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Reactivity Studies of Para-Hydrogen with μ_3-Quinolyl Triosmium Clusters

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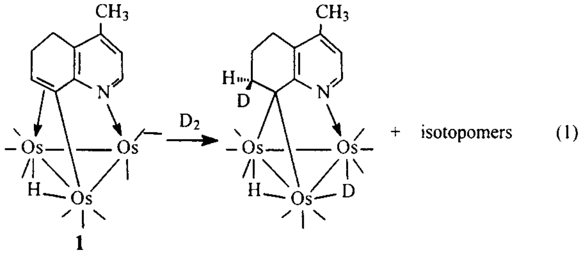
Summary: The reactions of the cluster complexes $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_7(4\text{-}CH_3)N)(\mu\text{-}H)$*(**1**),* $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(n\text{-}NH_2)N)(\mu\text{-}H)$ *(n = 3, **2**, n = 5, **3**),* $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6(4\text{-}C(CH_3)_2CN)(5\text{-}NH_2)N)(\mu\text{-}H)$ *(**4**), and* $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6(4\text{-}C(CH_3)_2CN)(5\text{-}F)N)(\mu\text{-}H)$ *(**5**) with para-hydrogen have been studied at ∼3 atm and 90−110 °C. In all cases, reaction at the metal core is the initial product and polarization enhanced polyhydride intermediates are observed. The chemical shifts and relative intensities of these resonances are used to extract mechanistic information about the reactivity of **1**−**5**. As with previous studies on related electron-deficient complexes, **3**−**5** show reactivity that is very sensitive to the substituent in the 5-position.*

Introduction

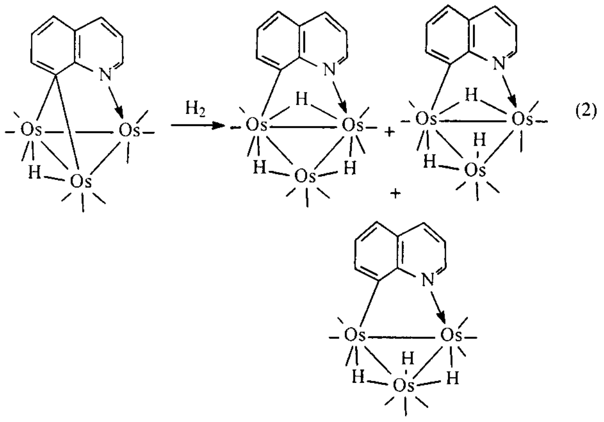
The use of para-H_2 as a tool for understanding the reactivity and catalytic behavior of organometallic complexes has been an area of intense interest.[1] In the case of mono- and dinuclear complexes, valuable insight into hydride connectivity and exchange, as well as the structural identification of short-lived intermediates, has been realized.

Most recently, para-hydrogen has provided detailed information of the dynamics of the hydrogenation of the lightly stabilized trimetallic clusters $Os_3(CO)_{10}(CH_3CN)_2$[2] and $Ru_3(CO)_{11}(CH_3CN)$.[3] In the course of our studies of the reactivity of μ_3-η^3-quinolyl complexes of triosmium clusters, several reactivity patterns that we thought could be further elucidated by reaction with para-hydrogen were observed.[4]

First, the reaction of the σ−π-vinyl complex $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_6H_7(4\text{-}CH_3)N)(\mu\text{-}H)$ (**1**) with D_2 revealed exclusive deuterium incorporation into the 7-position of the quinoline ring and random incorporation of a second deuterium in the resulting dihydride complex (eq 1).[4] Although initial reaction at the metal core seemed the most likely pathway, this was difficult to rationalize in light of the results of the labeling study. One could not rigorously exclude a concerted D_2 addition across the ligand cluster framework or a radical chain mechanism initiated at C(7), because a trihydride intermediate was not observable.[4]



Second, we have observed that reaction of the electron-deficient metal cluster $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6)N)(\mu\text{-}H)$ with H_2 gives three isomeric trihydrides as the final products (eq 2).[5] Here, two questions arose. Do the three isomeric trihydrides form simultaneously, or is one isomer followed by slower isomerization to the other two?



In addition, we have observed that substitution at the 5-position of electron-donating or electron-withdrawing groups has a dramatic effect on the reactivity of these complexes with two-electron donors.[6] For example, no reaction with $2e^-$ donors is observed when an amino group is substituted in the 5-position, but the normal coordination of $2e^-$ donors is observed when the amino group is substituted in the 3- or 6-position. The question

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(1) For a recent review, see: Duckett, S. B.; Sleigh, C. J. *J. Prog. Magn. Reson. Spec.* **1999**, *34*, 71.

(2) Aime, S.; Gobetto, R.; Canet, D. *J. Am. Chem. Soc.* **1998**, *120*, 6770.

(3) Aime, S.; Dastrù, W.; Gobetto, R.; Viale, A.; Canet, D. *J. Phys. Chem. A* **1999**, *103*, 9702.

(4) Rosenberg, E.; Arcia, E.; Kolwaite, D. S.; Hardcastle, K. I.; Ciurash, J.; Duque, R.; Gobetto, R.; Milone, L.; Osella, D.; Botta, M.; Dastrù, W.; Viale, A.; Fiedler, J. *Organometallics* **1998**, *17*, 415.

(5) Rosenberg, E.; Kabir, S. E.; Kolwaite, D.; Hardcastle, K. I.; Crosswell, W.; Grindstaff, J. *Organometallics* **1995**, *14*, 3611.

(6) Rosenberg, E.; Bergman, B.; Bar Din, A.; Smith, R.; Gobetto, R.; Milone, L.; Viale, A.; Dastrù, W. *Polyhedron* **1998**, *17*, 2975.

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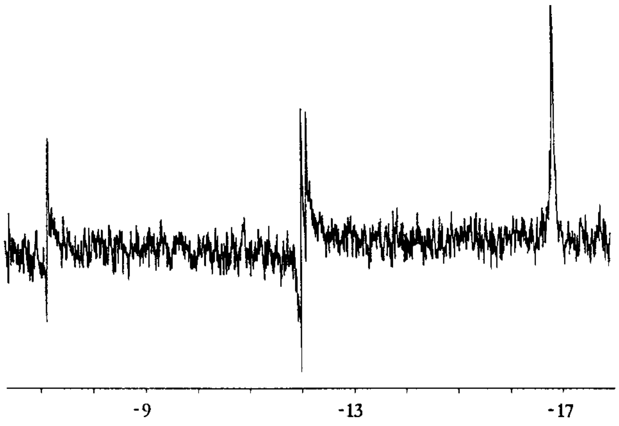
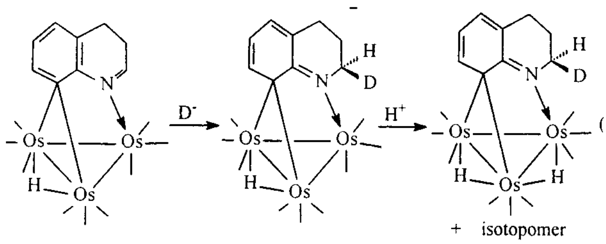


Figure 1. ^1H NMR of the hydride region of compound **1**, showing the polarized trihydride intermediates after treatment with para-hydrogen at 100 °C and 3 atm in toluene. The unpolarized resonance at the right is the hydride resonance of the starting material.

here is whether this reactivity carries over into the reaction of these complexes with H_2.

Finally, we previously reported that reaction of the partially hydrogenated electron-deficient complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_8N)(\mu\text{-}H)$ with D^-/H^+ gives initial attack of D^- at the 2-position followed by protonation at the metal core[5] (eq 3). Here we wondered whether reaction with H_2 would result in reaction directly at the C=N bond and whether substitution at the 5-position would have any effect on the reactivity of this structural type, as it does for the fully aromatized analogue $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_8N)(\mu\text{-}H)$.



(3)

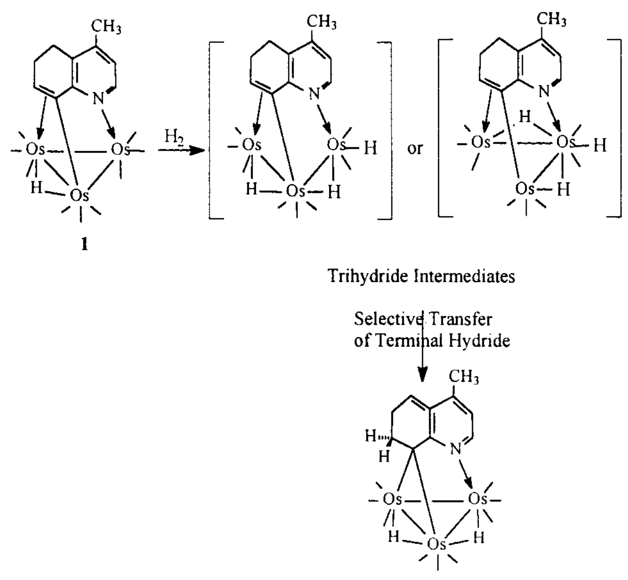
We anticipated that reaction of these complexes, with para-dihydrogen, might shed some light on the questions raised above. We report the results of these initial studies, which further illustrate the usefulness of para-dihydrogen as a mechanistic probe.

Results and Discussion

The reaction of the $\sigma-\pi$ vinyl $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_7(4\text{-}CH_3)N)(\mu\text{-}H)$ (**1**) with para-H_2 at 100 °C in toluene reveals the presence of three polarized signals in the hydride region, one in the terminal region (−7.1 ppm) and two in the bridging region (−12.25 and −12.10 ppm). The two bridging hydrides are at distinctly different chemical shifts than those observed in the final dihydride product (−13.86 and −13.99 ppm, respectively, Figure 1)[5]

The polarization on the terminal and one of the bridging hydrides is slightly stronger. We can therefore say that these hydrides derive directly from the para-H_2 molecule, while the other derives its polarization from cross polarization effects. Another possible explanation is that the observed intermediate is fluxional (in fact the signals are broadened).

Scheme 1



The observation of a trihydride clearly shows that H_2 addition at the metal core is the first step in the reduction of **1**. That one of these hydrides is in the terminal region nicely rationalizes the results of the labeling experiments (eq 1). On reaction with D_2, selective occupation of the terminal site should be favored because the higher stretching frequency of the terminal hydride has larger energy level spacings (1/2 hν), resulting in a thermodynamic isotope effect for the bond with the larger reduced mass (M−D over M−H).[7] Furthermore, selective transfer of the terminal deuteride to form a C−D bond would also involve a thermodynamic isotope effect if the metal-to-ligand hydrogen transfer is partially reversible.[7] These two effects combined account for the observed specificity of the labeling experiment previously reported (Scheme 1).[4] The proposed trihydride intermediate would require cleavage of a metal−metal bond to maintain consistency with the effective atomic number rule. There is considerable precedent for metal−metal bond cleavage being associated with hydrogen addition to electron precise trimetallic clusters.[8]

The reaction of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(3\text{-}NH_2)N)(\mu\text{-}H)$ (**2**) with para-dihydrogen at 100 °C and 3 atm in toluene gave three sets of three polarized hydride resonances in addition to residual unpolarized starting material. The most intense set gave resonances at −13.08, −13.45, and −13.56 ppm. Two sets of three resonances of approximately equal but lower intensity were observed at −8.90, −10.95, and −13.32 and at −10.36, −10.95, and −12.50 ppm (Figure 2). The resonances were grouped according to the overall pattern previously found for the final products of the hydrogenation of **1** (eq 2).[5] The resonance at −10.95 ppm appeared significantly broader than the rest and was therefore interpreted to result from two overlapping resonances from the two lower intensity sets.[5] Upon further diffusion of para-hydrogen into the solution over a period of 1 h, no

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[7] Rosenberg, E. *Polyhedron* **1989**, *8*, 383.

[8] Rosenberg, E.; Kabir, S. E.; Day, M.; Hardcastle, K. I. *Organometallics* **1994**, *13*, 4437.

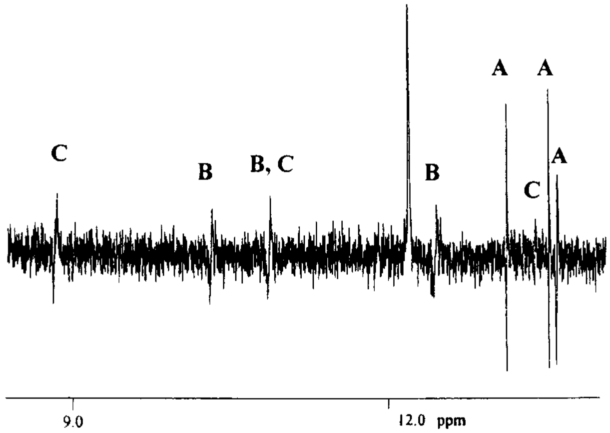


Figure 2. ^1H NMR of the hydride region of **2** showing the polarized isomeric trihydride products after treatment with para-hydrogen at 100 °C and 3 atm in toluene. The three sets of hydrides assigned to each isomer are marked A, B, and C. The unpolarized peak is residual starting material.

change in the relative intensity of these sets of resonances was seen. This result simply reports that initial formation of the final ratio of the three trihydride products is rapid on the time scale of these experiments. No reaction was seen below 100 °C, and so we conclude that formation of the three product hydrides is fast from whatever the initial H_2 adduct was. More significantly, the reaction of $Os_3(CO)_9(C_9H_5(5\text{-}NH_2)N)(\mu\text{-}H)$ (**3**), which is isostructural with **2** except for the position of the amine, with para-dihydrogen gave no reaction up to 110 °C. From this result, we can conclude that the reaction of H_2 with the electron-deficient clusters of structural type **3** follows the same pattern as the reaction of these complexes with amines, phosphines, and nitriles, where reaction with these nucleophiles is completely shut down in the case of **3**.[6] Furthermore, the ratio of the three trihydride clusters is approximately the same as obtained from the prolonged reaction of this type of cluster with H_2.[5]

The complete lack of reactivity toward H_2 of **3** is mitigated by a partial hydrogenation of the heterocyclic ring, as evidenced from the reaction of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6(4\text{-}C(CH_3)_2CN)(5\text{-}NH_2)N)(\mu\text{-}H)$ (**4**) with para-H_2. On reaction with para-H_2 under the same conditions as for **2** and **3**, the formation of a hyperpolarized trihydride species, with one terminal and two bridging hydrides at −8.78 and −11.10 and −13.58 ppm (Figure 3), is observed. A second set of two less polarized hydrides is also found at −11.82 and −13.52 ppm. The complete lack of a third polarized hydride suggests that these two hydrides belong to a species in which one H atom has been transferred to the organic molecule. In fact there is a new resonance in the aliphatic region (4.55 ppm), nonpolarized, that can be attributed to a compound in which the C=N bond has been reduced (Scheme 2). However, in this case, we do not know if the formation of the trihydride species precedes the formation of the dihydride species or if we are observing two parallel processes.

More interestingly, the substitution of the strongly electron donating $-NH_2$ group in the 5-position with F, a strongly electronegative group, in $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6(4\text{-}C(CH_3)_2CN)(5\text{-}F)N)(\mu\text{-}H)$ (**5**) changes the reactivity of the cluster toward H_2 completely. In this case the addition of the para-H_2 molecule to the cluster is so fast that no polyhydride intermediates are detected. We observe only the intense negative signal assignable to $H_2Os_3(CO)_{10}$ on the basis of its chemical shift (−11.5 ppm). Three weakly polarized hydrides are also observed in the bridging region. The resonances of the starting material have nearly disappeared, while new resonances of low intensity appear in the aromatic region. The reaction mechanism proposed (Scheme 3) rationalizes the observed spectrum (Figure 4). This mechanism involves the cleavage of the organic molecule from the cluster and the formation of hyperpolarized $H_2Os_3(CO)_{10}$. To form $(\mu\text{-}H)_2Os_3(CO)_{10}$ from **5**, a source of CO is required. It seems reasonable to propose that the initially formed $48e^-$ cluster (Scheme 3) loses CO to give a $46e^-$ cluster. This rationalizes the presence of the observed triply bridging hydride species. We know that the intense negative signal must result from an unobserved intermediate in which the longitudinal relaxation processes are different for the two hydrides (Scheme 4)[2,9] As a consequence of the presence of this intermediate,the A_2 spin system of para-hydrogen is

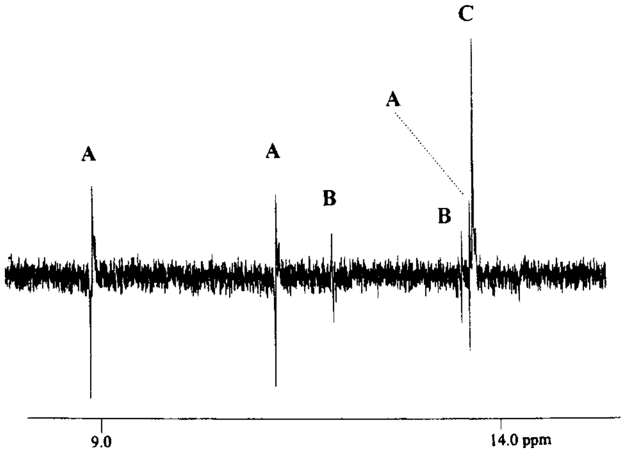


Figure 3. ^1H NMR of the hydride region of **4** after treatment with para-hydrogen at 100 °C and 3 atm in toluene. The trihydride intermediate is marked A, the proposed dihydride product is marked B, and the residual starting material is marked C.

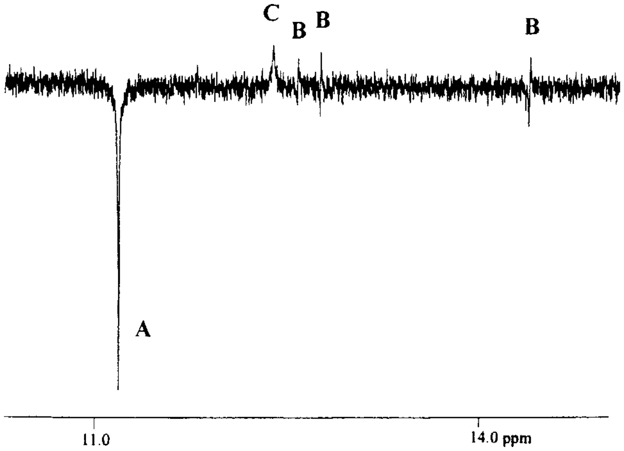
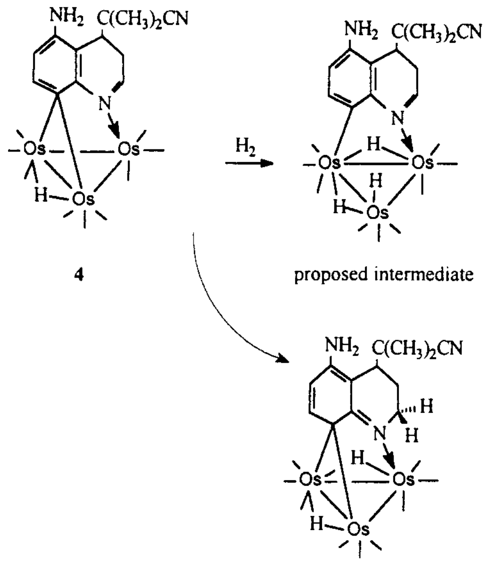
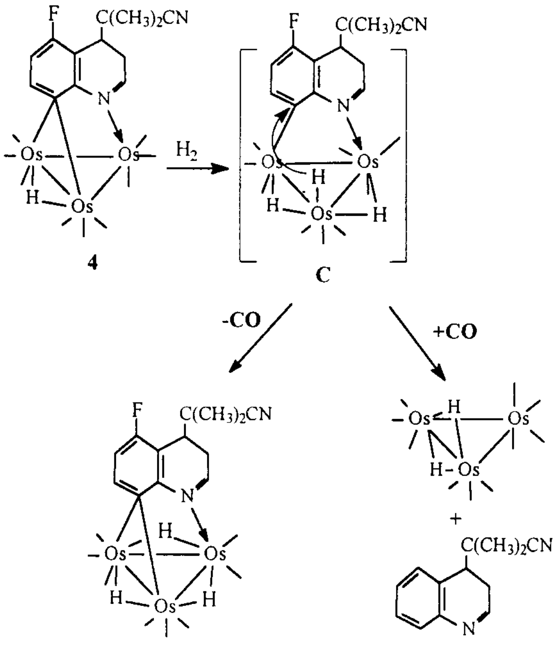


Figure 4. ^1H NMR of the hydride region of **5** after treatment with para-hydrogen at 100 °C and 3 atm in toluene. The negatively polarized peak assigned to $Os_3(CO)_{10}(\mu\text{-}H)_2$ is marked A. The triply bridged trihydride coproduct is marked B, and the starting material is marked C.

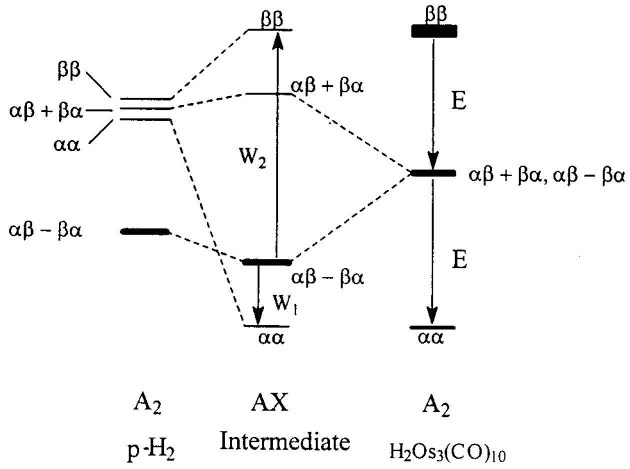
Scheme 2



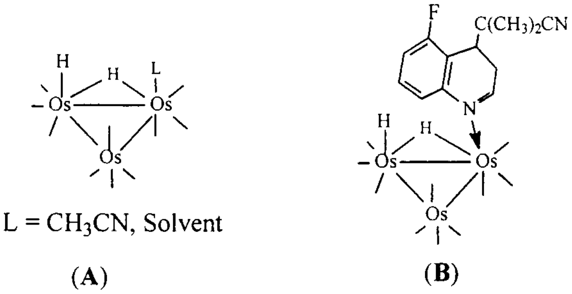
Scheme 3



Scheme 4



Scheme 5



transformed into an AX spin system (the intermediate) and then back into an A_2 spin system in the final product ($H_2Os_3(CO)_{10}$). Due to the transient presence of the AX system, symmetry is broken and polarization evolves, through various relaxation mechanisms, such that the upper states are populated and an emission signal is observed (Scheme 4). In all the reported cases the intermediate involved is like that shown in Scheme 5A in which L is CH_3CN or a solvent molecule.[9] In the present case the unsymmetrical intermediate that differentiates the longitudinal relaxation rates for the two hydrides must be a species in which the organic ligand is still coordinated to the cluster (Scheme 5 B). Thus substitution of a fluorine in 5-position results in an apparent facile cleavage of the organic ligand from the cluster, a process not previously observed for structural type **5**.[4]

This preliminary report demonstrates that para-hydrogen can be a useful probe for the observation of initial intermediates in organometallic clusters. Further studies on the dynamics and the evolution with time of the processes are currently underway.

Experimental Section

The complexes **1**−**4** were synthesized by published literature procedures.[4,5,10] Proton NMR were obtained on a JEOL EX-400 spectrometer. Para-enriched hydrogen was prepared by storing H_2 over Fe_2O_3 at −196 °C for 3−4 h. The experimental procedure was carried out in 5 mm screw cap vials containing 5−10 mg of sample and 0.5 mL of toluene-d_8. The tube was evacuated and then filled with para-hydrogen to a pressure of 3 atm. The tube was then shaken thoroughly and the sample placed in the NMR probe and monitored as the temperature was increased in 20 °C intervals until the onset of reaction was observed. Spectral monitoring was continued until polarization decay was observed, usually 5−10 min.

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(10) Rosenberg, E.; Bergman, B.; Holmquist; R.; Smith, R.; Ciurash, J.; Hardcastle, K.; Visi, M. *J. Am. Chem. Soc.* **1998**, *120*, 12818.