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Hydrocarbon-Soluble, Isolable Ziegler-Type $Ir(0)_n$ Nanoparticle Catalysts Made from $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ and 2−5 Equivalents of $AlEt_3$: Their High Catalytic Activity, Long Lifetime, and $AlEt_3$-Dependent, Exceptional, 200 °C Thermal Stability

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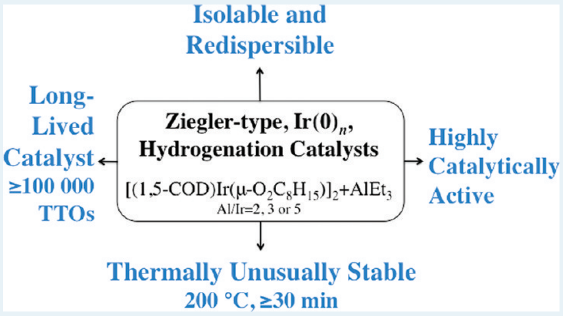
Supporting Information



ABSTRACT: Hydrocarbon-solvent-soluble, isolable, Ziegler-type $Ir(0)_n$ nanoparticle hydrogenation catalysts made from the crystallographically characterized $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ precatalyst and 2−5 equiv of $AlEt_3$ (≥2 equiv of $AlEt_3$ being required for the best catalysis and stability, vide infra) are scrutinized for their catalytic properties of (1) their isolability and then redispersibility without visible formation of bulk metal; (2) their initial catalytic activity of the isolated nanoparticle catalyst redispersed in cyclohexane; (3) their catalytic lifetime in terms of total turnovers (TTOs) of cyclohexene hydrogenation; and then also and unusually (4) their relative thermal stability in hydrocarbon solution at 200 °C for 30 min. These studies are of interest since $Ir(0)_n$ nanoparticles are the currently best-characterized example, and a model/analogue, of industrial Ziegler-type hydrogenation catalysts made, for example, from $Co(O_2CR)_2$ and ≥2 equiv of $AlEt_3$. Eight important insights result from the present studies, the highlights of which are that $Ir(0)_n$ Ziegler-type nanoparticles, made from $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ and $AlEt_3$, are (i) quite catalytically active and long-lived; (ii) thermally unusually stable nanoparticle catalysts at 200 °C, vide infra, a stability which requires the addition of at least 3 equiv of $AlEt_3$ ($Al/Ir = 3$), but where (iii) the $Al/Ir = 5$ $Ir(0)_n$ nanoparticles are even more stable, for ≥30 min at 200 °C, and exhibit 100 000 TTOs of cyclohexene hydrogenation. The results also reveal that (iv) the observed nanoparticle catalyst stability at 200 °C appears to surpass that of any other demonstrated nanoparticle catalyst in the literature, those reports being limited to ≤130−160 °C temperatures; and reveal that (v) $AlEt_3$, or possibly surface derivatives of $AlEt_3$, along with $[RCO_2{\cdot}AlEt_3]^-$ formed from the first equiv of $AlEt_3$ per 1/2 equiv of $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ are main components of the nanoparticle stabilizer system, consistent with previous suggestions from Shmidt, Goulon, Bönnemann, and others. The results therefore also (vi) imply that either (a) a still poorly understood mode of nanoparticle stabilization by alkyl Lewis acids such as $AlEt_3$ is present or, (b) that reactions between the $Ir(0)_n$ and $AlEt_3$ occur to give initially surface species such as $(Ir_{surface})_x{-}Et$ plus $(Ir_{surface})_x{-}Al(Et)_2Ir$, where the number of surface Ir atoms involved, $x = 1{-}4$; and (vii) confirm the literature's suggestion that the activity of Ziegler-type hydrogenation can be tuned by the Al/Ir ratio. Finally and perhaps most importantly, the results herein along with recent literature make apparent (viii) that isolable, hydrocarbon soluble, Lewis-acid containing, Ziegler-type nanoparticles are an underexploited, still not well understood type of high catalytic activity, long lifetime, and unusually if not unprecedentedly high thermal stability nanoparticles for exploitation in catalysis or other applications where their unusual hydrocarbon solubility and thermal stability might be advantageous.

KEYWORDS: *Ziegler-type nanoparticle catalysis, Ir(0) nanoparticles, stabilization, olefin hydrogenation*

INTRODUCTION

Ziegler-type, hydrocarbon-solvent-soluble hydrogenation catalysts are formed, by definition,[1] from a nonzero valent group 8−10 transition metal precatalyst such as the industrial example[1,2] of $Co(neodecanoate)_2$ plus a trialkylaluminum cocatalyst, for example, $AlEt_3$. These catalysts are used industrially to produce hydrogenated styrenic block copolymers at a level of ~1.7 × 10^5 metric tons/year.[2,3] Ziegler-type hydrogenation catalysts made from third-row elements of the same column metal (i.e., Ir as an analogue of Co Ziegler-type hydrogenation catalysts) are also important,[1] such third-row metals allowing more robust, more easily characterized catalysts.[4]

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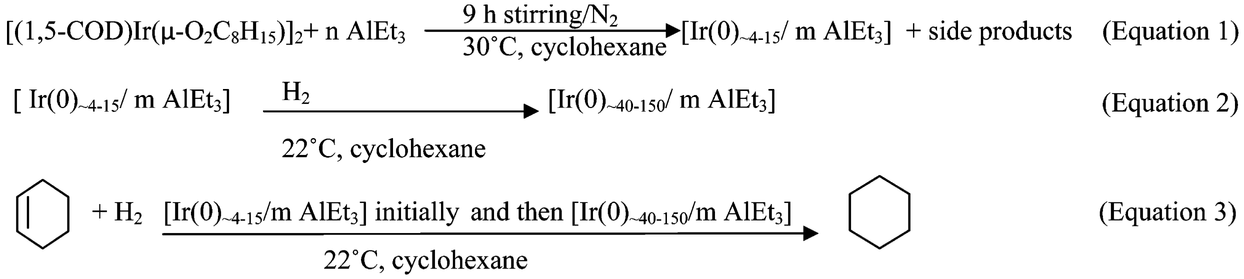
Scheme 1. Ziegler-Type Hydrogenation Catalyst Preparation, and Subsequent Cyclohexene Hydrogenation, from $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ Plus $AlEt_3$, Al/Ir = 2, 3, or 5[a]



$$[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2 + n\,AlEt_3 \xrightarrow[30^\circ C,\ \text{cyclohexane}]{9\text{ h stirring}/N_2} [Ir(0)_{\sim 4\text{-}15}/\,m\,AlEt_3] + \text{side products} \quad \text{(Equation 1)}$$

$$[Ir(0)_{\sim 4\text{-}15}/\,m\,AlEt_3] \xrightarrow[22^\circ C,\ \text{cyclohexane}]{H_2} [Ir(0)_{\sim 40\text{-}150}/\,m\,AlEt_3] \quad \text{(Equation 2)}$$

$$+\,H_2 \xrightarrow[22^\circ C,\ \text{cyclohexane}]{[Ir(0)_{\sim 4\text{-}15}/m\,AlEt_3]\ \text{initially and then}\ [Ir(0)_{\sim 40\text{-}150}/m\,AlEt_3]} \quad \text{(Equation 3)}$$

[a] Conditions for catalyst preparation (eq 1) are cyclohexane solvent, [Ir] = 1.4 mM, 30°C, N_2 atmosphere. Conditions for cyclohexene hydrogenation (eqs. 2 and 3) are cyclohexane solvent, [Ir] = 1.2 mM (except where noted otherwise), $[\text{cyclohexene}]_{\text{initial}}$ = 1.65 M, 22.0 ± 0.1 °C, 40 ± 1 psig H_2. The side products in eq 1 include 1,5-COD, $O_2C_8H_{15}^-$, and $(n - m)$ $AlEt_3$ $(n \geq m)$ or their combinations.

We recently reported high activity Ziegler-type nanoparticle hydrogenation catalysts made from the crystallographically characterized $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ precatalyst[3] plus $AlEt_3$, Al/Ir = 1, 2, 3, or 5,[4] Scheme 1. (An Al/Ir = 1 catalyst means 1 equiv of $AlEt_3$ is added per Ir, i.e., 1 equiv of $AlEt_3$ is added to 0.5 equiv of the $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ precatalyst dimer). Subsequent studies, using X-ray absorption fine structure spectroscopy (XAFS), Z-contrast scanning transmission electron microscopy (STEM) plus matrix assisted laser desorption ionization mass spectroscopy (MALDI MS), revealed that subnanometer particles of an estimated mean-size range of $Ir(0)_{\sim 4-15}$ are formed initially as a result of simply mixing $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$ at Al/Ir = 1, 2, 3, or 5 (Scheme 1, eq 1). Regardless of the Al/Ir ratio examined (Al/Ir = 1−5) or the initial [Ir] concentration ([Ir] = 1.0−7.0 mM), the initially formed $Ir(0)_{\sim 4-15}$ particles were then shown to transform under H_2/cyclohexene hydrogenation catalysis conditions (Scheme 1, eq 2),[4] to $Ir(0)_{\sim 40-150}$ Ziegler-type nanoparticles[5−8] according to XAFS, STEM and MALDI MS characterization results—a new, hydrocarbon soluble, AlR_3-dependent type of catalytically active nanoparticle,[1,4] vide infra. Concomitant with this transformation to *fcc* $Ir(0)_{\sim 40-150}$ Ziegler-type nanoparticles, an increase in the catalytic activity in cyclohexene hydrogenation is observed.[4] The combined kinetic, plus XAFS, STEM, and MALDI MS characterization, studies both before and after catalysis provide the best evidence to date that Ziegler-type $Ir(0)_n$ nanoparticles both exist and appear to be the fastest catalysts in Ziegler-type hydrogenations.[1,4] The finding of kinetically dominant catalysis by Ziegler-type nanoparticles is significant since it answers a 50-year old question about the nature of the true catalyst under Ziegler hydrogenation catalysis conditions.[1] Indeed, nanoparticles (or, when these catalysts were first discovered, "colloids"[9−21]) have been discussed as the possible true catalysts for 50 years now, but definitive demonstration that Ziegler-type nanoparticles are both present and are the most active catalysts in Ziegler-type hydrogenation catalysis[1,2] was previously lacking.[1,4]

The Ziegler-type nanoparticle catalysts are unusual in that they are hydrocarbon soluble. They are further unusual as at least ostensibly an example of "weakly ligated/labile-ligand nanoparticles",[5−7,22] in this case nanoparticles in which the only possible ligands are cyclohexane, $AlEt_3$ Lewis acid (or its nanoparticle surface-derivatives), carboxylates such as $C_7H_{15}CO_2^-$ and H_2 (and/or metal hydrides) plus cyclohexene. All these are either relatively weak ligands, or the actual reagents of the desired reaction (H_2 plus cyclohexene hydrogenations), other than the $AlEt_3$ (and the combination $[C_7H_{15}CO_2\cdot AlEt_3]^-$ for the first equivalent of $AlEt_3$ per $1/2$ $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$, eq 1, vide supra). Significantly, the high stability of the $Ir(0)_n$ nanoparticles reported herein at ratios ≥2 of $AlEt_3$ per $1/2[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ would seem to indicate a robust interaction between the $Ir(0)_n$ nanoparticle and the $AlEt_3$, vide infra. Restated, Ziegler-type nanoparticles appear to be an unusual type of little recognized, and hence underexploited, nanoparticle catalyst, ones used industrially but hidden for a 50-year period because of a lack of knowledge of the probable true catalyst.[1,2]

It became, therefore, of significant interest to examine the catalytic activity, lifetime, and thermal stability of these hydrocarbon soluble, $Ir(0)_n$ Ziegler-type nanoparticles, as a function of the Al/Ir molar ratio of the $AlEt_3$ cocatalyst and Ir metal precatalyst.[1] Just how active, long-lived, and thermally stable are these unusual, hydrocarbon soluble, AlR_3 containing nanoparticles? Relevant here is the previously developed, so-called "five-criteria method"[23−26] to rank the formation and then stabilizing abilities of various anions, solvents, cations, and polymers for catalytically active nanoparticles, a method developed specifically with $Ir(0)_n$ nanoparticles.[27]

Herein, a necessarily modified version[28] of the five-criteria ranking method[23−27] is developed and then used to evaluate the catalytic properties of the $Ir(0)_n$ Ziegler-type nanoparticle hydrogenation catalysts made from $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$, as a function of Al/Ir ratios from primarily 2−5 (with 0−1 being examined in control reactions). Those modified evaluation criteria used herein are (i) the isolability and then redispersibility of the resultant nanoparticle catalyst without visible formation of bulk metal—historically a demanding test of nanoparticle stability;[23−26] (ii) the initial catalytic activity of the isolated catalyst redispersed in cyclohexane; (iii) the catalytic lifetime; and then also (iv) the thermal stability of the catalyst solution as determined by the ability of the stabilizing species to keep the nanoparticles in solution at 200 °C for 30 min without the visible formation of bulk metal. The enhanced (vide infra) thermal stability of the Ziegler-type nanoparticle catalyst solutions is important, since industrial applications of Ziegler-type hydrogenation catalysts report catalyst preparation temperatures up to 250 °C, and then polymer hydrogenations up to 180 °C.[1,29,30] However, no prior study has examined the thermal stability of a firmly established Ziegler-type nanoparticle catalyst, in our case an $Ir(0)_n$ catalyst, under controlled conditions.

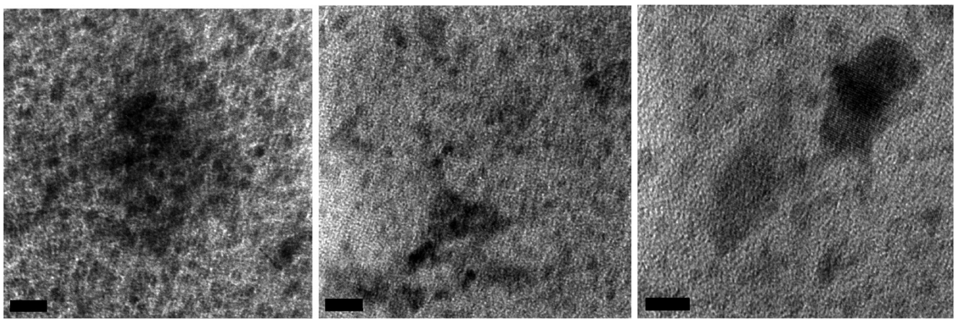


Figure 1. Representative TEM images for the Al/Ir = 2, 3, and 5 catalysts taken from cyclohexane solutions of initially isolated, but then redispersed, catalysts prepared with $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$, Al/Ir = 2 (left), Al/Ir = 3 (middle) and Al/Ir = 5 (right). The scale bar is 5 nm in each case. The images show nanoparticles with equivalent average sizes within experimental error of 1.4 ± 0.7 nm (left), 1.5 ± 0.5 nm (middle), and 1.7 ± 0.4 nm (right) for the respective Al/Ir = 2, 3, and 5 catalysts.

Table 1. Compilation of Data for the Ziegler-Type Hydrogenation Catalysts Made from $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ Plus $AlEt_3$[a]

entry	Al/Ir ratio	redispersibility in cyclohexane[b]	catalytic activity of the redispersed catalyst (mmol H_2/h)[c,d]	TTO[c,e]	TOF_{ave}[c,e] (TTO/time) (h^{-1})	appearance after heating at 200 °C	catalytic activity at 22 °C after heating at 200 °C (mmol H_2/h)[f,g]	appearance after hydrogenation of the 200 °C treated catalyst
1	2	yes	10(3)	180 000	3500	brown solution, black particles	24(9)	brown solution, black particles
2	3	yes	7(2)	155 000	1100	brown solution, brown particles	5(4)	brown solution, black particles
3	5	yes	3(1)	100 000	700	clear, brown solution	6(4)	*clear, brown solution*
			Lower Al/Ir Ratios—Controls Studying Less Stable Catalysts					
4	1	partially	19(4)	[370 000][h]	3600	colorless solution, black particles	25(5)	gray solution, black particles
5	0	no	ND[i]	[230 000][h]	2600	ND	ND	ND

[a] Conditions for all hydrogenations are as follows: cyclohexane solvent; [Ir] = 1.2 mM; $[\text{cyclohexene}]_{initial}$ = 1.65 M; 22.0 ± 0.1 °C; and 40 ± 1 psig H_2, unless otherwise noted. The catalytic activity data given in the table are the average of three separate hydrogenation runs carried out under identical conditions. For the data shown in the format "$x(y)$", x = the average of three separate runs, and y = the standard deviation (1σ) of those 3 runs. [b] "Yes" means all the isolated material dissolved (i.e., no undissolved particles remained in the medium). "Partially" means some visually observable particles are present in the solution after redispersion. [c] Measured in cyclohexane solvent. The reported values are uncorrected for the number of surface atoms and, therefore, are lower limits to the true TTOs and TOFs per available surface active site. [d] Initial rate. [e] A 60-fold lower concentration of Ir ([Ir] = 0.02 mM was used for the TTO and TOF_{ave} measurements vs the [Ir] = 1.2 mM for catalytic activity or other measurements in columns 4, 7, 8, and 9). Hence, the size and n value of these $\text{Ir}(0)_n$ nanoclusters may be somewhat different than those in columns 4, 7, 8, and 9, although our prior work shows that concentrations from [Ir] = 1.0 to 7.0 mM yield $\text{Ir}(0)_{\sim 40-150}$ nanoparticles.[4] [f] Maximum catalytic rate observed during the corresponding hydrogenation. [g] Measured in dodecane solvent. [h] The "partial" to "no" redispersibility for these control study entries with 0−1 equiv of $AlEt_3$ means that the TTO values are not just for nanoparticles (i.e., reflect significant contributions from bulk metal) and, therefore, are placed in [brackets]. [i] ND: Not determinable.

■ RESULTS AND DISCUSSION

$\text{Ir}(0)_{\sim 40-150}$ "Ziegler Nanoparticle" Catalyst Synthesis and Cyclohexene Hydrogenation. Our review of the literature of Ziegler-type catalysis[1] reveals that the following variables have significant effects on the catalytic activity and other properties of the catalyst:[4] the Al/Ir ratio; the order and rate of addition of the precatalyst and cocatalyst; the solvent used; aging of the initial catalyst material; and whether or not the olefin substrate is present during the initial precatalyst and cocatalyst addition step. Hence, and as detailed in the Experimental Section and based on our published experience,[4] the Ziegler-type $\text{Ir}(0)_n/AlEt_3$ hydrogenation catalysts were prepared from $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ and $AlEt_3$, by adding quickly (over 2 s) a cyclohexane solution of $AlEt_3$ to a cyclohexane solution of $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$, all while vigorously stirring at 30 °C under N_2. This resultant solution was then aged[1,4] by further stirring for 9 h under N_2 at 30 °C (Scheme 1, eq 1).

Cyclohexene hydrogenation was used as a test reaction to measure the activity and lifetime of $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$, Al/Ir = 2, 3, or 5, catalysts, Scheme 1, eqs 2 and 3. These catalysts were also tested for their thermal stability by first preparing the catalyst solution in dodecane solvent and then performing a cyclohexene hydrogenation at room temperature. The resulting catalyst solution was then kept at 200 °C for 30 min, followed by a test of cyclohexene hydrogenation activity back at room temperature of the resultant, thermalized nanoparticles. The transmission electron microscopy (TEM) images of the post catalyst samples were also obtained, vide infra.

Redispersibility, Catalytic Activity, and Lifetime in Cyclohexane of Ziegler-Type Hydrogenation Catalysts Made from $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ Plus $AlEt_3$, Al/Ir = 2, 3, or 5. All three catalysts made from $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ and

$AlEt_3$, Al/Ir = 2, 3, or 5, are isolable as brown/black powders by evaporation of the volatiles under vacuum. The isolated catalysts are then fully redispersible in cyclohexane hydrocarbon solvent without visible formation of bulk metal, Figure 1 (Table 1, entries 1−3, column 3).[31]

For the redispersed catalysts (Al/Ir = 2, 3, or 5), hydrogenations start immediately and continue in a slightly sigmoidal fashion until consumption of the cyclohexene is complete, Figure 2, with catalytic activities of 10(3), 7(2) and 3(1) mmol H_2/h[32] for the Al/Ir = 2, 3, and 5 catalysts, respectively (Table 1, entries 1−3, column 4). The TEM results in Figure 1 show that the redispersed $Ir(0)_n$ Ziegler-type catalysts for the Al/Ir = 2 and Al/Ir = 5 ratios are the same size within experimental error as those synthesized as described above and then used in cyclohexene hydrogenation.[4] The Al/Ir = 2, 3, or 5 catalysts provide 180 000, 155 000 and 100 000 turnovers over the course of 52 h, 144 and 150 h, respectively, with average TOF (= TTO/total time before deactivation) of the rather high values of 3500, 1100, and 700 h^{-1}, respectively, before deactivation (Table 1, entries 1−3, columns 5 and 6).

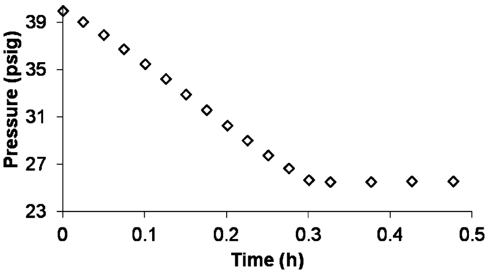


Figure 2. Plot of the H_2 pressure vs time data for cyclohexene hydrogenations starting from $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$, Al/Ir = 2, catalyst after it was isolated and redispersed in cyclohexane. Conditions for hydrogenations are as follows: cyclohexane solvent; [Ir] = 1.2 mM; $[\text{cyclohexene}]_{\text{initial}}$ = 1.65 M; 22.0 ± 0.1 °C; and 40 ± 1 psig H_2.

Comparison to Earlier Literature $Ir(0)_n$ Nanoparticle Catalysis Data. The observed hydrogenation activities of the redispersed Al/Ir = 2, 3, and 5 catalysts (Table 1, entries 1−3) are as high as (and in some cases higher than) any previously reported $Ir(0)_n$ nanoparticle catalysts (Table 2, Entries 1−6),[24−26,33,34] comparisons made under identical conditions of precatalyst and cyclohexene concentration as well as initial H_2 pressure (but, necessarily, involving a solvent change from cyclohexane for the data in Table 1 vs acetone for the data in Table 2). In addition, the lifetimes of catalysts made with Al/Ir = 2 and Al/Ir = 3, 180 000 and 155 000 turnovers, respectively, are longer than those of all other $Ir(0)_n$ nanoparticle catalyst systems previously ranked via the five-criteria method (Table 2, Entries 1−6, column 5).[24−26,33] In short, the Ziegler-type hydrogenation catalysts made with 2, 3, or 5 equiv of $AlEt_3$ are high activity, and longer lifetime, $Ir(0)_n$ nanoparticle catalysts, in comparison to previously reported $Ir(0)_n$ nanoparticle catalysts.

Thermal Stability in Dodecane at 200 °C. The Ziegler-type hydrogenation catalysts made from $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$, prepared in dodecane[35] (boiling point: 215 °C) and aged in solution for 9 h, were tested for their stability against agglomeration at 200 °C for 30 min (see the Supporting Information, Figure S3, for a representative hydrogenation curve using the heat-treated catalyst).[36] Importantly, using a high Al/Ir ratio up to 5 has a significant effect on the thermal stability of the resulting Ziegler-type hydrogenation catalyst, inhibiting agglomeration even after heating at 200 °C for 30 min. In comparison, the Al/Ir = 2 catalyst contained visually observable black bulk metal in a brown solution at the end of 30 min heating at 200 °C (Table 1, entry 1, column 7). Cyclohexene hydrogenation[37] with that Al/Ir = 2, 200 °C thermally treated catalyst revealed a still brown solution, but visually observable black bulk (Table 1, entry 2, column 9) verified by TEM, Figure 3. Heating the Al/Ir = 3 catalyst solution at 200 °C results in the appearance of brown Ir(0) particles (as verified by XPS, Supporting Information, Figure S5) in a brown solution (Table 1, entry 2, column 7), the brown particles being indicative of precipitated $Ir(0)_n$ nanoparticles.[38,39] At the end of the subsequent hydrogenation using the heat-treated Al/Ir = 3 catalyst, black Ir(0) bulk is again visually observable in the solution (Table 1, entry 2, column 9), a product again verified by TEM, Figure 4.

In contrast, the Al/Ir = 5 catalyst remains clear brown both at the end of the 30 min at 200 °C and at the end of the subsequent hydrogenation (Table 1, Entry 3, columns 7 and 9, Figure 5). These observations are significant, as they reveal that at a Al/Ir = 5 ratio, the $AlEt_3$ stabilizer (i.e., plus any nanoparticle surface species derived from the $AlEt_3$) are able to stabilize the $Ir(0)_n$ nanoparticles in solution sufficiently to prevent the formation of bulk metal even after 200 °C heating and subsequent hydrogenation catalysis. The results reveal the high thermal stability of at least $Ir(0)_n$ Ziegler-type nanoparticle catalysts along with the key role of the higher Al/Ir ratio in achieving that stability. Significantly, the $Ir(0)_n/AlEt_3$ nanoparticle catalysts appear to be more thermally stable[40,41] vs any

Table 2. Summary of Key Literature Data for $Ir(0)_n$ Nanoparticle Catalysts in Solution[a]

entry	catalyst system	redispersibility in acetone	catalytic activity of redispersed catalyst (mmol H_2/h)	TTO	ref
1	$[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ + $[Bu_4N]_2HPO_4$ + 1 equiv of PS[a]	yes	5(1)	53 000	25
2	$[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ + $[Bu_4N]_{(8n+1)}[P_2W_{15}(TiOH)_3O_{59}]_n$ + 1 equiv of PS	yes	2.3(2)	29 000	24
3	$[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ + $[Bu_4N]C_2H_3O_2$	partial	0.9(2)	[81 000]	24
4	$[Bu_4N]_5Na_3[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]$ + 1 equiv of PS	yes	2.2(2)	68 000	24, 33
5	$\{[(1,5\text{-COD})Ir{\cdot}HPO_4]\}_n$ + 1 equiv of PS	yes	0.8(1)	[150 000]	25
6	$[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ + 1 equiv of $[Bu_4N]_9\{H[P_2W_{17}O_{61}]\}$ + 1 equiv of PS	yes	0.6(1)	71 000	26

[a] Conditions for all hydrogenations are as follows: acetone solvent; [Ir] = 1.2 mM; $[\text{cyclohexene}]_{\text{initial}}$ = 1.65 M; 22.0 ± 0.1 °C; and 40 ± 1 psig H_2 initially. PS: Proton Sponge, 1,8-bis(dimethylamino)naphthalene. TTO values given in [brackets] are upper limits to the TTOs due solely to nanoparticles because of the presence of bulk metal.

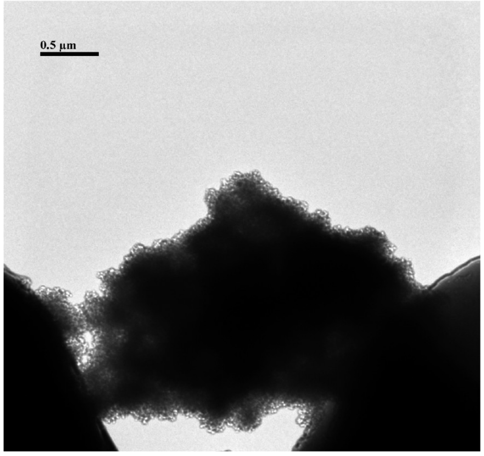


Figure 3. Bright-field TEM image on a sample of the Al/Ir = 2 Ziegler-type hydrogenation catalyst made from $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$, heat-treated at 200 °C, and then a drop of solution was withdrawn from the reaction's culture tube at the end of hydrogenation catalysis and placed on a TEM grid. The image shows bulk Ir metal (note the 0.5 μm = 500 nm scale bar).

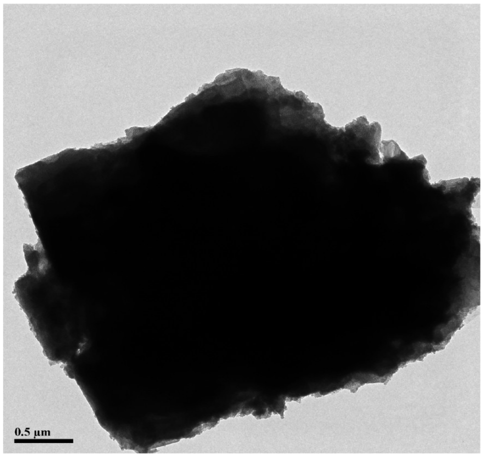


Figure 4. Bright-field TEM image on a sample of the Al/Ir = 3 Ziegler-type hydrogenation catalyst made from $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$, heat-treated at 200 °C, and then a drop of solution was withdrawn from the reaction's culture tube at the end of hydrogenation catalysis and placed on a TEM grid. The image shows bulk Ir metal (note the 0.5 μm = 500 nm scale bar).

demonstrated soluble nanoparticle catalyst that at least we can find in the current literature. Previous reports of the highest thermal stability of solutions of claimed nanoparticle catalysts appear to be limited to the ≤130−160 °C range[42−51]—although it should be noted that those reports typically lack the type of strong evidence provided elsewhere that the $\text{Ir}(0)_n$ Ziegler-type nanoparticles studied herein are the true catalysts.[4]

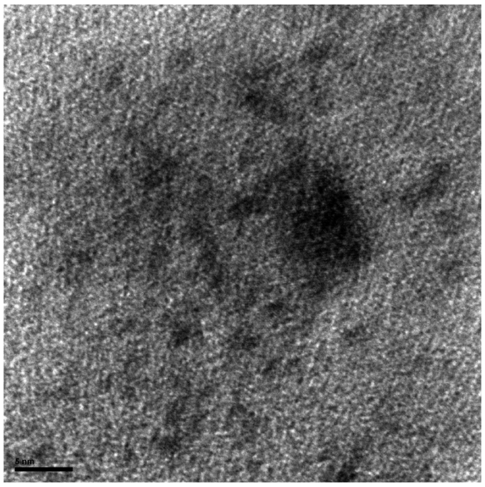


Figure 5. TEM image taken from a homogeneously appearing cyclohexane solution of catalyst prepared with $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$, Al/Ir = 5, after hydrogenation with heat-treated catalyst. The image shows nanoparticles of 1.9 ± 0.3 nm, that is, on average $\text{Ir}_{\sim 250}$, with no evidence for bulk metal (the scale bar is 5 nm).

Control Studies with the Al/Ir = 1 and Al/Ir = 0 Catalysts. The following three observations with an Al/Ir = 1 catalyst show that >1 equiv of $AlEt_3$ per Ir is required to obtain a highly stable catalyst. Specifically, for the Al/Ir = 1 catalyst (i) there are visually observable black particles of bulk Ir(0) in the brown solution and on the stirbar after cyclohexene hydrogenation; (ii) there is only a partial redispersibility in cyclohexane of the isolated catalyst (i.e., isolated by removing the volatiles under vacuum to give a brown suspension, but one with visually observable, bulk-metal particles) (Table 1, entry 4, column 3); and (iii) there are visually observable black particles after 30 min of heating at 200 °C in dodecane, which also yields a colorless, and therefore nanoparticle-free, solution (Table 1, entry 4, column 7). Furthermore, the presence of bulk metal in the postcatalysis solution of the Al/Ir = 1 catalyst means that the relatively high TTO value of [370 000] over the course of 104 h at 22.0 ± 0.1 °C contains a significant contribution from bulk metal (see the Supporting Information for a more detailed discussion on the Al/Ir = 1 catalyst). Control experiments with the Al/Ir = 0 catalyst confirms that the initially formed $\text{Ir}(0)_n$ nanoparticles are unstable against agglomeration in the absence of $AlEt_3$: a clear, colorless, and therefore nanoparticle free solution with visually observable black bulk Ir metal results (see the Supporting Information for a more detailed discussion of the Al/Ir = 0 catalyst).

The results make clear the stability enhancing effects of added $AlEt_3$. The ability of Lewis acids to stabilize nanoparticles has general, albeit not well understood, precedent in the studies of Shmidt,[52−55] Goulon,[56] and Bönnemann[57−61] as detailed on pp 13−17 of our 2010 review.[1] What remains poorly understood, in comparison to what is known in a review of nanoparticle stabilization,[22] is why Lewis acids such as $AlEt_3$—even if in combination with the RCO_2^- component of the precatalyst to make the anionic (i.e., DLVO-theory type[22]) stabilizer $[RCO_2\cdot AlEt_3]^-$—are anywhere near as effective a nanoparticle stabilizer as is observed.

The fact that the stabilization is highest at higher (e.g., 5:1) Al/Ir ratios (i.e., 4 equiv beyond the 1 RCO_2^- present, and thus beyond the consumption of 1 $AlEt_3$, to make 1 equiv of $[RCO_2\cdot AlEt_3]^-$) implies, significantly, the little appreciated hypothesis that the Lewis acidic $AlEt_3$ alone appears to be a good stabilizer,[62−64] although again Shmidt's pioneering work[52−55] provides early evidence for this hypothesis if that work is carefully examined (see the discussion on p 13 elsewhere[1]). It is presently unknown whether the stability enhancing, concomitantly rate decreasing, effects of added $AlEt_3$ are simply indicating that $AlEt_3$ is binding at the catalytically active site,[65] or if there is some other more complex phenomenon involved (e.g., some structural or compositional change, or both, induced by the added excess AlEt$_3$[4,66,67]. Noteworthy here is that one can envisage Ir$_n$:→AlEt$_3$ species (where a Al−Et→Ir dative bond back to the Ir$_n$ surface may be a key, additional component of that bonding). Also conceivable are the formation of surface species such as (Ir$_{\text{surface}}$)$_x$-Et plus (Ir$_{\text{surface}}$)$_x$-Al(Et)$_2$Ir where the number of surface Ir atoms involved could be x = 1, 2, 3, or 4, for example, as well as (Ir$_{\text{surface}}$)$_x$-H hydrides from β-H elimination from any putative (Ir$_{\text{surface}}$)$_x$-Et. Hence, one important finding of the present work and the work of Shmidt,[52−55] Goulon,[56] Bönnemann[57−61] and others discussed elsewhere[1] is that future studies of AlR$_3$-stabilized nanoparticles are of considerable interest. The needed studies of the surface composition of Ziegler-type nanoparticles promise to be challenging, however.

Reflection on the observations uncovered by this research suggests several hypotheses for future research, specifically: (i) that either the expected to be electrophilic, Lewis acidic Ir(0)$_n$ surface is much more strongly stabilized by the Lewis acidic AlEt$_3$ than one might have first expect; or possibly (ii) that reactions with the Ir(0)$_n$ surface and AlEt$_3$ occur such as those suggested above. It is also possible (iii) that the true catalyst is a fragment, for example, a hydride species (at present we are investigating the catalysis of the combination of AlEt$_3$ plus the previously unknown[68] [(1,5-COD)Ir(μ-H)]$_4$). Our recent XAFS plus kinetic studies argue fairly strongly against the "a fragment is the true catalyst" explanation, however, since faster catalysis is seen when larger Ir(0)$_n$ nanoparticles are being formed and fewer Ir$_4$-sized subnanometer particles can be detected.[4] Additional studies of these and other hypotheses are needed and promise to reveal novel insights about nanoparticle stabilization by added AlR$_3$ or other Lewis acids.

■ SUMMARY AND CONCLUSIONS

The main conclusions of this study are as follows:

(i) Hydrocarbon soluble, Ir(0)$_n$ Ziegler-type nanoparticles made from [(1,5-COD)Ir(μ-O$_2$C$_8$H$_{15}$)]$_2$ and AlEt$_3$ are highly active, long-lived and thermally unusually stable—if not unprecedentedly stable—nanoparticle solution catalysts. Their TTO lifetimes are higher than any known Ir(0)$_n$ nanoparticles, even those of the premier, P$_2$W$_{15}$Nb$_3$O$_{62}^{9-}$ polyoxoanion, "electrosteric" stabilized[24,33] Ir(0)$_n$ nanoparticles.

(ii) Thermal stability at 200 °C requires addition of at least 3 equiv of AlEt$_3$, and the stability of the resulting catalyst increases at Al/Ir = 5. The addition of ≥2 equiv of AlEt$_3$ is necessary to prevent agglomeration of the Ir(0)$_n$ Ziegler-type nanoparticles to bulk Ir(0) metal during room temperature cyclohexene hydrogenation catalysis.

(iii) The Al/Ir = 5 Ir(0)$_n$ nanoparticles are stable for ≥30 min at 200 °C, and exhibit 100 000 TTOs of cyclohexene hydrogenation. The observed nanoparticle catalyst stability at 200 °C appears to surpass that of any other demonstrated nanoparticle catalyst that we can find, those literature reports being limited to ≤130−160 °C temperatures.

(iv) The results strongly suggest that AlEt$_3$, or possibly derivatives of it, are a main component of the stabilizer.

(v) The results imply that either (a) a little understood mode of nanoparticle stabilization by alkyl Lewis acids such as AlEt$_3$ is present (i.e., and in addition to the anionic, DLVO-theory type of stabilization expected for [RCO$_2$·AlEt$_3$]$^-$ formed from the first equivalent of added AlEt$_3$), or (b) that reactions between the Ir(0)$_n$ and AlR$_3$ occur to give species such as the (Ir$_{\text{surface}}$)$_x$−Et and (Ir$_{\text{surface}}$)$_x$−Al(Et)$_2$Ir detailed earlier. It is also conceivable that (c) some other species is the true catalyst in the reaction, possibly an iridium hydride fragment (which could then, for example, have a Lewis base/Lewis acid interaction between the Ir−H and the AlEt$_3$), although the evidence to date argues against this third possibility.[4] Additional studies are, however, warranted and promise to uncover new insights, most likely into the novel stabilization mode of Ziegler-type nanoparticles.

(vi) The results confirm that the activity of Ziegler-type hydrogenation catalyst can be tuned by the Al/Ir ratio, a point apparent in the extant literature.[1] Our results show that, in addition to their catalytic activity, the catalytic lifetime and thermal stability of Ziegler-type hydrogenation catalysts are also strongly influenced by, and thus can be tuned by, the Al/Ir ratio.

(vii) Finally and most importantly, the valuable prior studies of Shmidt,[52−55] Goulon,[56] and Bönnemann,[57−61] plus the result herein and our other, recent publications[4] and critical review,[1] make apparent that hydrocarbon soluble, Lewis-acid containing, Ziegler-type nanoparticles are an underexploited type of highly active, long lifetime and unusually high stability nanoparticle for use in catalysis or other applications where their unusual hydrocarbon solubility and thermal stability might be advantageous.

Overall, the results help confirm the existence of Ziegler-type nanoparticles, highlight their hydrocarbon solubility, and highlight their high, Al/Ir ratio-tunable catalytic activities and lifetimes while also revealing their exceptionally high thermal stability at 200 °C. It is hoped that these results will open the door to the other possible applications of Ziegler-type nanoparticles in catalysis and, possibly, other areas.

In our studies in progress we are concentrating on another historically difficult question in this area,[1] namely precisely what happens to the AlEt$_3$ after mixing [(1,5-COD)Ir(μ-O$_2$C$_8$H$_{15}$)]$_2$ and AlEt$_3$, as well as any insights that may give about the nature of the true catalyst(s). We are also striving to bring to completion our multiyear studies of the precise form and catalytic properties of other Ziegler-type hydrogenation catalysts made from various combinations of industrial precatalysts[63] such as Co and Ni salts and commonly used cocatalysts such as AlMe$_3$, Al(t-Bu)$_3$, or alumoxanes and their derivatives.

■ EXPERIMENTAL SECTION

Materials, Stock Solutions, and Instrumentation. All manipulations were performed under N$_2$ in a Vacuum Atmospheres drybox (≤5 ppm O$_2$ as monitored by a Vacuum Atmospheres O$_2$-level monitor) or using a Schlenk line. All glassware was dried overnight in an oven at 160 °C, cooled under vacuum in a desiccator, and then transferred into the drybox while still in the desiccator and under vacuum, since H$_2$O is known to be detrimental to Ziegler-type hydrogenation catalysts.[1] Cyclohexane (Sigma-Aldrich, 99.5%, H$_2$O < 0.001%) and dodecane (Sigma-Aldrich, anhydrous, ≥99%, water content ≤0.003%) were dried over activated molecular sieves for 2 days prior to use. Molecular sieves (Acros, 3 Å) were activated by keeping at 200 °C for 8 h under vacuum. AlEt$_3$ (Strem Chemicals, 93%, in 100 g steel cylinder) was used as received.

Cyclohexene (Aldrich, 99%) was distilled over Na under N_2(g) and transferred into the drybox under air-free conditions. Silicone oil (Dimethyl Silicone, Thomas Scientific) was used as received. Hydrogen gas (General Air, 99.5%) was passed through an indicating moisture trap (Scott Specialty Gas), a disposable O_2 cartridge (Trigon), and an indicating O_2 trap (Trigon) before use in hydrogenations. $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ was prepared by W. Morgan Alley in our laboratories following our previously published procedure.[3] It was characterized, and its purity checked, by ^{1}H and ^{13}C NMR that matched the literature.[3]

^{1}H NMR. The spectra of sample solutions in benzene-d_6 (Cambridge Isotope Laboratories, Inc., 99.5%, w/o TMS) were taken on a Varian Inova 400 instrument and worked out with MestRec software when needed. Observed chemical shifts were referenced to the proton resonance of the benzene-d_6 solvent.

TEM. Sample solutions for TEM were prepared at Colorado State University by first diluting 0.1 mL of a catalyst solution to 0.6 mL using cyclohexane in a 5 mL glass vial. TEM grids (ultrathin carbon film supported by a holey carbon film on a 400 Mesh copper grid, Ted Pella, Inc.) were then immersed into a sample solution, and dried under an N_2 atmosphere in the drybox for ~1 min. The grids were then placed in 5-mL glass vials, double-sealed under N_2 in the drybox, and then sent to Dr. JoAn Hudson at Clemson University for imaging at ≥0.5 M magnification on a Hitachi H7600T operated at 120 kV.

Procedures and Cautions for Handling the Pyrophoric $AlEt_3$. ***Caution!*** *$AlEt_3$ is a well-known pyrophoric reagent. $AlEt_3$ ignites spontaneously when in contact with air. It, as with all pyrophoric reagents, is more dangerous when flammable solvents are present (e.g., cyclohexane or dodecane, herein). $AlEt_3$ and solvents are even more dangerous the larger the amounts being employed.*

Hence, the required safety considerations were carefully designed and followed, including: (i) first reading the MSDS safety sheet on $AlEt_3$; (ii) working with the minimal amounts of pyrophoric and flammable reagents possible; (iii) using the $AlEt_3$ only in a drybox or in Fisher-Porter (F−P) bottle under N_2 atmosphere. The F−P bottle was sealed using Swagelock quick-connects before taking it out of the drybox.

$AlEt_3$ Stock Solution (36 mM). A stock solution was prepared in the drybox by adding neat $AlEt_3$ (0.529 mL, 0.834 g/mL) using a 1.000 mL gastight syringe into 50 mL cyclohexane in a 100 mL volumetric flask. The resulting solution was diluted to 100 mL using cyclohexane.

Hydrogenation Solution Preparation and Catalytic Cyclohexene Hydrogenation with As-Prepared Catalysts. Catalyst solutions, 1.44 mM in Ir, were individually prepared in a drybox at 30 °C. An example procedure follows for the preparation of catalyst solution with $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ and $AlEt_3$, Al/Ir = 1: A 1.60 mg portion of $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ was weighed into a 20 mL screw-cap glass vial and then dissolved in 2.4 mL of cyclohexane forming an orange-red solution. A 5/8 × 5/16 in. Teflon-coated magnetic stir bar was then placed in the 20 mL screw-cap glass vial, and the solution was stirred for 1 min at 1.0×10^3 rpm as measured with a Monarch Instruments Pocket-Tachometer. A $AlEt_3$ solution (0.1 mL, 36 mM; ***Caution!*** *Pyrophoric material, vide supra, in combination with flammable solvents.*) was then quickly added to the Ir(I) solution within 2 s using a 0.5 mL gastight syringe while vigorously stirring.[1] The original orange-red color of the $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ solution changed to tawny yellow at the end of $AlEt_3$ addition. This tawny yellow solution was stirred under N_2 in the drybox for 9 h. At the end of 9 h, the solution appeared clear brown with no visually observable particles. The solution was then transferred into a new 22 × 175 mm Pyrex borosilicate culture tube containing a new 5/8 × 5/16 in. Teflon-coated magnetic stirbar. Cyclohexene (0.5 mL) was added using a 1.0 mL gastight syringe, and the resulting hydrogenation solution (1.65 M in [cyclohexene] and 1.2 mM in [Ir]) was stirred for an additional 1 min.

The procedure and apparatus used for catalytic hydrogenations of cyclohexene have been described in detail elsewhere.[33,69,70] Briefly, a culture tube containing the hydrogenation solution was placed in a F−P bottle, which was then sealed and brought out of the drybox. The F−P bottle was placed in a bath set at 22.0 ± 0.1 °C. Stirring was started at 1000 ± 10 rpm using a Fauske Super magnetic stirplate, and the F−P bottle was connected to a pressurized H_2 line using TFE-sealed Swagelok quick-connects. The F−P bottle was purged 15 times (1 purge/15 s) with H_2 that had passed through an indicating moisture trap (Scott Specialty Gas), a disposable O_2 cartridge (Trigon), and an indicating O_2 trap (Trigon). The pressure in the F−P bottle was then set to 40 psig, and then the data collection was initiated. Hydrogen pressure vs time data was collected using a pressure transducer (Omega PX 624-100 GSV) interfaced via an Omega D1131 analog to digital converter to a PC running LabVIEW 7.0. Data was subsequently handled using MS Excel. The maximum hydrogenation rate of catalysts before and after catalyst isolation was calculated from each kinetic curve by a linear-least-squares fit to the data points in the highest activity (highest slope) region ($R^2 \geq 0.999$ for the reported data). The maximum hydrogenation rates of redispersed catalysts occur at the beginning of the hydrogenation (i.e., the maximum rate equals the initial rate), so those (maximum) rates were calculated via linear-least-squares fits to the initial, linear regions of the redispersed catalysts hydrogenation curves ($R^2 \geq 0.999$ for the reported data).

For hydrogenations with $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$, Al/Ir = 2, 3, or 5, orange-red $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ (1.60 mg) was dissolved in a total of 2.3, 2.2, or 2.0 mL cyclohexane, respectively. Then, 0.2, 0.3, or 0.5 mL, respectively, of a stock $AlEt_3$ solution (36 mM) was added using a 1.0 mL gastight syringe. At the end of 9 h aging in the drybox, all the catalysts made with 1, 2, 3, or 5 equiv of $AlEt_3$ turned to brown without visually observable bulk metal. At the end of cyclohexene hydrogenation, the catalyst solutions prepared with 2, 3, or 5 equiv of $AlEt_3$ were still brown with no visually observable particles in contrast to the Al/Ir = 1 catalyst solution which did contain bulk metal particles in the solution and on the stirbar.

Isolation and Redispersion Procedure and Hydrogenation Using Redispersed Catalyst. After hydrogenation, the F−P bottle was detached from the line and taken inside the drybox. The catalyst solution and the stirbar were then transferred into a new 20 mL screw-cap glass vial. Volatiles were removed under vacuum to yield a black powder which was dried under vacuum for 2 h. Cyclohexane (2.5 mL) was then added to this isolated, black powdered catalyst, and the resulting solution was stirred for 2 min. This solution was completely transferred (i.e.; without leaving any observable particles in the glass vial) into a new 22 × 175 mm Pyrex borosilicate culture tube containing a new 5/8 × 5/16 in.

Teflon-coated magnetic stirbar. Fresh cyclohexene (0.5 mL) was added using a 1.0 mL gastight syringe, and the resulting hydrogenation solution (1.65 M in [cyclohexene] and 1.2 mM in [Ir]) was stirred for an additional 1 min.

Catalytic Lifetime Measurements. The catalytic lifetime measurements were performed according to a previously published procedure.[23,26] In the drybox, the orange-red crystals of $[(1,5\text{-COD})\text{Ir}(\mu\text{-O}_2\text{C}_8\text{H}_{15})]$ (0.319 mg, 0.72 μmol) were weighed into a 20 mL screw-cap glass vial. Then, AlEt_3 (20 μL, 36 mM) was quickly added in 1 s using a 50 μL syringe. The resulting solution was stirred for 30 min. The catalyst solution was then diluted with 10 mL of cyclohexene and transferred into a new 22 × 175 mm Pyrex borosilicate culture tube containing a new 5/8 × 5/16 in. Teflon-coated magnetic stirbar using a disposable polyethylene pipet. Further cyclohexene (26 mL, to bring the total cyclohexene volume to 36 mL, corresponding to a total of 488 000 total turnovers) was added using a 10 mL syringe while vigorously stirring. The culture tube containing the hydrogenation solution was placed in a F−P bottle, which was then sealed and brought out of the drybox. The F−P bottle was placed in a water bath set at 22.0 ± 0.1 °C. Stirring was started at 1000 ± 10 rpm using a Fauske Super magnetic stirplate and the F−P bottle was connected to a pressurized H_2 line using TFE-sealed Swagelok quick-connects. The F−P bottle was purged 15 times (1 purge/15 s) with H_2 that has passed through an indicating moisture trap (Scott Specialty Gas), a disposable O_2 cartridge (Trigon), and an indicating O_2 trap (Trigon). A timer was started, and the pressure in the F−P bottle was set to 40 ± 1 psig.

The reaction was monitored by periodically withdrawing 0.1 mL aliquots of the reaction solution and then analyzing that aliquot by ^{1}H NMR spectroscopy. The aliquots were taken from the reaction solution while the F−P bottle was connected to the H_2 line as follows: the purge valve was opened to air while the H_2 gas at 40 psig pressure was still flowing. A gastight syringe with a ~25 cm needle was first purged with H_2 gas by inserting the tip into flowing H_2 gas between Swagelok quick-connects on the brass pressure head of the F−P bottle. The syringe was filled with H_2 and then emptied while under H_2. This procedure was repeated five times to ensure exclusion of air when the tip of the needle was inserted into the reaction solution. Then 0.1 mL of the reaction solution was withdrawn with the syringe and quickly transferred into an NMR tube including 1.0 mL C_6D_6.

Thermal Stability Experiments. Thermal stability experiments were carried out using dodecane as solvent because of its high boiling point (215 °C vs 81 °C for cyclohexane). The catalyst and hydrogenation solutions, except AlEt_3 solution, were prepared in dodecane using the procedure detailed above when cyclohexane was used as the solvent and under the section heading "Hydrogenation Solution Preparation and Catalytic Cyclohexene Hydrogenations". The AlEt_3 stock solution in cyclohexane (36 mM) (that is, not in dodecane) was used in the thermal stability experiments. A cyclohexene hydrogenation (called initial cyclohexene hydrogenation hereafter) was carried out as detailed above, but now in dodecane solvent. At the end of the initial cyclohexene hydrogenation the 22 °C water bath was replaced with a silicone oil bath set at 200 ± 2 °C. The H_2 pressure in the F−P bottle was decreased to ~20 psig and the F−P bottle was placed in silicone-oil bath. The pressure in the F−P bottle was continuously monitored during heating. The solution in the F−P bottle was kept at 200 °C for 30 min and then cooled down to room temperature under H_2. The F−P bottle was then brought into the drybox, and 0.5 mL of cyclohexene was added. Next, the F−P bottle was taken out of the drybox, connected to H_2 line, and purged 15 times (1purge/15 s) with H_2 that had passed through an indicating moisture trap (Scott Specialty Gas), a disposable O_2 cartridge (Trigon), and an indicating O_2 trap (Trigon). A second cyclohexene hydrogenation was then carried out to test the activity of the 200 °C, 30 min, heat-treated catalyst.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures for control studies (i) measuring the maximum rate of cyclohexene hydrogenation as a function of cycles of catalyst isolation and then redispersion, (ii) determining the effect of aging the Ziegler-type hydrogenation catalyst made from $[(1,5\text{-COD})\text{Ir}(\mu\text{-O}_2\text{C}_8\text{H}_{15})]_2$ plus AlEt_3, Al/Ir = 2, in dodecane; and (iii) determining the effect of using Al/Ir = 1 and Al/Ir = 0 ratios on catalyst activity and stability. Hydrogenation curves with heat-treated Ziegler-type hydrogenation catalyst made from $[(1,5\text{-COD})\text{Ir}(\mu\text{-O}_2\text{C}_8\text{H}_{15})]_2$ plus AlEt_3, Al/Ir = 2. Control hydrogenations determining the H_2 gas-to-solution, mass-transfer-limited (MTL) rate of the hydrogenation apparatus used in the present work. High resolution XPS spectrum of Ir 4f peaks of brown particles from the Al/Ir = 3 catalyst after heating at 200 °C for 30 min. ^{1}H NMR spectrum of neat AlEt_3 and that of catalyst solution prepared with $[(1,5\text{-COD})\text{Ir}(\mu\text{-O}_2\text{C}_8\text{H}_{15})]_2$ plus AlEt_3, Al/Ir = 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(7) Consistent with those definitions,[5,6] the nomenclature used herein is "nanoparticles" to define species for which (only) the size distribution is known, but the composition and structure of the nanoparticles are not known. Alternatively, the term "nanocluster" is reserved for atomically precise, compositionally and structurally atomically characterized (nano)clusters.

(8) The $\text{Ir}(0)_n$ *nanoparticles* studied herein begin in the $\text{Ir}(0)_{\sim 40-150}$ size range,[4] and are a bit larger, $\text{Ir}(0)_{\sim 250}$ post the 200 °C heat treatment as demonstrated in Figure 5.

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(27) The original five-criteria method, developed and then applied to rank the efficacy of a given additive (e.g., anions, solvent, cations, or polymers) to achieve the kinetically controlled formation and then stabilization and catalytic activity of the resultant nanoparticles, consists of the following: (i) the ability to exhibit high level of kinetic control as measured quantitatively by the k_2/k_1 ratio for the nucleation [$A \rightarrow B$ (rate constant k_1)], then autocatalytic surface growth [$A + B \rightarrow 2B$ (rate constant k_2)] mechanism of formation of transition metal nanoparticles under H_2; (ii) the ability to form near-monodisperse (≤15% size dispersion) nanoparticles as evidenced by TEM; (iii) the ability to allow isolation from solution and then complete redispersion without visible formation of bulk metal—a telling test of nanoparticle stability; (iv) the ability of the isolated nanoparticles to exhibit high catalytic activity in cyclohexene hydrogenation once redispersed in the solution; and (v) the ability to allow long catalytic lifetime in the test reaction of cyclohexene hydrogenation as measured by the catalytic total turnovers (TTOs).

(28) The previous 5-criteria method[27] had to be modified somewhat for the present studies since the Ziegler-type nanoparticles examined herein are preformed quickly upon simple mixing the $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ with the $AlEt_3$. This, in turn, means that the kinetic criteria which ranks the ability of the various anions or other ligands and additives (such as polymers) to influence the *nanoparticle formation kinetics* is no longer readily measurable without, for example, stopped-flow kinetics (i.e., kinetic studies not important to the present work whose focal point is nanoparticle catalytic activity, thermal stability and lifetime).

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(30) A patent[29] reports that a Ziegler-type hydrogenation catalyst made from $Co(O_2CR)$ and $Zn(O_2CR)_2$ plus $AlEt_3$, prepared at temperatures of 0−200 °C is a fast, highly efficient catalyst (the hydrogenation of 100 mL of propionitrile is reported to be complete in 11.5 h with a 99.5% conversion to propylamines). Although propionitrile hydrogenation at temperatures from 0 to 300 °C are claimed, the specific examples of hydrogenations (of various substrates) are at only 155, 160, or 180 °C, and not up to 300 °C. In addition, the nature of the active catalyst was not determined, so it is not clear what the true catalyst actually is at these temperatures and in this patent.

(31) Control experiments were performed, on a Ziegler-type hydrogenation catalyst made from $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$ (Al/Ir = 2) in cyclohexane, to determine the effect of number of catalyst isolation and then redispersion cycles on the hydrogenation rate of the catalyst. Interestingly, the catalyst appears to become slightly more active up to the third cycle of isolation and redispersion (5 ± 2, 8 ± 1, and 9 ± 1 mmol H_2/h, respectively, for once-redispersed, two-times-redispersed, and three-times-redispersed catalysts), although the results are rigorously the same within a 2σ experimental error (i.e., at 2× the reported 1σ error bars just above). The catalyst retains its activity (~9 mmol/h) after redispersion two through eight times (see the Supporting Information for additional details).

(32) Original cyclohexene hydrogenation data is obtained in units of loss of psig H_2/h. The data in units of psig H_2/h are then converted as follows to mmol H_2/h using the ideal gas law formula ($PV = nRT$) and the necessary data for our apparatus: $P(\text{psig } H_2) \times 0.0891 \times 1000)/14.7 = n \text{ (mmol } H_2) \times 0.082 \times 295$ where $R = 0.082$ L atm/mol K, $T = 295$ K and 1 atm = 14.7 psi and V(volume of F-P bottle used) = 0.0891 L.

(33) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891−4910.

(34) Aiken, J. III; Finke, R. G. *Chem. Mater.* **1999**, *11*, 1035−1047.

(35) Control experiments performed on Ziegler-type hydrogenation catalyst made from $[(1,5\text{-COD})\text{Ir}(\mu\text{-}O_2C_8H_{15})]_2$ plus $AlEt_3$ (Al/Ir = 2) in *dodecane* showed that aging the catalyst for 9 h at room temperature appears to decrease slightly the activity of the catalyst (although the results are the same within experimental error if the cited 1σ error bars are expanded by 2× to 2σ values): the catalyst prepared in dodecane, and then immediately used for cyclohexene hydrogenation, exhibits a hydrogenation rate of 1.1 ± 0.1 mmol H_2/h, whereas the catalyst aged 9 h has a hydrogenation rate of 0.7 ± 0.1 mmol H_2/h (see the Supporting Information for the corresponding hydrogenation curves). In comparison, the catalyst prepared in *cyclohexane* and aged for 9 h at room temperature is a somewhat faster catalyst compared to the unaged, immediately prepared catalyst[4] (see also the Supporting Information provided with that paper[4]).

(36) Initial survey experiments reveal that an active catalyst is obtained in dodecane (i) when the 9 h aged catalyst was thermally treated and then used for cyclohexene hydrogenation (i.e., without performing a cyclohexene hydrogenation before the 200 °C thermal treatment); (ii) when the as-prepared catalyst was thermally treated and then used directly for cyclohexene hydrogenation (i.e., without the 9 h aging); and (iii) when the catalyst solution is prepared with cyclohexene added before the 200 °C thermal treatment. See the Supporting Information for additional details.

(37) The heat-treated catalyst with an Al/Ir ratio of 2 is highly active for cyclohexene hydrogenation with average maximum rate of 24(9) mmol H_2/h (Table 1 and Supporting Information, Figure S3). A fast hydrogenation started immediately in that experiment, and continued with an almost linear rate until the consumption of cyclohexene was complete (Supporting Information, Figure S4). The observed linear hydrogenation kinetics reveal that the catalysis has reached the H_2 gas-to-solution mass transfer limited (MTL) rate of even our well-stirred apparatus (~1000 rpm stir-bar stirring)—that is, that H_2 is consumed as fast as it is delivered from the gas phase to solution in our apparatus. Consistent with this interpretation, an independent determination of the H_2 gas-to-solution MTL rate under our reaction conditions, stirring rate, and for our specific apparatus revealed that H_2 gas-to-solution MTL occurs at ~20(5) mmol H_2/h for our apparatus (Supporting Information, Figure S4). Hence, the true activity of the heat-treated Al/Ir = 2 catalyst is greater than or equal to the observed rate of 24(9) mmol H_2/h.

(38) Aiken, J. D. III; Finke, R. G. *J. Am. Chem. Soc.* **1999**, *121*, 8803−8810 , and references therein.

(39) Somewhat analogously, a brown precipitate of $Ir(0)_n$ and $Rh(0)_n$ nanoparticles also settles out of solution during cyclohexene hydrogenation catalysis by $Ir(0)_{\sim 300}$ nanoparticles[38] formed by placing $[Bu_4N]_5Na_3[(1,5\text{-COD})Ir \cdot P_2W_{15}Nb_3O_{62}]$ or $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh \cdot P_2W_{15}Nb_3O_{62}]$ and cyclohexene under 40 psig H_2, a result that has been ascribed to the conversion of cyclohexene into the somewhat less polar cyclohexane as a result of the hydrogenation reaction. Note, however, that these polar polyoxoanion, $P_2W_{15}Nb_3O_{62}{}^{9-}$-stabilized nanoparticles are expected to have little solubility in nonpolar solvents like cyclohexane, at least with Bu_4N^+ counter-cations.

(40) Lin, Y.; Finke, R. G. *J. Am . Chem. Soc.* **1994**, *116*, 8335−8353.

(41) For the case of either $Ir(0)_{\sim 300}{}^{33}$ or $Ir(0)_{\sim 900}{}^{40}$ nanoparticles stabilized by the "electrosteric", premier/"Gold Standard" anionic,[22] $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion stabilizer,[22−26] acetone solutions show limited stability and agglomeration to bulk metal above 60 °C. Hence, it is apparent that the thermal stability of $Ir(0)_n$ nanoparticles with added $AlEt_3$ in hydrocarbon solvents at 200 °C exceeds that of at least these classic, anionically (DLVO-theory[22]) stabilized nanoparticles.[33,40]

(42) Beller, M.; Fischer, H.; Kühlein, K.; Reisinger, C.-P.; Hermann, W. A. *J. Organomet. Chem.* **1996**, *520*, 257−259.

(43) $Pd(0)_n$ nanoparticles *unstable* at 130−140 °C have been reported,[42] ones where 490,000−500,000 TTOs of Heck reaction catalysis were obtained by adding preformed $Pd(0)_n$ slowly to the 130−140 °C reaction solution as a way to combat the nanoparticle instability at the 130−140 °C temperatures. Note, however, that the actual catalyst in these reactions was not established and remains controversial.[44]

(44) Phan, N. T.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609−679.

(45) Reetz, M. T.; Lohmer, G. *Chem. Commun.* **1996**, 1921−1922.

(46) Reetz, M. T.; Breinbauer, R.; Wedemann, P.; Bringer, P. *Tetrahedron* **1998**, *54*, 1233−1240.

(47) Two studies[45,46] report nanoparticles stable for at least some (generally unstated) numbers of catalytic turnovers in the 130−160 °C range, and which involve longer chain alkyl-ammonium cations as part of the stabilization system. However, the actual catalyst in these studies was not established.

(48) Klingelhöfer, S.; Heitz, W.; Greiner, A.; Oestreich, S.; Förster, S.; Antonietti, M. *J. Am. Chem. Soc.* **1997**, *119*, 10116−10120.

(49) Pd_n nanoparticle stabilities of up to 140 °C for 3 days while undergoing Heck coupling reactions using OAc^- plus amphiphilic block copolymers, specifically polystyrene-block-poly-4-vinylpyridine (PS-*b*-P4VP), have been reported.[48] Note, however, that Figures 2 and 3 in this paper show autocatalytic curves. This means that either the PS-*b*-P4VP-stabilized Pd_n nanoparticles are not the true catalyst or that a reaction byproduct (the H^+X^- formed) is involved in the catalytic reaction (e.g., the H^+X^- byproduct should protonate the pyridine in the PS-*b*-P4VP stabilizer, thereby causing it to decoordinate from the metal, in turn giving a more active catalyst, consistent with the observed reaction kinetics).

(50) Wilcoxon, J. P.; Williamson, R. L.; Baughman, R. *J. Chem. Phys.* **1993**, *98*, 9933−9951.

(51) A report of $Au(0)_n$ nanoparticles prepared in the presence of various nonionic (such as ethoxylated alcohols), anionic (such as bir(2-ethylhexyl)sulfosuccinate), and cationic (such as didodecyldimethylammonium) surfactants and stable to agglomeration up to 100 °C has appeared, but the $Au(0)_n$ nanoparticles were not shown to be catalysts.[50]

(52) Nindakova, L. O.; Shmidt, F. K.; Saraev, V. V.; Shainyan, B. A.; Chipanina, N. N.; Umanets, V. A.; Belonogova, L. N.; Toryashinova, D. -S. D. *Kinet. Catal.* **2006**, *47*, 54−63.

(53) Shmidt, F. K.; Nindakova, L. O.; Shainyan, B. A.; Saraev, V. V.; Chipanina, N. N.; Umanetz, V. A. *J. Mol. Catal. A: Chem* **2005**, *235*, 161−172.

(54) Belykh, L. B.; Goremyka, T. V.; Skripov, N. I.; Umanets, V. A.; Shmidt, F. K. *Kinet. Catal.* **2006**, *47*, 367−374.

(55) Schmidt, F. K.; Ratovskii, G. V.; Dmitrieva, T. V.; Ivleva, I. N.; Borodko, Y. G. *J. Organomet. Chem.* **1983**, *256*, 309−329.

(56) Goulon, J.; Georges, E.; Goulon-Ginet, C.; Chauvin, Y.; Commereuc, D.; Dexpert, H.; Freund, E. *Chem. Phys.* **1984**, *83*, 357−366.

(57) Bönnemann, H.; Waldofner, N.; Haubold, H.-G.; Vad, T. *Chem. Mater.* **2002**, *14*, 1115−1120.

(58) Angermund, K.; Buhl, M.; Dinjus, E.; Endruschat, U.; Gassner, F.; Haubold, H.-G.; Hormes, J.; Kohl, G.; Mauschick, F. T.; Modrow, H.; Mortel, R.; Mynott, R.; Tesche, B.; Vad, T.; Waldofner, N.; Bönnemann, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4041−4044.

(59) Angermund, K.; Buhl, M.; Endruschat, U.; Mauschick, F. T.; Mortel, R.; Mynott, R.; Tesche, B.; Waldofner, N.; Bönnemann, H.; Kohl, G.; Modrow, H.; Hormes, J.; Dinjus, E.; Gassner, F.; Haubold, H.-G.; Vad, T.; Kaupp, M. *J. Phys. Chem. B* **2003**, *107*, 7507−7515.

(60) Bönnemann, H.; Waldofner, N.; Haubold, H.-G.; Vad, T. *Rev. Roum. Chim.* **1999**, *44*, 1003−1010.

(61) Wen, F.; Bönnemann, H.; Mynott, R.; Spliethoff, B.; Weidenthaler, C.; Palina, N.; Zinoveva, S.; Modrow, H. *Appl. Organomet. Chem.* **2005**, *19*, 827−829.

(62) ^1H NMR confirms that intact $AlEt_3$ (∼3 equiv per Ir) is present in the catalyst solution prepared with $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ and $AlEt_3$ when using Al/Ir = 5 (see the Supporting Information, Figures S6 and S7 for ^1H NMR spectra of catalyst prepared with $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ and 5 equiv of $AlEt_3$ vs that of pure $AlEt_3$.).

(63) Alley, W. M.; Hamdemir, I. K.; Wang, Q.; Frenkel, A.; Li, L.; Yang, J. C.; Menard, L. D.; Nuzzo, R. G.; Özkar, S.; Yih, K. H.; Johnson, K. A.; Finke, R. G. *Langmuir* **2011**, *27*, 6279−6294.

(64) Note here that care was taken to minimize the H_2O level to minimize alumoxane (i.e., Al-O-Al compound) production, and controls[63] show that added H_2O to the Al/Co = 2 or 3 catalyst solution prepared with $Co(neodecanoate)_2$ and $AlEt_3$ decreases the catalytic activity.[63] Prior studies by Shmidt and co-workers[52,53] show that presence of n = 0.5−1.5 equiv (per Co) of water of crystallization in a $Co(acac)_2 \cdot n(H_2O)$ plus $AlEt_3$ catalyst system decreases the catalyst stability and increases the amount of precipitate seen attributed to the formation of alumoxanes and their derivatives.

(65) A catalytic inhibiting effect has been observed when the precatalyst $\{[(1,5\text{-COD})Ir \cdot HPO_4]\}_n$ is examined in the presence of added $[Bu_4N]_2HPO_4$. The catalytic activity of precatalyst is 1.0(1) mmol H_2/h before the catalyst was isolated and redispersed, while the addition of 1, and then separately 4, equiv of $[Bu_4N]_2HPO_4$ to the precatalyst $\{[(1,5\text{-COD})Ir \cdot HPO_4]\}_n$ lowers the catalytic activity to 0.20(5) and 0.10(5) mmol H_2/h, respectively.[25] It was concluded that "...increasing the concentration of $HPO_4{}^{2-}$ results in a higher coverage of the $Ir(0)_n$ nanoparticle surface, thereby, inhibiting the catalytic reactions of the Ir(0) active sites...".[25]

(66) An alternative hypothesis for the lower hydrogenation activity at higher $AlEt_3$ concentrations (i.e.; Al/Ir = 2, 3, or 5 when compared to Al/Ir = 1) is that a difference in size of the $Ir(0)_n$ nanoparticles is the main factor behind the different catalytic activities. However, this alternative explanation can be ruled out since the same size nanoparticles are observed within experimental error for each of the Al/Ir = 1, 2 and 5 catalysts[4] (see also the Supporting Information for that paper[4]).

(67) Reactions between $AlEt_3$ and precatalyst components are known in the literature of Ziegler-type hydrogenation catalysts. For example, when starting with $M(acac)_2$, where acac: acetylacetonate and M: Co, Pt or Pd, and AlR_3 (R: Me or Et),[54,57,58] the suggested products are $R_2Al\text{-}O\text{-}C(CH_3){=}CH\text{-}C(Et)(CH_3)\text{-}O\text{-}AlR_2$, and $R_2Al\text{-}O\text{-}C(Et)(CH_3)\text{-}CH(AlEt_2)\text{-}C(Et)(CH_3)\text{-}O\text{-}AlR_2$.

(68) Yih, K.-H.; Hamdemir, I. K.; Mondloch, J. E.; Bayram, E.; Özkar, S.; Vasic, R.; Frenkel, A. I.; Anderson, O.; Finke, R. G. *Inorg. Chem.* **2012**, *51*, 3186−3193.

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