

S U P P O R T I N G I N F O R M A T I O N

A Test of the Transition-Metal Nanocluster Formation and Stabilization Ability of the Most Common Polymeric Stabilizer, Poly(vinylpyrrolidone), As Well As Four Other Polymeric Protectants

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Nanocluster Preparation from [(1,5-COD)Ir(CH₃CN)₂][BF₄] With and Without Added PVP at Higher Concentrations. As noted in the main text, these experiments were carried out at higher concentrations (3.5 mM instead of the 1.2 mM concentration used for the reactions run with [Bu₄N]₅Na₃(1,5-COD)Ir•P₂W₁₅Nb₃O₆₂), to avoid significant weighing and balance errors. In order to be sure that the 5 criteria were within error for both concentrations (and therefore the 3.5 mM data set would be comparable to the 1.2 mM data for reactions with the [Bu₄N]₅Na₃(1,5-COD)Ir•P₂W₁₅Nb₃O₆₂ precursor), the 5 criteria were evaluated for with 40 equivalents of dried MW_{ave}=10,000 g/mol PVP at both 1.2 mM and 3.5 mM [Bu₄N]₅Na₃(1,5-COD)Ir•P₂W₁₅Nb₃O₆₂ precursor.

Table S1. Compilation of the data for 1.2 and 3.5 mM [Bu₄N]₅Na₃(1,5-COD)Ir•P₂W₁₅Nb₃O₆₂ precursor.

Precursor	Polymer	Conc. (mM)	k ₂ /k ₁ ^a	Size (Å)	Redisp ?	Catalytic Activity ^b	TTO ^c
[(1,5-COD)Ir(CH ₃ CN) ₂][BF ₄]	dried, 10k	1.2	6.7(5)x10 ³	agg.	yes	6.0(3)x10 ⁵	[12,000]
[(1,5-COD)Ir(CH ₃ CN) ₂][BF ₄]	dried, 10k	3.5	8.6(4)x10 ³	agg.	yes	6.2(3)x10 ⁵	[13,000]

(a) The k₂ values which are part of this ratio are corrected by the mathematically required stoichiometry factor of 1400 as detailed elsewhere.¹ (b) mmol h⁻¹ mol Ir⁻¹. (c) Due to the formation of bulk metal, the values in [] brackets are upper limits to the true nanoparticle TTOS.

As shown in Table S1, the two concentrations yield data within error of each other as measured by the 5 criteria. Consequently, an accurate comparison may be made between the systems with an initial [Bu₄N]₅Na₃(1,5-COD)Ir•P₂W₁₅Nb₃O₆₂ concentration of 1.2 mM and the PVP systems with initial [(1,5-COD)Ir(CH₃CN)₂][BF₄] concentration of 3.5 mM.

¹ Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382.

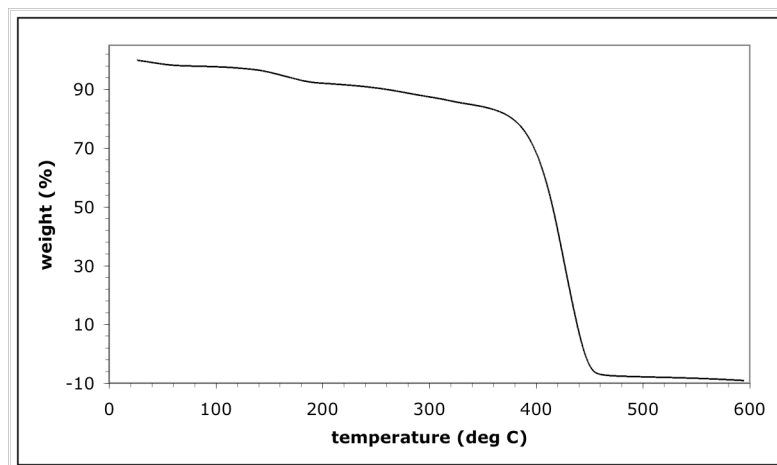


Figure S1. Thermal gravimetric analysis (TGA) of as-received $MW_{ave}=10,000$ g/mol PVP. A 2.2% weight loss is observed up to 100 °C, corresponding to 0.14 mol H_2O per mol PVP. This, in turn, corresponds to 11 equivalents H_2O per Ir atom when 40 eqv of $MW_{ave}=10,000$ g/mol PVP per eqv Ir is used. This and the evidence in the main text shows that commercially obtained PVP should be dried before use in nanocluster syntheses.

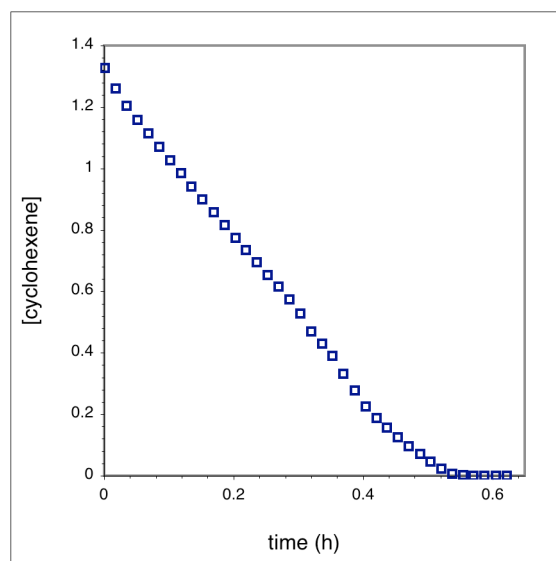


Figure S2. Kinetic curve for hydrogenation of cyclohexene in propylene carbonate by [(1,5-COD)Ir(CH₃CN)₂][BF₄] in the presence of 40 equivalents of dried MW_{ave}=3,500 g/mol PVP.

This curve cannot be fit to the established autocatalytic nanocluster formation mechanism, $A \rightarrow B$, then $A+B \rightarrow 2B$. A significant, nucleation-rate-increasing effect appears to be present as indicated by the loss of the induction period (i.e., the apparent increase in k_1).

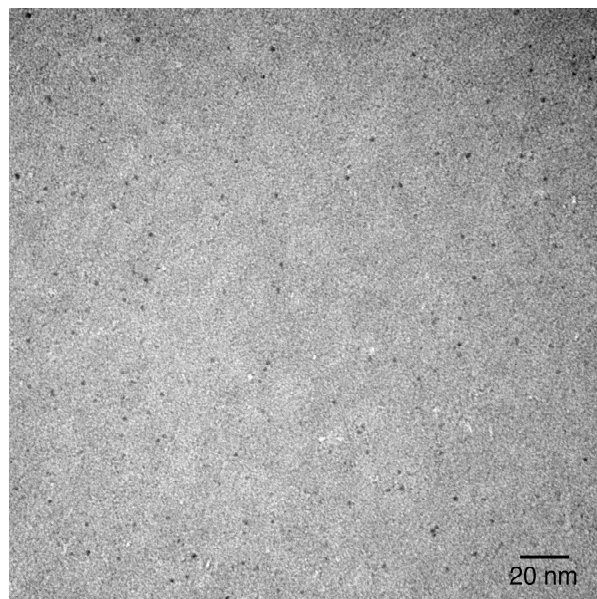


Figure S3. TEM of Ir(0) nanoclusters formed under the conditions in entry 9 of Table 1, namely $[\text{Bu}_4\text{N}]_5\text{Na}_3(1,5\text{-COD})\text{Ir}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ under 40 psig H_2 in the presence of dried 10,000 g/mol PVP. These nanoclusters are well separated and show a near-monodisperse size distribution of $\pm 14\%$.

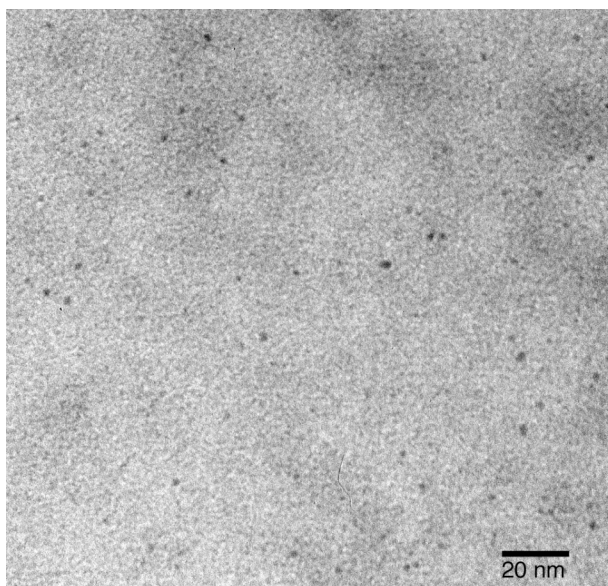


Figure S4. TEM of Ir(0) nanoclusters formed under the conditions in entry 10 of Table 1, namely $[\text{Bu}_4\text{N}]_5\text{Na}_3(1,5\text{-COD})\text{Ir}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ under 40 psig H_2 in the presence of undried 10,000 g/mol PVP. The nanoclusters display a larger, $\pm 29\%$ size distribution than the nanoclusters in Figure S3.

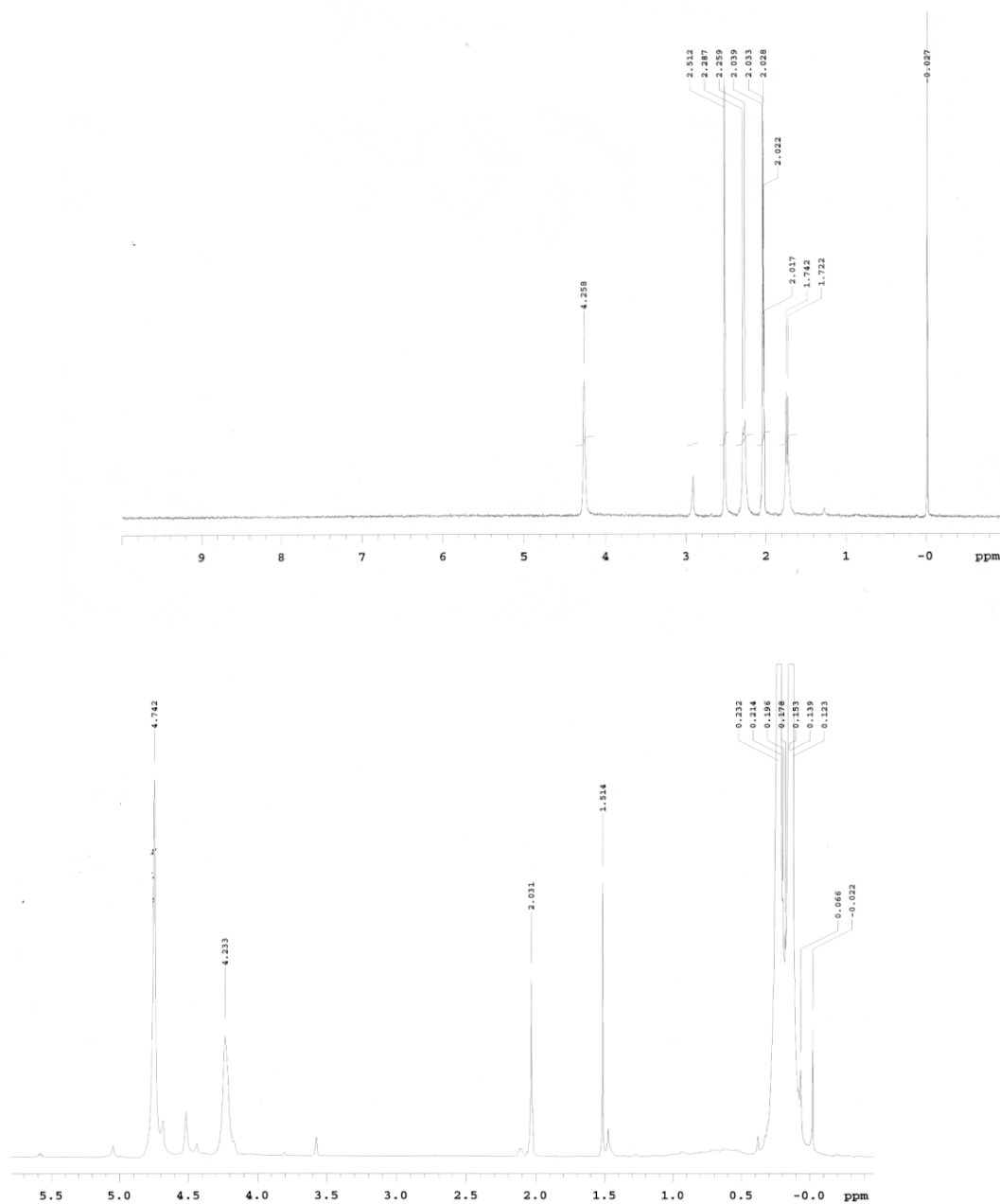


Figure S5. ^1H NMR spectra of $[(1,5\text{-COD})\text{Ir}(\text{CH}_3\text{CN})_2][\text{BF}_4]$ before (top) and after (bottom) the addition of 40 equivalents of undried PMHS. Among other changes, the vinylic protons present at $\delta=2.5$ in the top spectrum are not present in the bottom spectrum. This indicates a reaction between $[(1,5\text{-COD})\text{Ir}(\text{CH}_3\text{CN})_2][\text{BF}_4]$ and the 40 equivalents of undried PMHS.