Supporting information for

Generation of low-valent tantalum species by reversible C-H activation in a cyclometallated tantalum hydride complex

A. NMR spectroscopic analysis

A.1 Representative ^{1}H NMR spectrum of a mixture of **2a**/**2b**

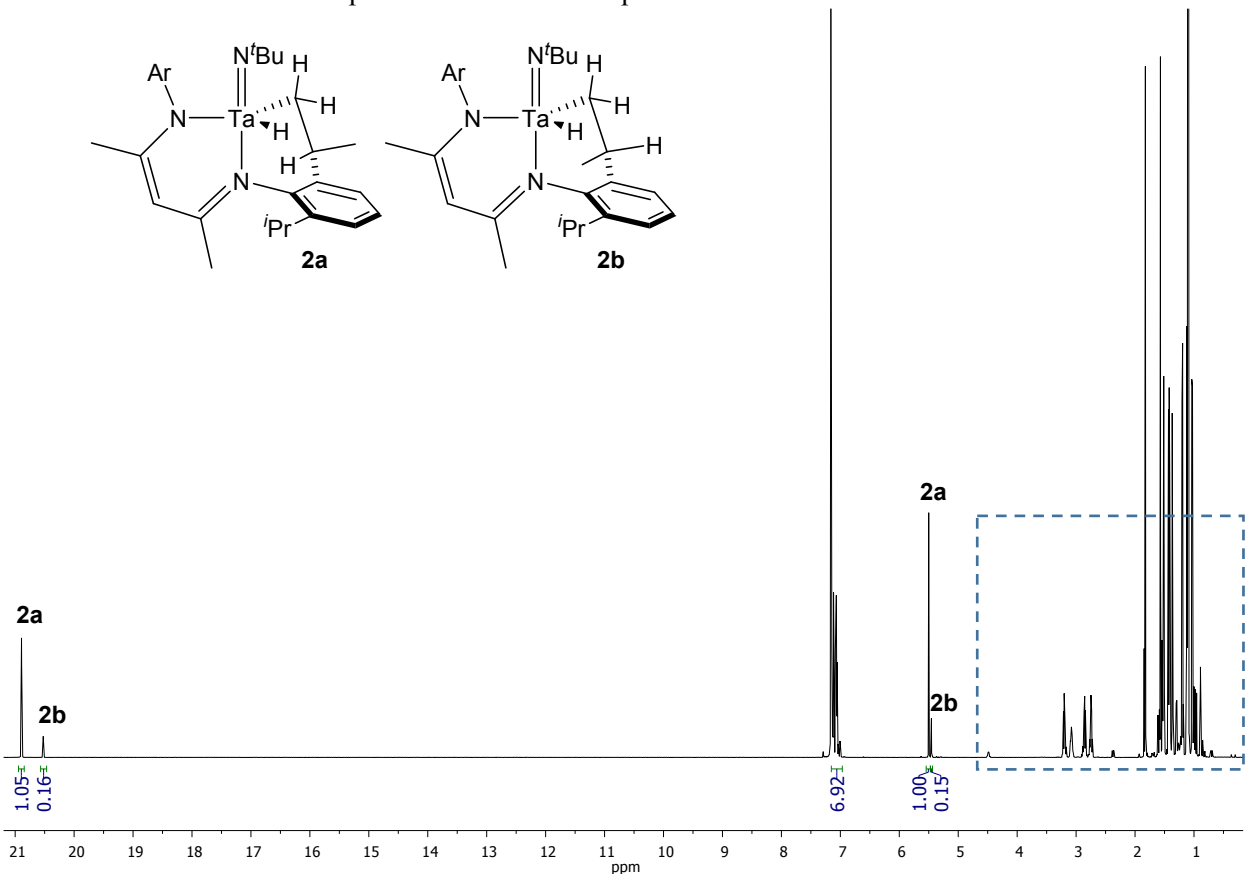

Figure S1 Representative ^{1}H NMR spectrum of an isolated 7:1 mixture of **2a** to **2b** showing hydride and BDI backbone methine resonances.

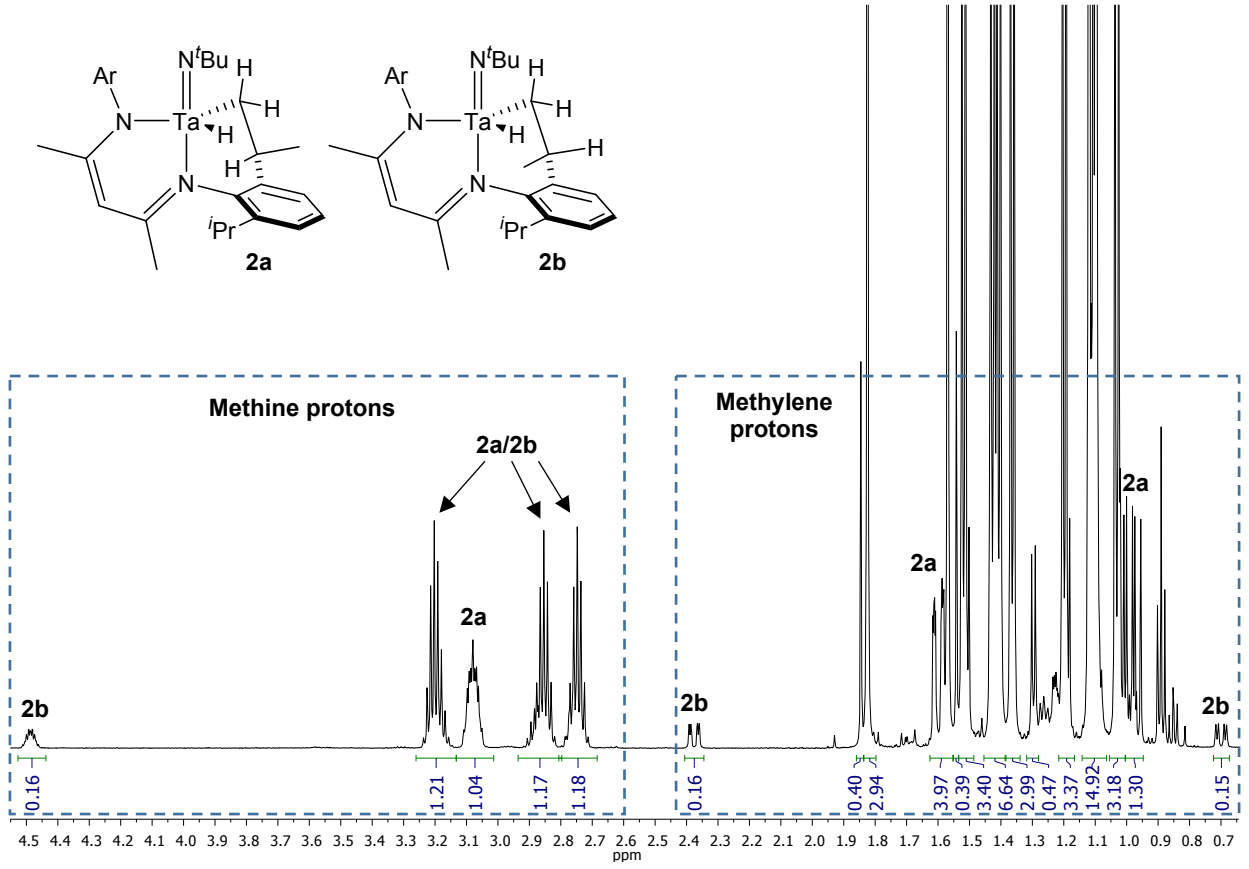

Figure S2 Zoom in on the region shown in Figure S1 showing the methine and diastereotopic methylene resonances for **2a** and **2b**.

A.2 Deuterium scrambling observed by ^{2}H NMR spectroscopy

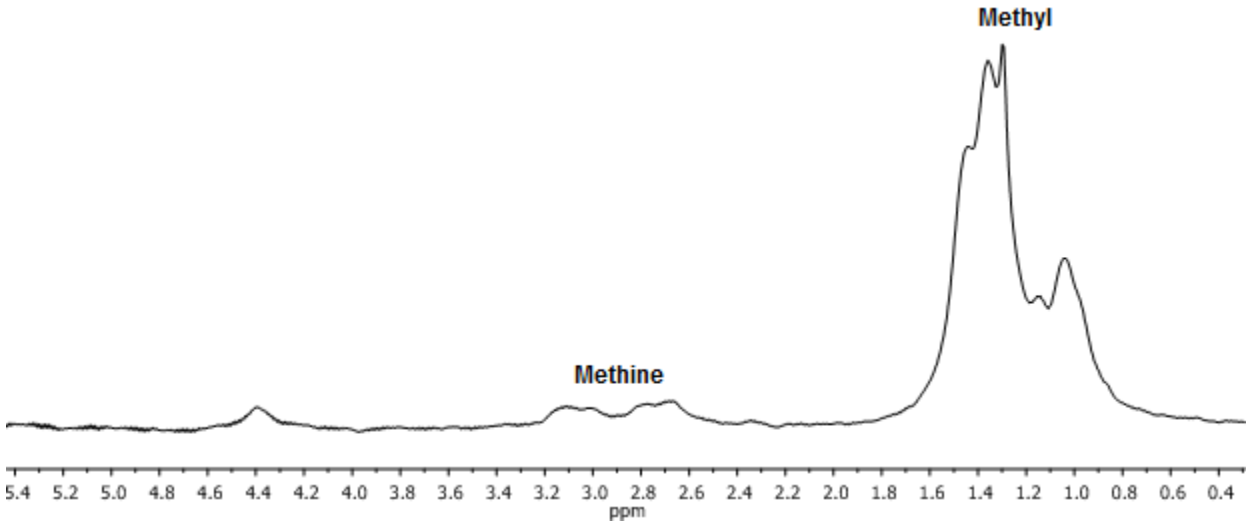

Figure S3 ^{2}H NMR spectrum of product isolated from reaction of **1** with 1 atm D_2 showing scrambling of deuterium into the methyl and methine groups of the BDI ligand.

A.3 Observation of intermediate **A** by ^{1}H NMR Spectroscopy

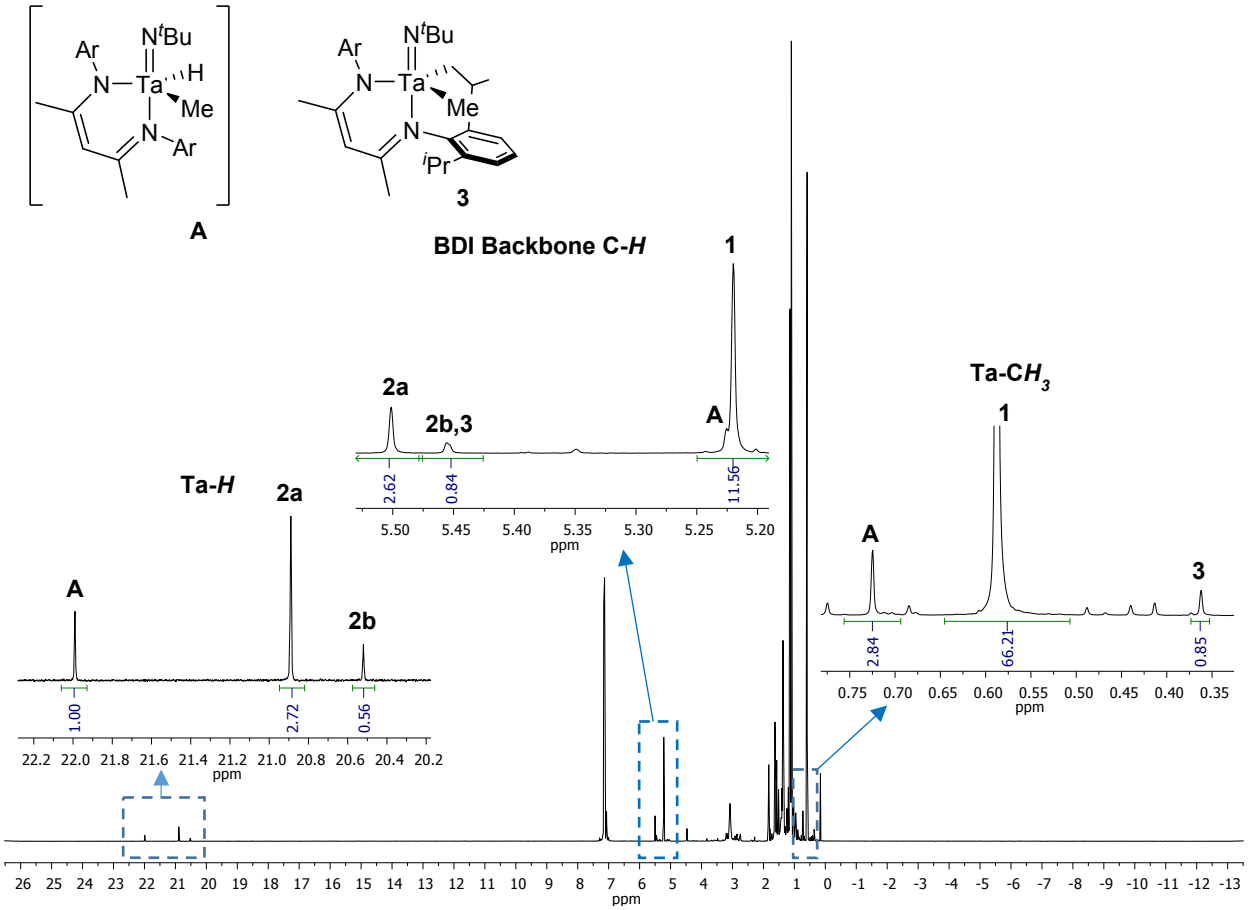

Figure S4 ^{1}H NMR spectrum taken after 90 minutes of introducing 1 atm of H_2 to an NMR tube containing **1**. Compound 1 is partially converted to a mixture of **2a**, **2b**, and **3**. Resonances attributed to intermediate **A** are shown.

B. X-ray crystallographic analysis

B.1 X-Ray crystal structure of **3**

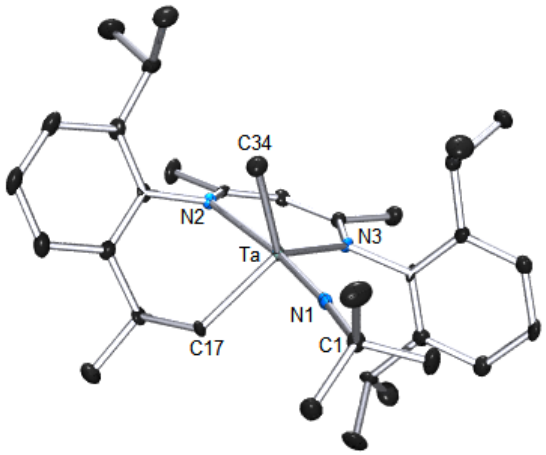

Figure S5 Molecular structure of **3** as determined by a single crystal X-ray diffraction study. The hydrogen atoms and the co-crystallized benzene molecule are omitted for clarity; the thermal ellipsoids are set at the 50% probability level. Selected bond lengths (Å): Ta(1)-C(34) 2.172(2), Ta(1)-N(1) 1.785(2), Ta(1)-N(2) 2.300(2), Ta(1)-N(3) 2.102(2), Ta(1)-C(17) 2.184(2). Selected bond angles (˚): N(3)-Ta(1)-C(34) 120.5(9), C(17)-Ta(1)-C(34) 115.7(1), N(3)-Ta(1)-C(17) 119.8(8), N(1)-Ta(1)-N(2) 173.1(1), C(1)-N(1)-Ta(1) 170.2(2).

B.2 Determination of τ parameter for **2a**

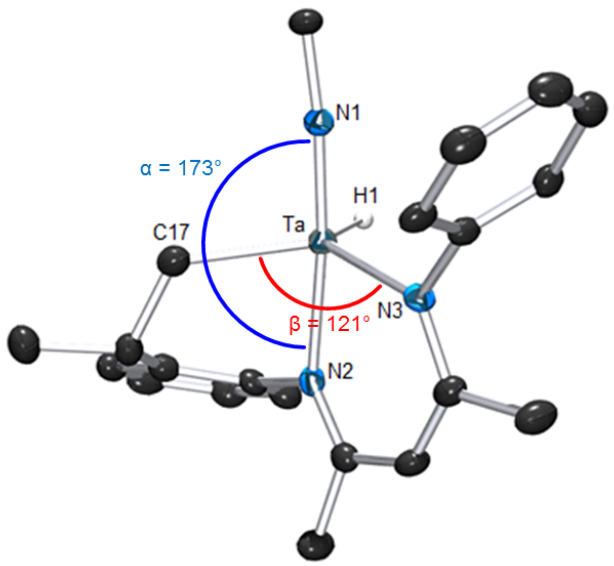

Figure S6 Molecular structure of **2a** showing the angles α and β used for determining the parameter τ using the equation τ = (α-β)/60° = 52°/60° = 0.87. The *tert*-butyl group and aryl groups have been truncated for clarity. A value of τ close to 1.0 indicates a nearly trigonal bipyramidal structure, whereas a value close to 0.0 indicates a nearly square pyramidal structure.