Supporting Information

Why Less Coordination Provides Higher Reactivity Chromium Phosphinoamidine Ethylene Trimerization Catalysts

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Computational Details

All calculations were performed in Gaussian 09 (see citation below). Geometry optimizations were carried out with unrestricted M06-L/6-31G**[LANL2DZ for Cr]. Vibrational frequencies were calculated to verify stationary points as minima or first-order saddle points (transition states) as well as determine thermochemical corrections at 298 K and experimental temperatures. Intrinsic reaction coordinate (IRC) calculations were used to verify connection between transition states and intermediates for TS1 and TS2. As discussed in the text, the M06-L functional was chosen because McGuinness and Britovsek showed that M06-L gave similar spinstate energies and reaction energies compared with G4(MP2,rel) and CCSD(T)/CBS wavefunction methods.¹ Cyclohexane, toluene, and methylcyclohexane solvents were modeled using the SMD continuum solvation model, which generally provides accurate estimates of ΔG_{solv} . On the optimized geometries, energies were then calculated with the def2-TZVP basis set so that final Gibbs free energies reported are: (U)M06-L/def2-TZVP//(U)M06-L/6-31G**[LANL2DZ for Cr]. Gibbs free energies are the sum of $E_{(def2-TZVP)} + \Delta E_{ZPE(6-31G^{**}[LANL2DZ \text{ for } Cr])} + \Delta U_{vib(6-31G^{**}[LANL2DZ])}$ for Cr]) + $\Delta U_{rot(6-31G^{*}[LANL2DZ \text{ for Cr}])} + \Delta U_{trans(6-31G^{*}[LANL2DZ \text{ for Cr}])} + nRT - T\Delta S_{vib(6-31G^{*}[LANL2DZ \text{ for Cr}])}$ $- T\Delta S_{rot(6-31G^{*}[LANL2DZ \text{ for } Cr])} - T\Delta S_{trans(6-31G^{*}[LANL2DZ \text{ for } Cr])} + \Delta G_{solv(def2-TZVP)}$. E is the total SCF energy. ΔE_{ZPE} is the zero-point energy (ZPE) correction. ΔU_{vib} , ΔU_{rot} , and ΔU_{trans} are thermal energy vibrational, rotational, and translational corrections. R is the gas constant. T is the temperature. $T\Delta S_{vib}$, $T\Delta S_{rot}$, and $T\Delta S_{trans}$ are temperature-dependent entropy vibrational, rotational, and translational corrections. $\Delta G_{\text{solv(large)}}$ is the solvation Gibbs free energy change. 3-D structures were generated using CYLview.²

Full G09 Reference: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 09, Revision B.01. Wallingford CT, 2009.

Summary of Experimental Conditions

Table S1 summarizes some of the experimental reaction conditions for catalysts **1a-8a**. The high pressure NMR kinetic studies reported by Sydora and Abu-Omar and were performed at 50 bar of ethylene, room temperature, 5 μ mol of Cr catalyst, cyclohexane solvent, and 600 eq of MMAO-3A.³ See Table S1 and the references for more details of **1a**, ⁴ **2**, ⁵ **3**, ⁶ **4**, ⁶ **5**, ⁷ **6**, ⁸ **7**, ⁹ and **8a**.⁴

complex	ethylene pressure (bar)	catalyst (µmol)	co-catalyst (equivalents)	solvent	T (°C)	Productivity (g/g Cr·h)	C ₆ [1-C ₆] (% mass)	Poly- ethylene (mass %)
1a	60	10	MMAO-3A (400-800)	cyclohexane	70	1,054,000	94 [>99]	Trace
1a ^a	50	5	MMAO-3A (600)	cyclohexane	25	-	-	-
2	40	1.3	MMAO-3A (500)	methyl- cyclohexane	60	672,000	94 [>99]	6.5
3	40	11	(600)	toluene	80	42,000	94 [>99]	0.1
4	40	11.3	(660)	toluene	120	27,000	93 [>99]	0.2
5	35	30	(1000)	toluene	50	5,200	99 [-]	1.8
6	25	20	(200)	toluene	80	2,800	96 [99]	<0.1
7	30	10	(100)	toluene	24	470	98 [99]	2
8a	60	10	MMAO-3A (400-800)	cyclohexane	55	0	trace	100

Table S1. Summary of experimental reaction conditions for ethylene trimerization Cr catalysts examined in this computational study. ^aReaction conditions for high pressure NMR kinetic experiments with **1a**.

Anionic (P,N) Ligand

We explored the possibility of phosphinoamidine ligand N-H deprotonation and the resulting **1c** catalyst with coordination to Cr (see below). An overall neutral Cr complex would mediate a Cr^{I/III} catalytic cycle while a cationic system would operate by a Cr^{II/IV} cycle. Scheme S1 displays the Gibbs free energy surfaces for the neutral and cationic catalyst models. The neutral Cr^{I/III} system energy span is mainly controlled by **TS2** with a barrier of 17.5 kcal/mol relative to **C**. This energy span is <2 kcal/mol higher in energy than the energy span calculated with the protonated ligand catalyst **1a**. This indicates that catalyst **1c**, compared to catalyst **1a**, could provide a nearly equivalent computational model to analyze productivity. Additionally, it is possible that both **1a** and **1c** can contribute to catalysis. With the deprotonated ligand and an overall cationic complex the **TS2** barrier is >30 kcal/mol, and suggest that this would not be a viable catalyst.



Scheme S1. Top: Gibbs free energy landscape of deprotonated N-H phosphinoamidine ligand and an overall neutral Cr catalyst complex with a $Cr^{I/III}$ cycle. Intermediate A and B are sextet spin and all other intermediates and TS are quartet. Bottom: Gibbs free energy landscape of deprotonated

N-H phosphinoamidine ligand and overall cationic Cr complex with a $Cr^{II/IV}$ cycle. Intermediate **A** and **B** are quintet spin and all other intermediates and TS are triplet. (kcal/mol)

N-Al

Alternative to phosphinoamidine ligand N-H deprotonation, we examined the *N*-dimethylaluminum ligand (shown below, **1c-AlMe**₂) that potentially results from MMAO exchanging an aluminum group for the N-H proton. Scheme S2 illustrates the Gibbs free energy surface with the **1c-AlMe**₂ catalyst. Not surprisingly based on the results with the anionic ligand, the **1c-AlMe**₂ energy surface is qualitatively and quantitatively very similar to the protonated N-H **1a** landscape. Again, this indicates that catalyst **1c-AlMe**₂ could also provide a computational model for productivity, and may contribute to catalysis along with **1a** and **1c**.



Scheme S2. Gibbs free energy landscape of N-dimethylaluminum substituted model. (kcal/mol) Cationic $Cr^{I/III}$ reaction channel. Intermediates **A** and **B** are sextet and all other intermediates and TS are quartet.

Ethylene Coordination

We explored all ethylene coordination structures starting with no ethylene coordinated to Cr (**0EC** shown in Scheme S3 below). All spin states were examined, and the sextet spin (S=5/2) was the lowest in energy for ethylene coordinated complexes preceding oxidative coupling. Our results are consistent with previous computational data reported by McGuinness, although McGuinness proposed sextet to quartet spin crossing is favorable with **3EC** and **4EC** coordinated complexes.¹⁰

The first ethylene coordination is favorable by 20.8 kcal/mol to form **A**. The second ethylene coordination forms **B** and is only lower in energy by 0.3 kcal/mol. These calculated coordination energies are consistent with Sydora and Abu-Omar's kinetic study indicating that only one ethylene coordination is reversible.³

We also considered oxidative coupling with additional ethylene coordination. For **3EC** the calculated barrier is 32.3 kcal/mol, which suggests it is unlikely to occur compared to **TS1**. Despite significant searching, we were unable to locate the transition state **2EC-TS1**. Ethylene coordinating to intermediate **E** is endergonic by 7.2 kcal/mol. β -hydrogen transfer with an additional ethylene coordinated (**1EC-TS3**) is 13.0 kcal/mol higher in energy than **TS3**.



Scheme S3. Ethylene coordination to Cr and alternative mechanistic pathways considered. **0EC**, **A**, and **B** are sextet spin, all other intermediates and TS are quartet. (kcal/mol)

Alternative Pathways to 1-Hexene and Alternative Products

Once the chromacycloheptane intermediate is generated, there are two possible pathways that we considered to form the 1-hexene product: β -hydrogen transfer (**TS3**) and stepwise β -hydride elimination (**TS4**) followed by reductive elimination (**TS5**), which are illustrated in Scheme S4. Consistent with previous computational studies,^{11,12} our calculations indicate that the β -hydrogen transfer pathway is the lower energy pathway to form the 1-hexene product. While **TS4** is 3.7 kcal/mol higher than **TS3**, if **G** is reached it is unlikely to produce 1-hexene through **TS5**. Instead, it will likely undergo migratory insertion **TS7** to form methylenecyclopetane **I** as the barrier is 4.4 kcal/mol lower in energy than **TS5**.



Scheme S4. Alternative mechanistic pathway to 1-hexene and alternative products. (kcal/mol)

Comparison of (P,N)Cr Energy Landscapes

Scheme S5 compares the enthalpy, Gibbs free energy, and entropy-scaled Gibbs free energy surfaces ($\Delta G_{S,corr}$) from intermediate **B** to **E** involving **TS1** and **TS2**. The major difference between these surfaces is the region surrounding **TS2**, which results from the gas-phase $-T\Delta S$ value that is potentially overestimated. Therefore, we examined the use of a 0.67 scaled ΔS term that Ziegler and co-workers¹³ demonstrated captures the entropic penalty for association and dissociation of ethylene under condensed phase catalytic conditions of Zr and Hf ethylene oligomerization reactions. The orange energy surface in Scheme S5 shows that the entropy scaling lowers the **TS2** barrier to 9.4 kcal/mol. The predicted TOF of the entropy-scaled Gibbs free energy is 250 mol 1-C₆·s⁻¹ that translates to a predicted total productivity mass of 7.6 x 10⁷ g·h⁻¹, which overestimates but is close to the experimental productivity value.



Scheme S5. Abbreviated Gibbs free energy, enthalpy, and entropy-corrected Gibbs free energy surface comparison of 1a performed at 1 atm and room temperature without pressure corrections. Intermediate **B** is sextet spin and all other intermediates and TS are quartet.

Ethylene Pressure Correction

As discussed in the main manuscript, we included ethylene pressure corrections to the calculated Gibbs free energy surfaces of **1a** because the kinetic experiments were run at high pressures of ethylene (50 bars).³

$$\Delta_r G = \Delta_r G^0 + RT \ln \frac{P_f}{P_i}$$

We also explored the ω B97X-D Gibbs free energy surface with ethylene pressure corrections shown in Scheme S6. Qualitatively, the surface is very similar to M06-L ethylene pressure corrected energy span. Scheme S6 displays the ω B97X-D energy surface. The predicted TOF is 1300 mol 1-C₆·s⁻¹ that translates to a predicted total productivity mass of 3.9 x 10⁸ g·h⁻¹ that slightly overestimates the experimental productivity.



Scheme S6. ω B97X-D pressure corrected Gibbs free energy surface. Intermediate **A** and **B** are sextet spin and all other intermediates and TS are quartet.

Ethylene Kinetic Order

Utilizing the energy span model it is possible to express the ethylene rate dependence using **A** and **B** turnover controlling intermediates and **TS1** and **TS2** as turnover controlling transition states. Each ground state-transition state pair can contribute to the total TOF and has a specific ethylene rate dependence. As an example, for the landscape shown in Scheme 4a, the following provides an estimate of 1.2 for the rate order of ethylene.

 $K_{i} = \mathbf{A} \times \mathbf{TS1}[C_{2}H_{4}]$ $K_{ii} = \mathbf{A} \times \mathbf{TS2}[C_{2}H_{4}]^{2}$ $K_{iii} = \mathbf{B} \times \mathbf{TS1}$ $K_{iv} = \mathbf{B} \times \mathbf{TS2}[C_{2}H_{4}]$ $k_{total} = (0.36 \times 0.13)[C_{2}H_{4}] + (0.36 \times 0.87)[C_{2}H_{4}]^{2} + (0.64 \times 0.13) + (0.64 \times 0.87)[C_{2}H_{4}]$ Ethylene dependent term sum: $(0.36 \times 0.13)[1] + (0.36 \times 0.87)[2] + (0.64 \times 0.87)[1] = 1.2$

Chromacyclopentane Ring Strain

We considered the stability of the chromacyclopentane intermediate as a potential impact on catalytic activity (Scheme S7). Initially we thought that the tridentate ligand $\mathbf{8}$ would lead to a more strained metallacycle. However, the Cr-C bond homolysis energy from the chromacyclopentane intermediate of $\mathbf{1a}$ was almost identical to $\mathbf{8}$ with only a 0.9 kcal/mol free energy difference. Therefore, stability of the chromacyclopentane intermediate does not affect catalyst activity.



Scheme S7. Bond homolysis energies of chromacyclopentane intermediate. Free energies in kcal/mol.

8a Amine Dissociation

To probe electronic and coordination effects that drastically slow down catalysis, we modeled catalyst **8a** with the amine arm dissociated to model a bidentate coordination environment. Scheme S8 displays the energy of amine dissociation for the mono(ethylene) coordinated intermediate A'.



Scheme S8. Energy penalty to dissociate an amine arm at the mono(ethylene) intermediate.

Considering the dissociated amine arm intermediate **A'** as the starting point of catalysis, a new Gibbs free energy surface was constructed displayed in Scheme S9. This energy span quantitatively mirrors the bidentate nature of **1a** and demonstrates the extra coordination at the Cr metal and the augmented electron density through the tridentate framework shuts down catalysis. The predicted TOF is 1.3 mol $1-C_6$ ·s⁻¹, which translates to a productivity of 3.9×10^5 g·h⁻¹.



Scheme S9. Gibbs free energy surface of dissociated amine ligand 8c. Intermediates A and B are sextet spin and all other intermediates and TS are quartet. (kcal/mol)

Spin Crossover

Bis(ethylene) coordinated Cr intermediate **B** is lowest in energy as a sextet spin state. The doublet and quartet spin states are >8 kcal/mol compared to the sextet. Oxidative coupling favors the quartet spin state while the doublet and sextet spin configurations are >8 kcal/mol relative to the quartet spin. Spin crossover facilitates catalysis by accessing lower energy intermediates and transition state barriers.



Scheme S10. Spin crossover provides lower energy pathways. Spin states in parentheses. (kcal/mol)

Truncated Models of 1a and 8a

To evaluate steric effects on activity, we computed truncated model versions of **1a** and **8a**. The energy spans of the smaller models **1b** and **8b** very closely reflected the parent compounds **1a** and **8a** respectively. The computed free energy surfaces for **1b** and **8b** are shown in Scheme S11. The energy span of **1b** is 33% and 67% controlled by **TS1** and **TS3** respectively with an overall barrier of ~14.8 kcal/mol, closely reflecting the energy span of **1a** which is 16.0 kcal/mol. For **8b**, the energy span is completely controlled by **TS2**, a barrier of 26.7 kcal/mol which closely resembles the 27.1 kcal/mol energy span of **8a**.



Scheme S11. Top: Free energy landscape for steric model. Intermediates A and B are sextet spin and all other intermediates and TS are quartet. **1b**. Bottom: Free energy landscape for **8b**. All intermediates and TS are quartet. (kcal/mol)











Scheme S12. Gibbs free energy surfaces at 298 K, 1 atm, and with solvents defined in Table S1. Complex 2, 5, 6: Intermediates A and B are sextet spin and all other intermediates and TS are quartet. Complex 3, 4, 7: All intermediates and TS are quartet. (kcal/mol)

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