Trajectory of Approach of a Zn–H Bond to Transition Metals

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Dedication ((optional))

Abstract: Through a dramatic advance in the coordination chemistry of the zinc–hydride bond, we describe the trajectory for the approach of this bond to transition metals. The dynamic reaction coordinate was interrogated through analysis of a series of solid state structures and is one in which the TM–H–Zn angle becomes increasingly acute as the TM–Zn distance decreases. Parallels may be drawn with the oxidative addition of boron–hydrogen and silicon–hydrogen bonds to transition metal centers.

Appreciation of the trajectory for the approach of carbon–hydrogen bonds to transition metals has led to a deeper understanding of catalytic processes involving the breaking of carbon–hydrogen bonds.[1] As the C–H bond advances towards the metal, formation of an intermediate α-complex can preface oxidative addition.[2] Many authors have described a continuum between the α-complex and oxidative addition product.[3,4] As the M–C distance decreases, the H–M–C angle becomes increasingly acute and electron density is transferred from both the d-orbitals of the metal and breaking C–H bond to the forming M–C and M–H bonds. Alkanes are not privileged in this regard, borane and α-silane complexes have an extensive chemistry and the relationship between them and the oxidative addition products metal boryls and metal silyls is well understood (Figure 1).[5]

In comparison there is only limited precedent for the coordination of zinc hydrides to transition metal centers. Kubas and Shriver have commented on the nature of hydride-bridged zincate complexes in solution.[6] The proposition that these species could dimerize by 3-center 2-electron bonds seeded ideas that ultimately led to the discovery of dihydrogen complexes.[7,8] A handful of heterobimetallic complexes containing transition metal and zinc centers bridged by hydride ligands are known.[9-14] The majority however, include more than one bridging hydride ligand clouding analysis of the TM–H–Zn group. Through kinetic protection of a zinc center with a sterically demanding ligand, we recently isolated a rare example of a heterobimetallic complex possessing an unsupported Cu–H–Zn moiety.[15] Here we describe an advance in the coordination chemistry of the zinc hydride bond to transition metals. Through analysis of a series of solid state structures and calculations, we describe the reaction trajectory for the approach of a single zinc–hydride bond to a transition metal.

Photolysis of a 1:1 mixture of the terminal zinc hydride 1 and either [TM(CO)]₃ (TM = Cr, Mo), [(η⁵-C₅H₅)₂CrH(CO)]₃, [(η⁵-C₅H₅Me)Mn(CO)]₃, or [(η⁵-C₅H₅)₂Co(CO)]₃ in benzene, toluene or THF solution with a 400 W Hg lamp resulted in clean conversion to the corresponding heterobimetallic complexes (Figure 2, 2a-b, 3a-b, 4a). While a similar protocol could not be used to synthesize the tungsten pentacarbonyl complex 2c, photolysis of [W(CO)]₃ in d₂-ThF for 6h followed by addition of 1 gave the desired product. The rhodium complex 5b was prepared by in situ generation of [Cp*Rh(H)(SiEt₃)(ZnBDI)] (5a)[10a] followed by photolysis in the presence of excess PMe₃ (BDI = (2,6′-Pr₂C₆H₄)(NCMe)₂CH). A series of increasingly electron-rich ligands were included on the transition metal fragments to allow variation of the electron density at the TM center.

The new heterobimetallic complexes 2-5 possess a Zn–H–TM functional group. Inspection of the solid state structures reveals a number of distinct coordination modes of the zinc hydride which may be differentiated by the formal shortness ratio (fsr) of the Zn–TM distance.[16] The formal shortness ratio normalizes the metal–metal distance and has been used to evaluate the intermetallic interaction in complexes containing two metals in close proximity.[16]

Figure 1. α-Complexes and Oxidative Addition.


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Data are consistent with formation of $\sigma$-zincare complexes of the “M(CO)$_3$” fragment in 2a–c. The Zn—M fsr is 1.08–1.09 and the Zn–H bond lengths, confirmed by DFT methods, range between 1.7–1.8 Å. Analogous $\sigma$-alane and $\sigma$-gallane complexes have been reported by Aldridge and coworkers.\cite{17} Soluble in hydrocarbon solvents the hydride ligands of 2a–c resonate between δ = -6 and -10 ppm in C$_6$D$_6$. The $^1$J$_{M-H}$ coupling constant of 54 Hz in 2c is observed in $^{13}$W satellites of the hydride resonances,\cite{18} while both cis and trans carbonyl ligands could be assigned based on HMBC NMR experiments.

Upon modification of ligand to include a $\pi$-coordinating hydrocarbon in 3a–b, a similar geometry of the Zn–H–M moiety is observed. The fsr of this series of 1.02–1.04, however, is smaller than that observed in 2a–c. In 3a–b both short Zn—CO distances [3a 2.423(3) Å; 3b, 2.548(3)] and the deviation of the M–C–O angle from 180° are consistent with the formation of semi-bridging carbonyl ligands. Infra-red spectroscopy supports the formulation and ν(CO) peaks may be assigned to terminal (3a, 1905 cm$^{-1}$; 3b, 1937 cm$^{-1}$) and semi-bridging carbonyls (3a, 1799 cm$^{-1}$; 3b, 1852 cm$^{-1}$).\cite{19} In 3a–b only a single $^{13}$C carbonyl resonance was observed suggesting fast exchange of terminal and semi-bridging carbonyl ligands on the NMR timescale. Comparison of the ν(CO) for 3b against the known series [(η$^2$-C$_5$H$_5$Me)Mn(CO)$_3$(L)] (L = CO, H–B, H–Al, H–Ga, H–Si, H–Ge, H–Sn) reveals that the carbonyl stretches are near identical to those reported for both $\sigma$-alane and four coordinate $\sigma$-borane complexes (Table S1). The latter $\sigma$-complexes have been described as having little or no back-bonding to the H–E bond from the transition metal center and based on vibration spectroscopy it appears 3b is no different.\cite{17,20}

The cobalt and rhodium analogues 4a and 5b possess a fsr of <1. This is consistent with the metal—metal distance being smaller than that of the sum of the single bond radii. The rhodium complex 5b also contains exceptionally long Zn—H distances of 2.1–2.2 Å and a very acute TM–H–Zn angle. 4a may represent a stretched $\sigma$-complex, while 5b is reminiscent of the rhodium dihydride [Cp*Rh(H)$_2$(SiEt$_3$)(ZnBD)) (5a). We have previously described 5a as the product of complete hydride transfer from zinc to rhodium.\cite{10a} The $^1$J$_{Rh-H}$ coupling constant of 35 Hz and ν(Rh–H) stretch of 1976 cm$^{-1}$ for 5b suggests a similar structure to 5a.

A plot of the experimentally determined fsr as a function of the TM–H–Zn angle for 2–5 is given in Figure 3. In all cases, the hydrogen atom was located in the fourier difference map during X-ray experiments and its position confirmed by DFT calculations (Figure S3). Accepting that a series of static solid state structures can be used to interrogate a dynamic reaction coordinate,\cite{3,21} the data show that as the zinc–hydride bond approaches the transition metal not only does the Zn–TM distance decrease but the TM–H–Zn angle becomes increasingly acute. In the solid-state data, the angle decreases from 106° to 76° as the fsr decreases from 1.09 to 0.97.

![Figure 2](image-url)  
**Figure 2.** The crystal structures of (a) 2b, 3a, 3b, 4a, and 5b. Along with tabulated data for the Zn–H, TM–Zn bond lengths and formal shortness ratio (fsr).

![Figure 3](image-url)  
**Figure 3.** Plot of the fsr versus the TM–H–Zn angle for complexes 2–5.
Calculations provide insight to the reaction trajectory. Inspection of the charges for the ground state structures of $2\text{-}5$ reveals that the hydrogen atom becomes less negatively charged as it approaches the transition metal. In conjugation, the Wiberg bond index of both TM–H and TM–Zn increase as that of Zn–H decreases and the magnitude of the (TM–H)$\rightarrow$Zn donor-acceptor interaction increases as assessed by second-order perturbation theory. QTAIM calculations support a progression from a α-zincane complex to a transition metal-zinc hydride complex. While curved bond critical paths along with bond critical points (bcp) can be identified between Zn–H and TM–H for 3a and 4a no Zn–TM bcp was apparent. For 5b, no Zn–H bcp is found while both TM–H and TM–Zn are apparent (Figure 4).

In summary, we have prepared and crystallographically characterized seven new zinc-—transition metal heterobimetallic hydrides. Through variation of the transition metal fragment a series of “snap-shots” of the reaction coordinate of the approach of a Zn–H bond toward a transition metal have been obtained. Calculations on each of the isolated complexes show that the reaction trajectory is characterized by the transfer of electron density from the breaking largely ionic Zn–H bond to forming, increasingly covalent, TM–H and TM–Zn bonds. The reaction trajectory is analogous to the oxidative addition of silanes and boranes to a transition metal.

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The reaction trajectory for the approach of a zinc–hydride bond to a transition metal is described.

Interrogation of dynamic reaction coordinate.
Seven new heterobimetallic complexes.
DFT and QTAIM calculations.

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