Supplementary Materials: Accessing Low-Valent Titanium CCC-NHC Complexes: Toward Nitrogen Fixation

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Figure S1: Stacked plot of the $^1$H NMR spectra for reoxidation of intermediate 3. A: $^1$H NMR spectrum of intermediate 3. B: $^1$H NMR spectrum of intermediate 3 after reoxidation. C: $^1$H NMR spectrum of 2 for reference.

Figure S2: Stacked plot of the $^1$H NMR spectra for reduction of 1 with Mg-metal followed by reoxidation with PhICl in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$\text{D}_2$). B: $^1$H NMR spectrum for 1. C: $^1$H NMR spectrum after reduction of 1 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl.

Figure S3: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl. Figure S4: Stacked plot of the relevant zoomed portions of $^1$H NMR spectra for reduction of 1 with Mg-metal followed by reoxidation with PhICl in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$\text{D}_2$). B: $^1$H NMR spectrum for 1. C: $^1$H NMR spectrum after reduction of 1 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl.

Figure S5: Stacked plot of the $^1$H NMR spectra for reduction of 1 with KC$\text{S}$ followed by reoxidation with PhICl in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$\text{D}_2$). B: $^1$H NMR spectrum for 1. C: $^1$H NMR spectrum after reduction of 1 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl.

Figure S6: Stacked plot of the relevant zoomed portions of $^1$H NMR spectra for reduction of 1 with KC$\text{S}$ followed by reoxidation with PhICl in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$\text{D}_2$). B: $^1$H NMR spectrum for 1. C: $^1$H NMR spectrum after reduction of 1 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl.

Figure S7: Stacked plot of the $^1$H NMR spectra for reduction of 2 with KC$\text{S}$ followed by reoxidation with PhICl in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$\text{D}_2$). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl.

Figure S8: Stacked plot of the relevant zoomed portions of $^1$H NMR spectra for reduction of 2 with KC$\text{S}$ followed by reoxidation with PhICl in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$\text{D}_2$). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl.

Figure S9: Stacked plot of the $^1$H NMR spectra for reduction of 2 with Mg-metal followed by reoxidation with PhICl in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$\text{D}_2$). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl. Figure S10: Pictures of NMR tubes from reduction of 2 with 1, 2 and 4 equivalents of KC$\text{S}$s respectively.

Figure S11: Stacked plot of the $^1$H NMR spectra for reduction of 2 with KC$\text{S}$ followed by reoxidation with PhICl in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$\text{D}_2$). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl.

Figure S12: Stacked plot of the $^1$H NMR spectra for reduction of 2 with KC$\text{S}$ followed by bubbling with CO in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$\text{D}_2$). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3. D: $^1$H NMR spectrum after 3 was bubbled with CO.

Figure S13: Stacked plot of the relevant zoomed portions of $^1$H NMR spectra for reduction of 2 with KC$\text{S}$ followed by bubbling with CO in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$\text{D}_2$). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3. D: $^1$H NMR spectrum after 3 was bubbled with CO.

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**Figure S2.** Stacked plot of the $^1$H NMR spectra for reduction of 1 with Mg-metal followed by reoxidation with PhICl$_2$ in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with CsD$_6$). B: $^1$H NMR spectrum for 1. C: $^1$H NMR spectrum after reduction of 1 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl$_2$.

**Figure S3.** $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl$_2$. 
Figure S4. Stacked plot of the relevant zoomed portions of $^1$H NMR spectra for reduction of 1 with Mg-metal followed by reoxidation with PhICI in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$_6$D$_6$). B: $^1$H NMR spectrum for 1. C: $^1$H NMR spectrum after reduction of 1 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICI.
Figure S5. Stacked plot of the $^1$H NMR spectra for reduction of 1 with KC$_8$ followed by reoxidation with PhICl$_2$ in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$_6$D$_6$). B: $^1$H NMR spectrum for 1. C: $^1$H NMR spectrum after reduction of 1 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl$_2$. 
Figure S6. Stacked plot of the relevant zoomed portions of $^1$H NMR spectra for reduction of 1 with KC8 followed by reoxidation with PhICl2 in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C6D6). B: $^1$H NMR spectrum for 1. C: $^1$H NMR spectrum after reduction of 1 to intermediate 3. D: $^1$H NMR spectrum after reoxidation of intermediate 3 with PhICl2.
Figure S7. Stacked plot of the $^1$H NMR spectra for reduction of 2 with KC$_8$ followed by reoxidation with PhICl$_2$ in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$_6$D$_6$). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3'. D: $^1$H NMR spectrum after reoxidation of intermediate 3' with PhICl$_2$. 
Figure S8. Stacked plot of the relevant zoomed portions of $^1$H NMR spectra for reduction of 2 with KC$_8$ followed by reoxidation with PhICl$_2$ in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with CsD$_6$). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3'. D: $^1$H NMR spectrum after reoxidation of intermediate 3' with PhICl$_2$. 
Figure S9. Stacked plot of the $^1$H NMR spectra for reduction of 2 with Mg-metal followed by reoxidation with PhICl₂ in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C₆D₆). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3’. D: $^1$H NMR spectrum after reoxidation of intermediate 3’ with PhICl₂.
Figure S10. Pictures of NMR tubes from reduction of 2 with 1, 2 and 4 equivalents of KCs respectively.
Figure S11. Stacked plot of the $^1$H NMR spectra for reduction of 2 with KC$_8$ followed by reoxidation with PhICl$_2$ in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$_6$D$_6$). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3'. D: $^1$H NMR spectrum after reoxidation of intermediate 3' with PhICl$_2$. 
Figure S12. Stacked plot of the $^1$H NMR spectra for reduction of 2 with KCs followed by bubbling with CO in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C$_6$D$_6$). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3'. D: $^1$H NMR spectrum after 3' was bubbled with CO.
Figure S13. Stacked plot of the relevant zoomed portions of $^1$H NMR spectra for reduction of 2 with KC₈ followed by bubbling with CO in no-D THF. A: $^1$H NMR spectrum for no-D THF (locked with C₆D₆). B: $^1$H NMR spectrum for 2. C: $^1$H NMR spectrum after reduction of 2 to intermediate 3. D: $^1$H NMR spectrum after 3 was bubbled with CO.