 33.3 kcal/mol greater

than the CO bond dissociation in **2-CO**, while the analogous difference in N₂ dissociation energies between **1-N₂** and **2-N₂** was calculated to be 16.1 kcal/mol.

Following our computational evaluation, we began to wonder if **1-N₂** could indeed be isolated. While DFT calculations indicated this tautomer is less stable than either isomer of **2-N₂**, its metal-N₂ bond strength of 23.2 kcal/mol suggested that it may be a stable adduct once precipitated or crystallized from solution under appropriate conditions. Following a number of efforts, we did find that a red crystalline precipitate could be generated by combining $\text{Na}[\text{Re}(\eta^5\text{-Cp})(\text{BDI})]$ under N₂ with 2,6-di-*tert*-butylphenol as a proton source at -78 °C in Et₂O solvent (Scheme 3). Isolation of this material allowed for an IR absorbance measurement to be taken, showing a distinct peak at 1928 cm⁻¹, which is in the range expected of the putative end-on Re(I) N₂ complex **1-N₂**.²⁸ An X-ray quality single crystal was also analyzed, which proved to be the target complex (Figure S21). The N₂ ligand in this compound displays a short N-N distance (1.138(6) Å) in line with a triply-bonded N₂ unit and a modest degree of backbonding from Re.



Scheme 3. Synthesis of **1-N₂**.

We found that while **1-N₂** does not persist in Et₂O or THF solutions at room temperature for more than ca. 5 minutes (quickly converting to the green hydride complex $\text{Re}(\text{H})(\eta^5\text{-Cp})(\text{BDI})$, concurrently with the visible evolution of gas from solution), the isolated compound is sufficiently stable in C₆D₆ to allow for its NMR spectroscopic characterization. The ¹H NMR spectrum of **1-N₂** is highly similar to that of **1-CO-B(C₆F₅)₃**, in that a broad set of doublets corresponding to the BDI-H methylene group can be observed (Supporting Information, Figure S7). This suggests that **1-N₂** is indeed the species in solution leading up to its decomposition to $\text{Re}(\text{H})(\eta^5\text{-Cp})(\text{BDI})$, and that (in line with our DFT calculations) no isomer of the metal hydride tautomer **2-N₂** is likely to be characterized by routine methods. Developing the synthesis of **1-N₂** also shows that the N₂ adduct of $\text{Na}[\text{Re}(\eta^5\text{-Cp})(\text{BDI})]$ formed at -78 °C is likely analogous to the anionic complexes that act as precursors for **1-CO** and **1-XyINC**.

We note the stability of **1-N₂** in aromatic solvent (complete decomposition takes place over several days), was unexpected, as **1-CO** and **1-XyINC** are readily converted to their hydride forms when dissolved under the same conditions. In the conversion of **1-N₂** to Re(H)(η^5 -Cp)(BDI) and free N₂, two distinct steps must occur: (1) migration of the hydrogen from the BDI-H ligand to the Re center, and (2) release of N₂ by Re. We consider N₂ ejection prior to hydrogen migration to be the more plausible of the two possible decomposition pathways, in part due to the significantly lower calculated bond strength of the Re-N₂ bond (23.2 kcal/mol) versus that of the BDI-H C-H bond in **1-N₂** (34.7 kcal/mol). While this C-H bond strength is similar in magnitude to those calculated for **1-CO** and **1-XyINC**, the Re-L bond strengths in these latter two complexes are significantly higher. In either case, it appears that **1-N₂** is kinetically stabilized in C₆D₆, as it is quite clear its decomposition, while slow, is spontaneous. As such, we posit that the strength of the electron acceptor must also be correlated to the kinetic barrier to proton-hydride tautomerization in addition to the thermodynamic differences between each pair of proton-hydride tautomers.

In conclusion, we have presented our observation of proton-hydride tautomerism in a series of neutral rhenium β -diketiminates. Experimental efforts suggest that a facile tautomeric equilibrium between metal hydride and BDI-H tautomers is dependent on the strength of the electron accepting ligand bound to Re. DFT studies were employed to model the variable impacts of the electron accepting ligand on this uncommon tautomerization process, which ultimately motivated the targeting, isolation, and characterization of a neutral rhenium(I) dinitrogen complex that was not initially assumed to be synthetically accessible.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ X-ray crystal structures determined for this work have been submitted to the Cambridge Crystallographic Data Centre (CCDC)

with deposition numbers 1943028-1943030. These data may be obtained free-of-charge at <https://ccdc.cam.ac.uk/>.

§ DFT calculations were performed using the wB97XD functional, a mixed def2 basis set, and a SDD core potential on Re. Complete details may be found in the Supporting Information.

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