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Supporting Information

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Mechanistic Insights into the Formation of InP Quantum Dots**

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I. Experimental details

Reagents: Octylamine (Fluka, 99%, dried over calcium hydride), Toluene d-8 (Cambridge Isotope Labs), 1,2-dichloromethane (Cambridge Isotope Labs), and diphenylmethane (Sigma, >99%, degassed) were placed into a nitrogen filled glovebox and stored over 4 Å molecular sieves prior to use. Myristic acid (Sigma, >99%), 1-octadecene (Tech grade, Sigma), hexanes (anhydrous, Acros) and Indium acetate (99.99%, Alfa Aesar) were used to synthesize Indium(III) myristate [$In(MA)_3$]. Trimethylsilyl chloride (Fluka, 99%, re-distilled) was used to synthesize TMS-OA and TMS-MA NMR reference compounds. Tris(trimethylsilyl) phosphine [$(TMS)_3P$, *caution pyrophoric*] was obtained from Strem and used as received. J-young NMR tubes (Chemglass, 600 mhz) were dried at 120 ˚C prior to use. All other glassware was dried at 180 ˚C. All samples were prepared under minimal lighting in a nitrogen filled glovebox (mBraun, <0.1ppm oxygen).

Synthesis of $In(MA)_3$: The synthesis of $In(MA)_3$ was performed as previously reported.[1] All solutions containing $In(MA)_3$ were additionally dried for two days over 4 Å molecular sieves to remove residual water.

NMR Solutions: Example of a typical solution preparation for OA:In (6 :1): Solution (A) 0.24 mmol of $In(MA)_3$, 1.44 mmol of OA, and 0.36 mmol of diphenylmethane were mixed in 6 ml of toluene-d_8. $In(MA)_3$ dissolves readily in the presence of amines. Without amines, the solution was heated to 60 ˚C to produce a homogeneous solution. The solutions were stored over 4 Å molecular sieves for two days prior to use. Solution (B) 0.12 mmol of $(TMS)_3P$ and 6 ml toluene-d_8 were combined and stored in the dark at -35 ˚C prior to use.

NMR Reaction Tubes: In a typical reaction 0.35 ml of solution (A) and 0.35 ml of solution (B) were injected into a J-young NMR tube in the glovebox. The NMR tube was then immediately transferred for NMR measurements. All samples were handled under minimal lighting to prevent decomposition of $(TMS)_3P$.

NMR Spectroscopy: All spectra were taken on 300 MHz or 500 MHz Varian INOVA NMR spectrometers using either a variable temperature broadband switchable probe or a variable temperature indirect detection probe.

Synthesis of TMS-MA: 10 mg of trimethylsilyl chloride was added to a stirred solution of 60 mg of myristic acid and 50 mg of tri-n-octylphosphine in 1 ml of toluene-d_8 and heated to 60 ˚C. No further purification was performed prior to ^1H NMR analysis (Figure S8).

Synthesis of TMS-OA: 10 mg of trimethylsilyl chloride was added to a stirred solution of 75 mg of octylamine (OA) in 1 ml of toluene-d_8. The solution was filtered to remove the OA-HCl salt prior to ^1H NMR analysis (Figure S9).

II. Kinetic analysis: general rate determinations

All kinetic data was obtained via integrals of the ^{1}H NMR spectra of the samples described above. Each spectrum in the series retained the same integration interval throughout for all times, and all integrals were referenced to an internal diphenylmethane standard.

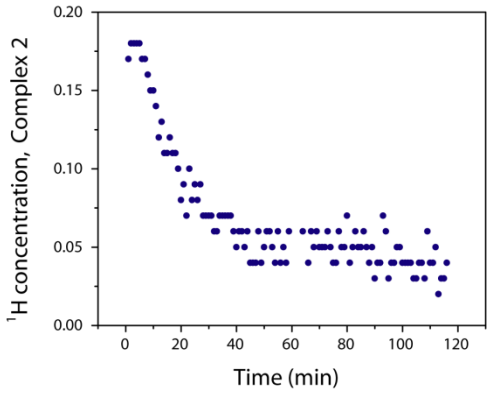

Figure S1. ^{1}H NMR concentration of Complex **2** during synthesis at 40 ˚C. The rise and fall of Complex **2** over time is consistent with the assignment of Complex **2** as an intermediate in the formation of InP QDs.

The only identifiable TMS-containing species are $(TMS)_3P$, TMS-MA, the intermediate $In(MA)_2P(TMS)_2$ (**2**), and the TMS-OA. The sum of these four species is constant throughout, indicating that our analysis accounts for all TMS groups introduced during the reaction.

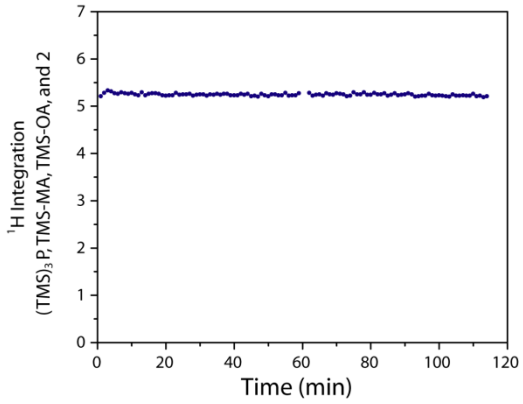

Figure S2. ^{1}H NMR integration of all identifiable TMS-containing species throughout the reaction. The overall concentration of TMS protons does not change during the course of the reaction.

We used the method of initial rates, using early time reaction data at < 15% conversion to fit a linear regression. The slope of the fit line gave the rate of the reaction. This rate was then used to determine an experimental rate constant, using relationship from the experimental rate law

$$k = \frac{\text{rate}}{[\text{In(MA)}_3]^x[(\text{TMS})_3\text{P}]^y}$$

From reactions run with variable $(TMS)_3P$ we found that $0 < x < 1$. A non-integer value for the order in $(TMS)_3P$ is plausible, as the TMS groups are each present with 1/3 the molar ratio of the $(TMS)_3P$ and as each TMS group on every possible intermediate likely has a different relative reactivity. The heterogeneous reactivity permits only the determination of the average order in $(TMS)_3P$ for the ensemble. We infer that for the conditions studied, on average no more than 1 P-containing species enters the transition state of the rate limiting step.

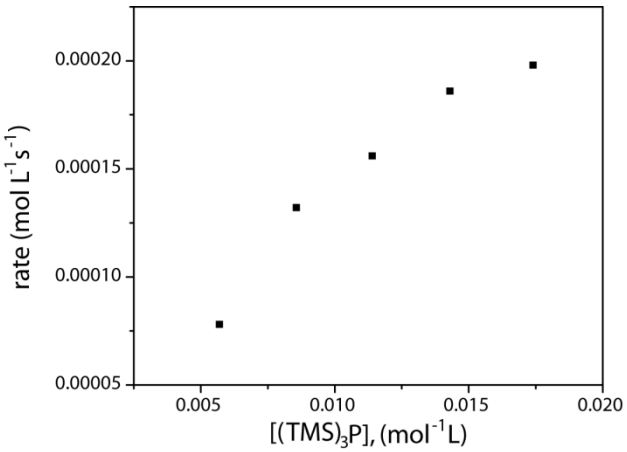

Figure S3. Plot of $(TMS)_3P$ concentration vs. rate (measured from the early time approximation) with a fixed concentration of $In(MA)_3$, 0.02 M at 25 ˚C. The rate does not follow a clear order dependence in $(TMS)_3P$ concentration.

Similarly, we found no evidence that the average order in $In(MA)_3$ is greater than 1 (ie $0 < y < 1$), and the bounds are also sensible for similar reasons as the order in $(TMS)_3P$.

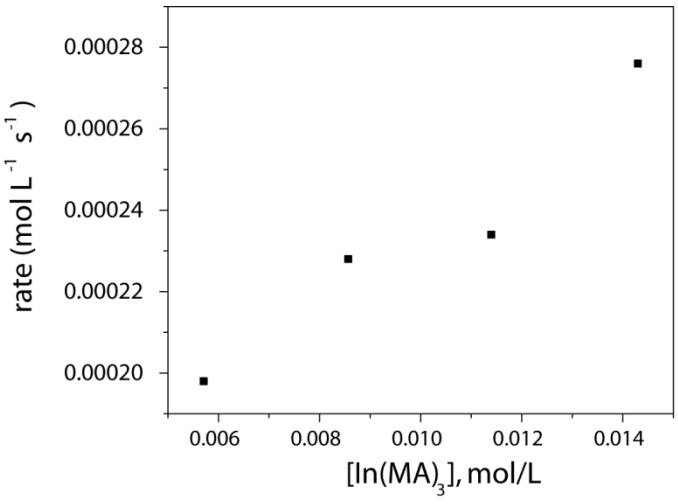

Figure S4. Plot of $In(MA)_3$ concentration vs. rate (measured from the early time approximation) with a fixed concentration of $(TMS)_3P$, 0.02 M at 25 ˚C. The rate does not follow a clear order dependence in $In(MA)_3$ concentration.

For Eyring analysis, the order in $(TMS)_3P$ and in $In(MA)_3$ is applied uniformly to each rate to estimate k, so any error in estimating x and y affects only the activation entropy, not the activation enthalpy. We obtained an upper bound on $\Delta S^{\ddagger}$ by computing k with $x = y = 1$. This upper bound on $\Delta S^{\ddagger}$ (-126 ± 4 J mol^{-1} K^{-1}) is still a large negative value, as noted in the manuscript.

III. Kinetic analysis: representative rate data

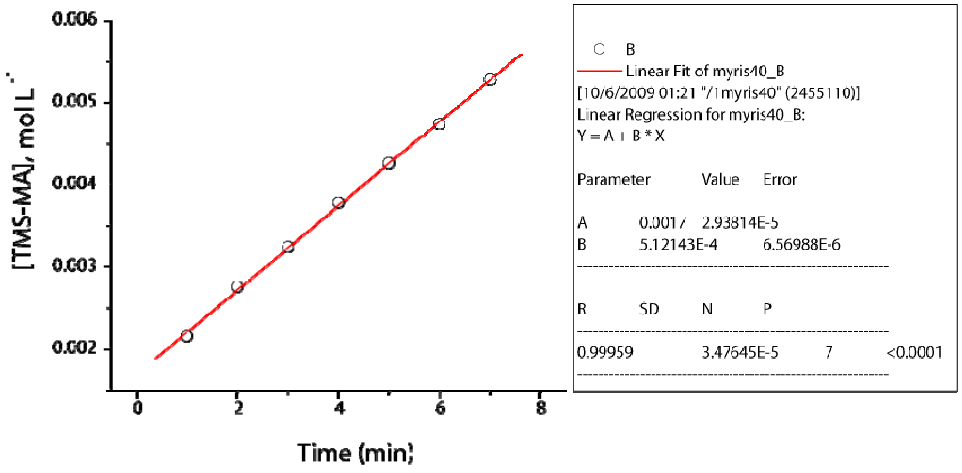

Figure S5. Evolution of TMS-MA concentration vs. time measured for <15% conversion as described above. This is the first replicate of 40 ˚C data for Eyring analysis. The slope, (5.12 mol L^{-1} min^{-1}) is the rate of reaction.

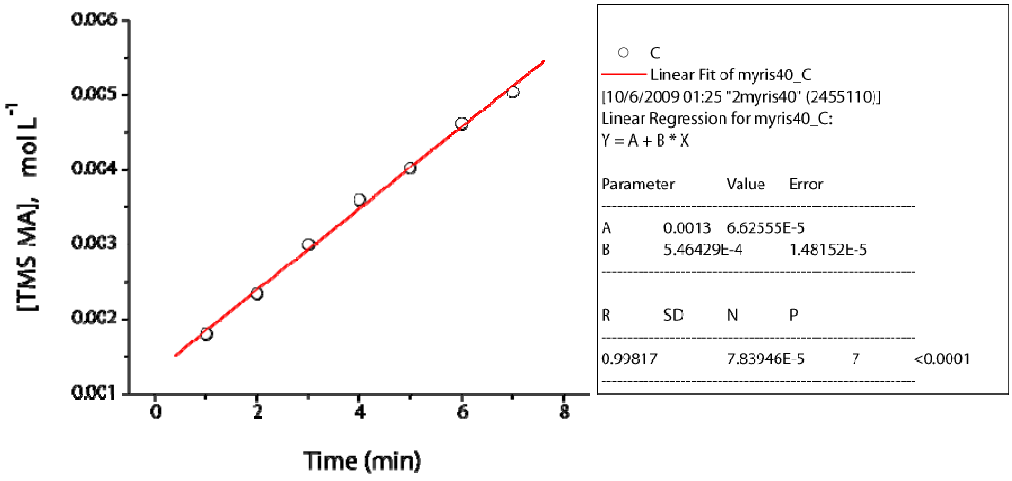

Figure S6. Evolution of TMS-MA concentration vs. time measured for <15% conversion as described above. This is the second replicate of 40 ˚C data for Eyring analysis. The slope, (5.46 mol L^{-1} min^{-1}) is the rate of reaction.

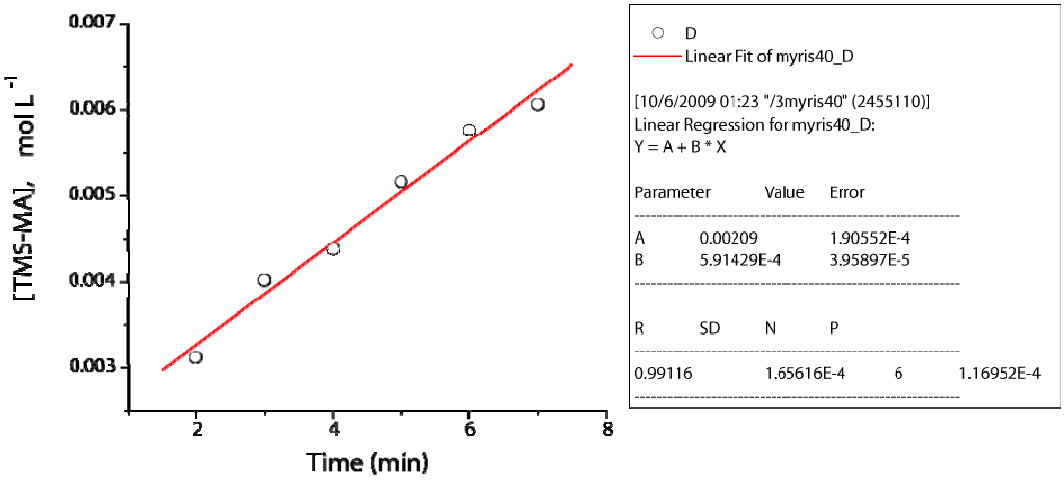

Figure S7. Evolution of TMS-MA concentration vs. time measured for <15% conversion as described above. This is the third replicate of 40 ˚C data for Eyring analysis. The slope, (5.91 mol L^{-1} min^{-1}) is the rate of reaction.

IV. Additional spectra

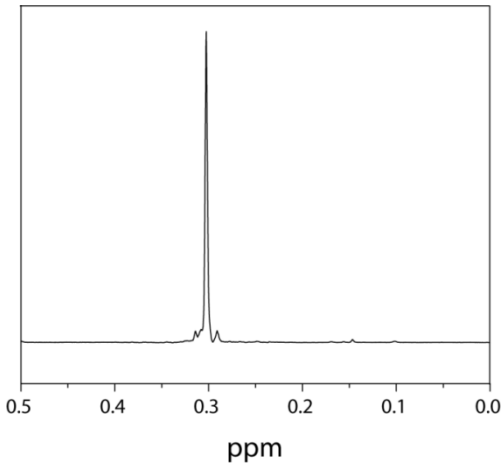

Figure S8. ^{1}H NMR of TMS-MA (0.303 ppm) in toluene-d_8 referenced to diphenylmethane (3.771 ppm).

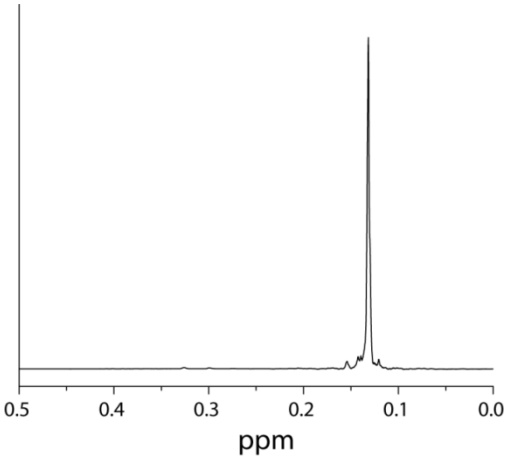

Figure S9. ^{1}H NMR spectrum of TMS-OA (0.132 ppm) in toluene-d_8 referenced to diphenylmethane (3.771 ppm).

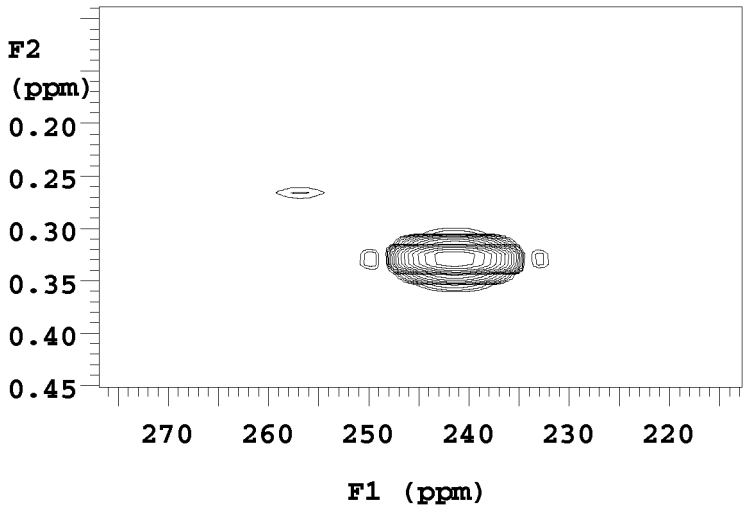

Figure S10. ^{31}P-^{1}H heteronuclear multiple bond coupling spectrum (HMBC) for the InP reaction mixture at 25 ˚C after 40 minutes. The only cross-coupled resonances correspond to $(TMS)_3P$ and intermediate **2**.

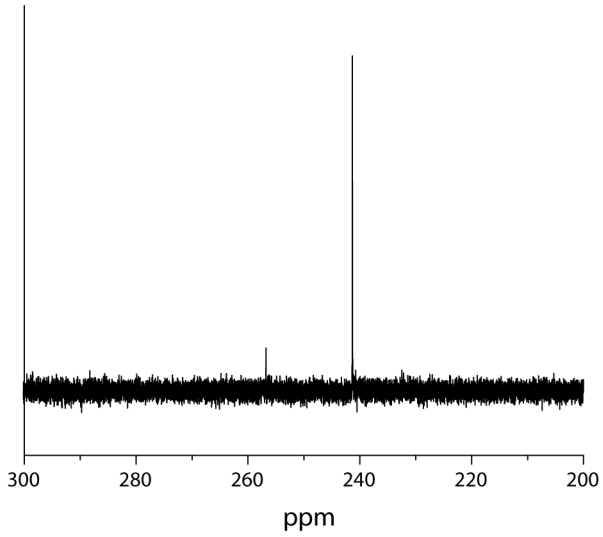

Figure S11. ^{1}H-decoupled ^{31}P spectrum for the InP reaction mixture after 30 min at 25 ˚C. Only resonances for $(TMS)_3P$ (241.3 ppm) and intermediate **2** (256.8 ppm) are visible. Chemical shifts are referenced to 85% H_3PO_4 (0 ppm).

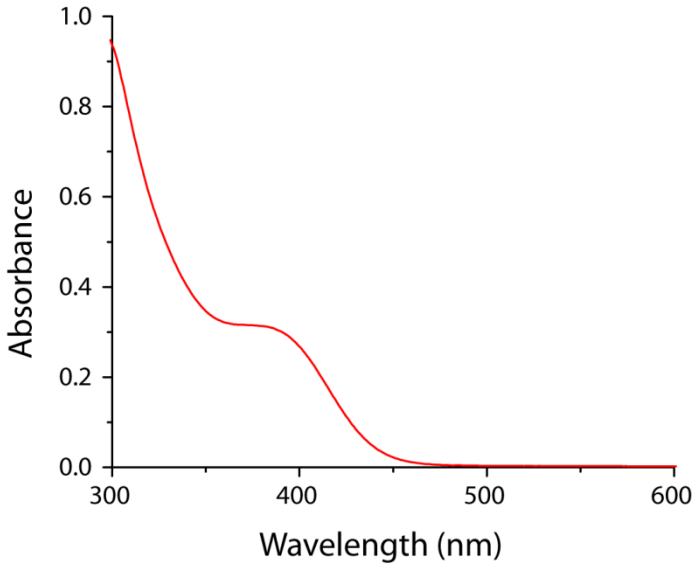

Figure S12. Absorbance spectra of InP QDs grown in an NMR tube at 40 ˚C for 60 minutes in the presence of octylamine.

V. References

[1] F. Wang, H. Yu, J. Li, Q. Hang, D. Zemlyanov, P. C. Gibbons, Wang, D. B. Janes, W. E. Buhro, *J. Am. Chem. Soc.* **2007**, *129*, 14327.