Electronic Supplementary Material for Dalton Transactions

Supporting Information for

Mechanistic Variety in Zirconium-Catalyzed Bond-Forming Reaction of Arsines

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Figure S-1. Second-order kinetic plot of the catalytic dehydrocoupling of diphenylarsine by catalytic $(N_3N)ZrAsPh_2$ (**2**) in benzene-d_6 solution ($[Ph_2AsH]_i$ = 0.95 M; T = 100 °C; R^2 (for fit line) = 0.9955).

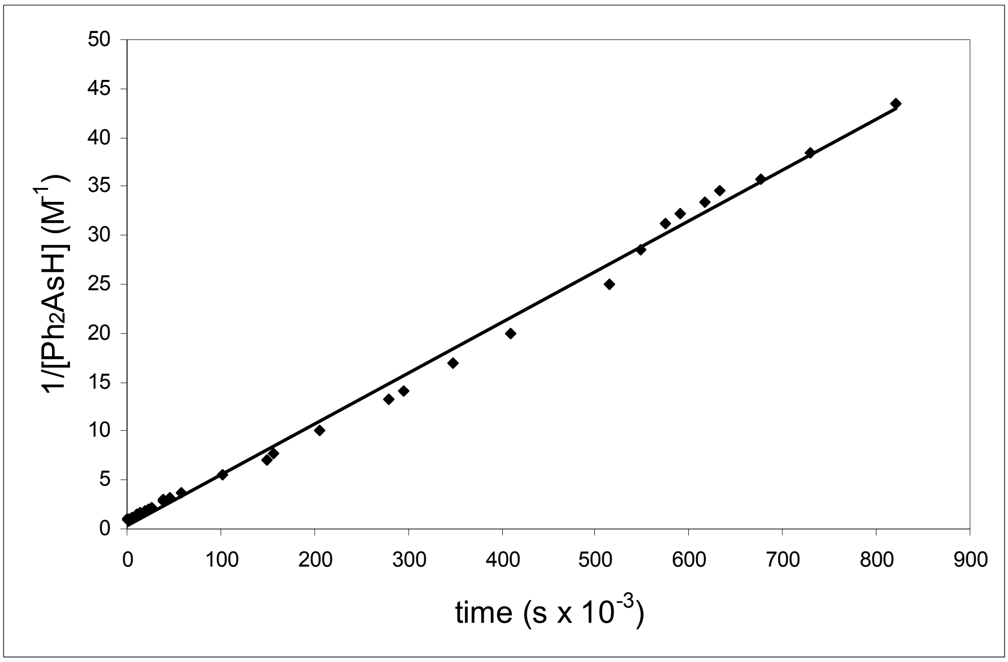

Figure S-2. Plot of the second-order observed rate constant (k_{obs}) versus concentration of arsenido complex $(N_3N)ZrAsPh_2$ (**2**) in the catalytic dehydrocoupling of Ph_2AsH. Approximately linear slope indicates a first-order dependence on [**2**] (R^2 (for fit line) = 0.9982).

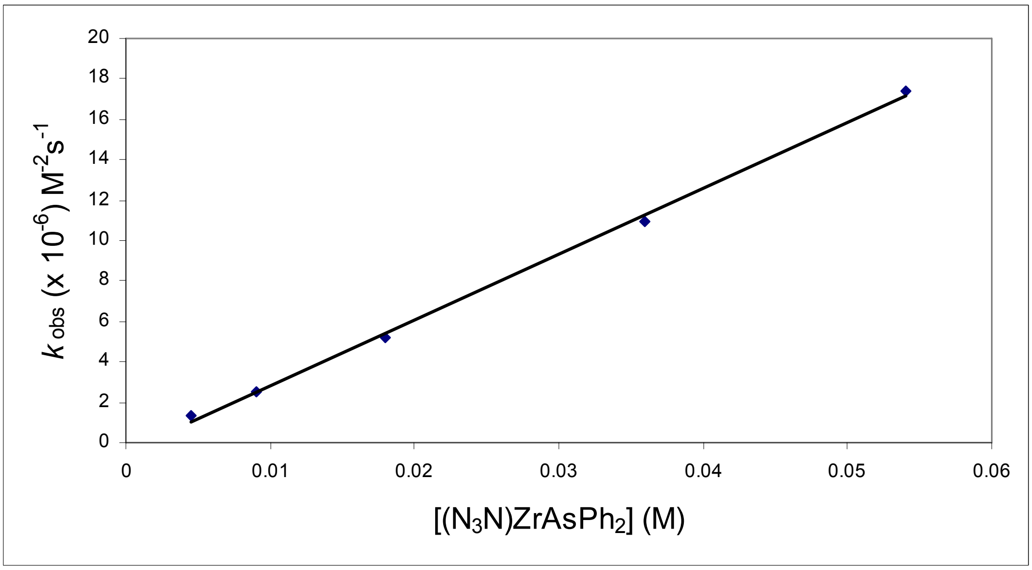

Figure S-3. Eyring plot of the catalytic dehydrocoupling of diphenylarsine by **2**, where k is the second-order rate constant measured by monitoring loss of Ph_2AsH for T = 89.5 – 130.0 °C (R^2 (for fit line) = 0.9809).

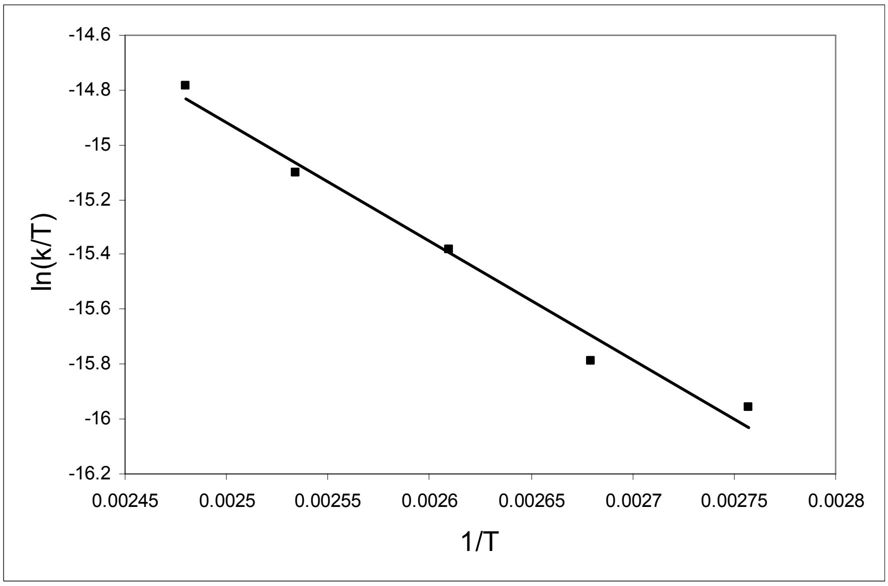

Figure S-4. Plot of the natural log of diphenylarsine concentration versus time for dehydrocoupling with catalytic $(N_3N)ZrAsPh_2$ (**2**) in benzene-d_6 solution ($[Ph_2AsH]_i$ = 0.95 M; T = 100 °C). Nonlinearity of the plot demonstrates that the catalysis is not first-order in Ph_2AsH.

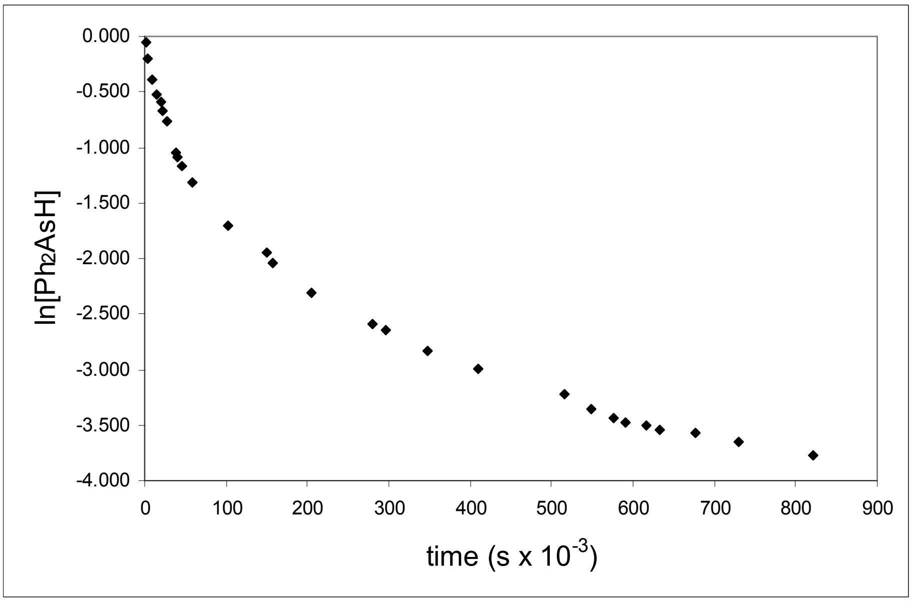

Figure S-5. First-order kinetic plot of the thermal decomposition of $(N_3N)ZrAsHMes$ (**9**) with 5 mol% of **1** in benzene-d_6 solution ($[\mathbf{9}]_i$ = 0.059 M; T = 90.2 °C; R^2 (for fit line) = 0.9985).

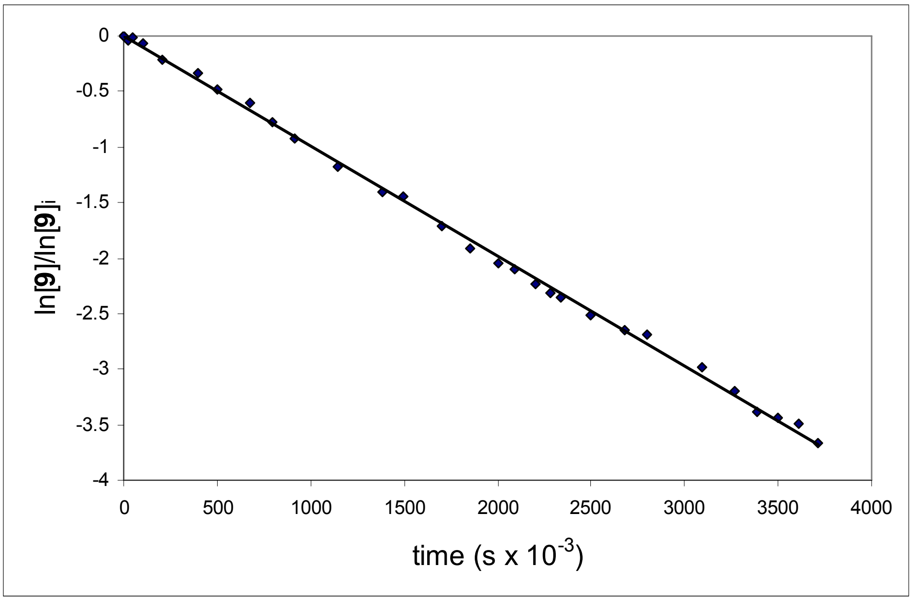

Figure S-6. Eyring plot of the thermal decomposition of $(N_3N)ZrAsHMes$ (**9**) with 5 mol% of **1** in benzene-d_6 solution, where k is the first-order rate constant measured by monitoring loss of **9** for T = 75.0 – 115.7 °C (R^2 (for fit line) = 0.9878).

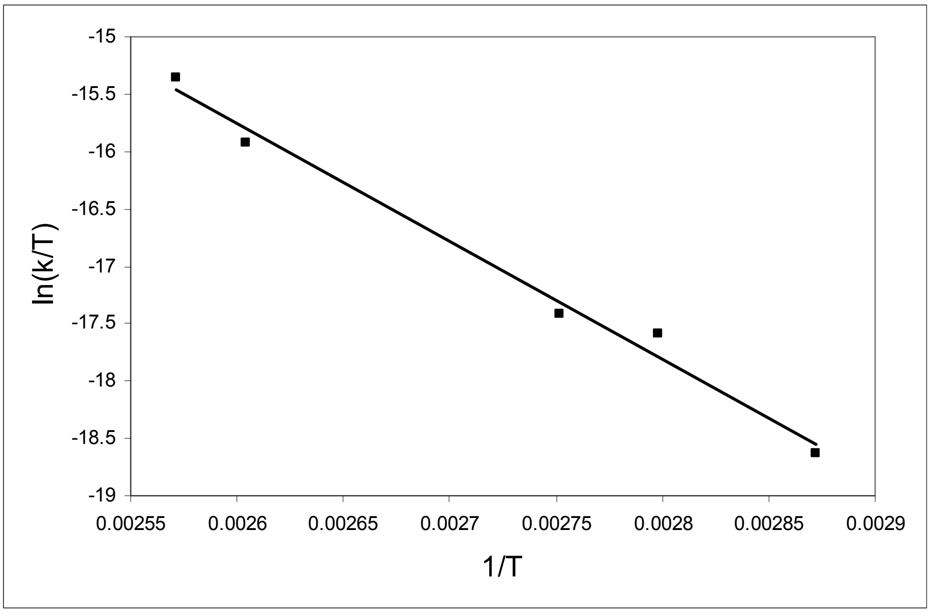

Figure S-7. Plot of the first-order rate constant for the thermal decomposition of $(N_3N)ZrAsHMes$ (**9**) benzene-d_6 solution ($[\mathbf{9}]_i$ = 0.059 M; T = 90.2 °C) as a function of either added complex **1** or added $MesAsH_2$. Rates were measured for 5–100 mol% of added reagent. At amounts less than 5 mol%, first-order decomposition of **9** was not consistently observed. These data suggest a zero-order dependence on these added reagents.