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Article

Model Ziegler-Type Hydrogenation Catalyst Precursors, $[(1,5\text{-COD})M(\mu\text{-}O_2C_8H_{15})]_2$ (M = Ir and Rh): Synthesis, Characterization, and Demonstration of Catalytic Activity En Route to Identifying the True Industrial Hydrogenation Catalysts

William M. Alley,[†] Chase W. Girard,[†] Saim Özkar,[‡] and Richard G. Finke*,[†]

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, and
Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

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The compounds $[(1,5\text{-COD})M(\mu\text{-}O_2C_8H_{15})]_2$ (COD = cyclooctadiene, M = Ir (**1**) or Rh (**2**), $O_2C_8H_{15}$ = 2-ethylhexanoate) were synthesized by addition of Bu_3NH(2-ethylhexanoate) or Na(2-ethylhexanoate) to acetone suspensions of $[(1,5\text{-COD})Ir(\mu\text{-}Cl)]_2$ or $[(1,5\text{-COD})Rh(\mu\text{-}Cl)]_2$, respectively. The synthesis of such well-defined second and third row model precursors is key to determining the true nature of commercial Ziegler-type hydrogenation catalysts (i.e., catalysts made from the combination of a non-zerovalent, group 8−10 transition metal precatalyst and a trialkylaluminum cocatalyst), an unsolved, ∼40 year old problem. The characterizations of **1** and **2** were accomplished by elemental analysis, melting point, FAB-MS, FT-IR, UV−vis, NMR spectroscopy, and single crystal X-ray diffraction. The complexes, $C_{32}H_{54}Ir_2O_4$ and $C_{32}H_{54}O_4Rh_2$, are isostructural: monoclinic, $P2_1/n$, $Z = 4$. The lattice constants for **1** are $a = 15.7748(5)$ Å, $b = 9.8962(3)$ Å, $c = 20.8847(7)$ Å, $\beta = 108.408(2)°$. The lattice constants for **2** are $a = 15.7608(4)$ Å, $b = 9.9032(3)$ Å, $c = 20.8259(5)$ Å, $\beta = 108.527(1)°$. Complexes **1** and **2** are dimeric, bridged by the 2-ethylhexanoates, and with one 1,5-COD ligand bound to each metal. The formally 16 electron metal atoms are in square ligand planes with dihedral angles between the planes of 56.5° for **1** and 58.1° for **2**. The M−M distances of 3.2776(2) and 3.3390(4) Å for **1** and **2**, respectively, fall in the range of similar structures thought to have some M−M interaction despite the lack of a formal M−M bond. Demonstration that active Ziegler-type hydrogenation catalysts are made when **1** or **2** combine with $AlEt_3$ is provided, results that open the door to the use of **1** and **2** as well-defined third and second row congeners, respectively, of Ziegler-type hydrogenation catalysts. These compounds have proven important in addressing the previously unsolved problem of the true nature of the catalyst in industrial Ziegler-type hydrogenation catalyst systems; their high yield synthesis and unequivocal characterization reported herein are the necessary first steps of that work.

Introduction

The selective catalytic hydrogenation of unsaturated sites in polymers, such as styrenic block copolymers, is an important industrial process used to improve the stability of the polymer toward both thermal and oxidative degradation by autoxidation processes.[1−3] According to one estimate, annual worldwide production of hydrogenated styrenic block copolymers probably exceeds 1.7×10^5 metric tons.[4] An industrially important family of catalysts developed during the late 1960s and early 1970s for the purpose of polymer hydrogenation is Ziegler-type *hydrogenation* catalysts, defined as those made from a non-zerovalent, group 8−10 transition metal precatalyst and a trialkylaluminum (e.g.,

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* To whom correspondence should be addressed. E-mail: rfinke@lamar.colostate.edu.

[†] Colorado State University.

[‡] Middle East Technical University.

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triethylaluminum) cocatalyst. As such, Ziegler-type *hydrogenation* catalysts are *used primarily for polymer hydrogenation*, not polymerization,[1,2,5−10] and should not be confused with Ziegler−Natta *polymerization* catalysts.

Surprisingly little fundamental information about Ziegler-type hydrogenation catalysts exists despite their ~40 year history of industrial application.[2,11,12] The single most important unanswered question is what is the true nature of Ziegler-type hydrogenation catalysts: are they single metal "homogeneous" or multiple metal "heterogeneous" catalysts?[13−15] The study of typically ill-defined industrial catalyst precursors alone has not led to a clear understanding of the true nature of these important industrial catalysts.[2,8,9,16]

Preparing well characterized, second and third row precursors, that yield model catalysts amenable to characterization by modern methods is the crucial first step in attaining new insights into the true nature of Ziegler-type hydrogenation catalysts.[17] Requirements for an ideal precursor are that it (i) fits the above definition of a Ziegler-type hydrogenation catalyst (i.e., that it is composed of a group 8−10 transition metal salt); (ii) has an anion such as 2-ethylhexanoate that is representative of those commonly employed industrially;[2] (iii) forms a catalytically active species for olefin hydrogenation upon combination with a typical alkylaluminum reagent such as $AlEt_3$; and (iv) is readily available, preferably inexpensive and easy to prepare reproducibly in a well characterized, pure form. Additional requirements for an ideal precursor are that it: (v) be soluble in solvents commonly used for olefin hydrogenation, such as cyclohexane for example; (vi) have an auxiliary ligand, such as 1,5-COD, which can be used as an analytical handle (e.g., to monitor conversion of the precatalyst to the catalyst);[18] (vii) employ a third row transition metal to allow transmission electron microscopy (TEM) to reliably image any polymetallic clusters that may be formed;[19] (viii) form the same fundamental type (i.e., homogeneous or heterogeneous) of catalyst made by industrially used precatalysts, and therefore, (ix) yield new insights into the Ziegler-type hydrogenation catalysts central to industrial polymer hydrogenation. A literature search revealed that complexes of the form $[(1,5\text{-COD})M(\mu\text{-}O_2C_8H_{15})]_2$ (COD = cyclooctadiene, M = Ir or Rh, $O_2C_8H_{15}$ = 2-ethylhexanoate) are perhaps ideal, previously unexploited, candidates for the desired precatalyst.[20−37] In addition, $[(1,5\text{-COD})M(\mu\text{-}O_2C_8H_{15})]_2$ (M = Ir or Rh) could prove to be of importance in a variety of other industrial applications.[38]

Herein we describe the synthesis, characterization, structural determination, and catalytic hydrogenation activity following the addition of $AlEt_3$ of complexes $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ (**1**) and $[(1,5\text{-COD})Rh(\mu\text{-}O_2C_8H_{15})]_2$ (**2**). The methods used for compositional and structural characterization are elemental analysis, mass spectrometry (MS), single crystal X-ray diffractometry, infrared (IR), UV−visible electronic absorption, and nuclear magnetic resonance (NMR) spectroscopy. In work to be reported separately,[17] we have used **1** and **2** as Ziegler-type hydrogenation catalyst precursors to investigate the problem of the true nature of industrial Ziegler-type polymer hydrogenation catalysts, a perplexing problem in the "is it homogeneous or heterogeneous catalysts?" area.[14] That subsequent work hinges on the high yield synthesis and unequivocal characterization of the $[(1,5\text{-COD})M(\mu\text{-}O_2C_8H_{15})]_2$ (M = Ir or Rh) precursors described herein.

Results and Discussion

Synthesis of $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ (1) and $[(1,5\text{-COD})Rh(\mu\text{-}O_2C_8H_{15})]_2$ (2). The syntheses of **1** and **2**, Scheme 1, were modeled after earlier syntheses of similar complexes which used $[(\text{diene})M(\mu\text{-}Cl)]_2$ (diene = 1,5-COD or norbornadiene (NBD), M = Ir or Rh), and Na^+, K^+, or Ag^+ carboxylate salts as starting materials, Supporting Information, Table S1. Control experiments were performed with longer reaction times while following the formation of

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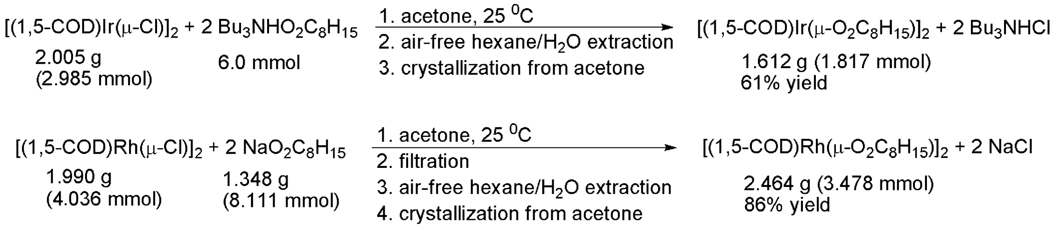
(20) The similarity of $[(1,5\text{-COD})M(\mu\text{-}O_2C_8H_{15})]_2$ compounds (M = Ir or Rh, $O_2C_8H_{15}$ = 2-ethylhexanoate) to industrial catalyst precursors such as Ni(2-ethylhexanoate)$_2$ made it very likely that they would form active Ziegler-type hydrogenation catalysts upon addition of $AlEt_3$ (as demonstrated herein). Additionally, complexes of the type $[(1,5\text{-COD})M(\mu\text{-carboxylato})]_2$ (COD = cyclooctadiene, M = Ir or Rh) were expected to be, and are, soluble in the same solvents as Ni(2-ethylhexanoate)$_2$ and other industrial catalyst precursors. Gas chromatographic (GC) analysis of cyclooctane (i.e., hydrogenated 1,5-COD) has proven to be an important analytical handle in past nanocluster syntheses from $(1,5\text{-COD})M^+$ (M = Rh, Ir) precursors.[18] It seemed especially promising to be able to use catalysts formed from the heavier, 3rd row transition metal Ir complex, as they would more likely be amenable for use with TEM to look for the presence of metal particles than catalysts made from lighter Co and Ni counterparts. The ability to compare the Ir compound to its Rh analogue, as well as to industrial Ni and Co catalysts, is an additional advantage of the present approach and precursors.

Scheme 1. Stoichiometry and Associated Reaction Conditions for the Synthesis Of **1** (Top) and **2** (Bottom)[a]



[a] Characterization for both compounds was accomplished using by elemental analysis, FAB-MS, single crystal X-ray diffraction, FT-IR, UV-Vis, and ^{1}H and ^{13}C spectroscopy, vide infra.

1 and **2** directly with ^{1}H NMR. The reactions proceeded rapidly at room temperature (complete reaction in $\leq$10 min). Additionally, identical product yields were obtained if the reaction time was 10 min or 9 days. The synthesis of **1** was also accomplished using either the Na$^+$ or Ag$^+$ salt of 2-ethylhexanoate. However use of the Na$^+$ salt requires an additional filtration step while use of the Ag$^+$ salt gave only limited amounts of **1**. Limited product formation was also observed in the attempted use of $Bu_3NHO_2C_8H_{15}$ to prepare **2**. The necessity of using Na$^+$ for the synthesis of **2** could result from different driving force requirements in the syntheses of **1** and **2**. The hexane/H_2O extraction step, shown in Scheme 1, was performed outside the drybox, with the exclusion of air accomplished using Ar pressure and cannula techniques, and rigorously degassed hexane and water. Compounds **1** and **2** were easily crystallized from acetone with slow cooling; performing the extractions thoroughly to remove the residual chloride salts and/or unreacted starting materials is important, however. Compounds **1** and **2** appear to be relatively air stable in crystalline form but not in solution.[39] These points are discussed in greater detail in the Supporting Information for the interested reader.

X-ray Crystal Structures of 1 and 2. The X-ray crystal structures of **1** and **2**, with atomic numbering schemes and thermal ellipsoids at a 30% probability level, are shown in Figures 1 and 2, respectively.[40] Compounds **1** and **2** both proved to be dimeric as expected,[41] and are isomorphous. Each molecule has two 2-ethylhexanoate ligands bridging the two metal centers. Each transition metal center in **1** and **2** is four-coordinate, bound to one of the oxygen atoms from each 2-ethylhexanoate and to the two olefinic bonds from a single $\eta^{2:2}$-1,5-COD. The centroids of the olefinic carbon

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(21) Although [(1,5-COD)M(μ-$O_2C_8H_{15}$)]$_2$ (M = Ir or Rh) are not commercially available, their ready synthesis also appeared promising. Chatt and Venanzi described the original synthesis of the acetate compound [(1,5-COD)Rh(μ-O_2CCH_3)]$_2$ from [(1,5-COD)Rh(μ-Cl)]$_2$ and potassium acetate.[26] The synthesis of other [(diene)Rh(μ-O_2CR)]$_2$ complexes have been reported using similar approaches, including those where the R group is CH_2Cl,[27] CH_2F,[27] or CF_3.[28−30] Other carboxylates used include benzoate,[30,31] L(+)-mandelate,[24] *N*-phenylanthranilate,[32] and salicylate.[33] Complexes with dienes other than 1,5-COD such as norbornadiene (NBD),[27,28,31,34,35] dicyclopentadiene,[27] (ethylene)$_2$,[30] or (cyclooctene)$_2$,[30] have been attained, usually by varying the [(diene)Rh(μ-Cl)]$_2$ starting material. Several comparable Ir compounds have been reported,[27,30,36] including a patent that described the synthesis of "Ir(cyclooctadiene)(2-ethylhexanoate)" by addition of triethylammonium 2-ethylhexanoate to [(1,5-COD)Ir(μ-Cl)]$_2$.[37] The previous literature describing syntheses of related Rh and Ir(1,5-COD)(μ-O_2CR)-type compounds is summarized in Supporting Information, Table S1.

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(38) The synthesis, characterization, properties, and uses of metal 2-ethylhexanoates and their derivatives have been recently reviewed by Mishra et al.[22] Metal 2-ethylhexanoates were described therein as "of great commercial importance" since they are used as driers in certain paints, lubricating agents, stabilizers for plastics, waterproofing agents, fuel additives, fungicides, in corrosion protection, and as desired precursors in materials science applications "to obtain nano-films, -composites, and -particles" by various deposition methods.[22] For this wide variety of uses, they enjoy the "advantages of being inexpensive, air-stable, non-toxic as well as commercially available for a wide number of elements."[22] Metal carboxylates used in catalytic applications include Ni(2-ethylhexanoate)$_2$ + $AlEt_3$ for industrial polymer hydrogenation,[1,2,22] $Rh_2(OAc)_4$ for olefin hydrogenation,[23] and [(COD)Rh(O_2CR)]$_2$ + PR'_3 for olefin hydrogenation,[24] or hydroformylation.[25]

(39) It was claimed that **1** in the viscous liquid form was air stable,[37] but this seems unlikely to be true, especially for air exposure at long time scales. Some air sensitivity is likely common for complexes of this type; for example, the related compound [$(C_2H_4)_2$Rh(μ-O_2CCH_3)]$_2$ was reported as "moderately air-sensitive."[30]

(40) It has been noted that "single-crystal X-ray data on 2-ethylhexanoate derivatives remain scarce since the long carbon chain favors disorder and, as a result, the obtained crystals are often of poor quality."[22] For this reason, the relative ease with which **1** and **2** yielded X-ray diffraction-quality single crystals is notable. However, the crystal structures of **1** and **2** conform to the above statement in that disorder in the 2-ethylhexanoate alkyl chain consisting of C25-C32 is pronounced.

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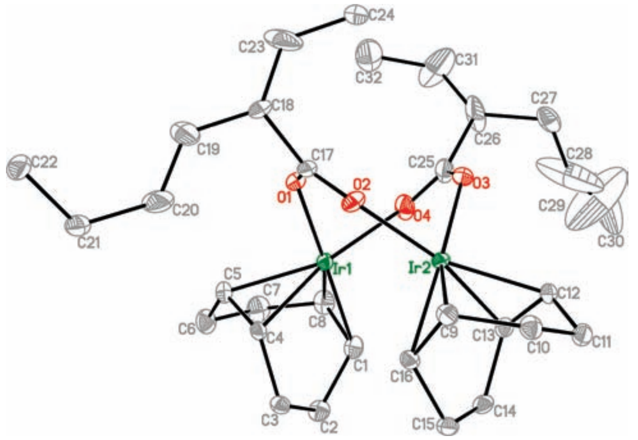

Figure 1. Single crystal X-ray diffraction structure and atomic numbering scheme for **1** with thermal ellipsoids at 30% probability. For the sake of clarity, hydrogen atoms are not shown. The large thermal ellipsoids for C_{28}, C_{29} and C_{30} (here and in Figure 2) are as expected for such floppy alkyl chains.

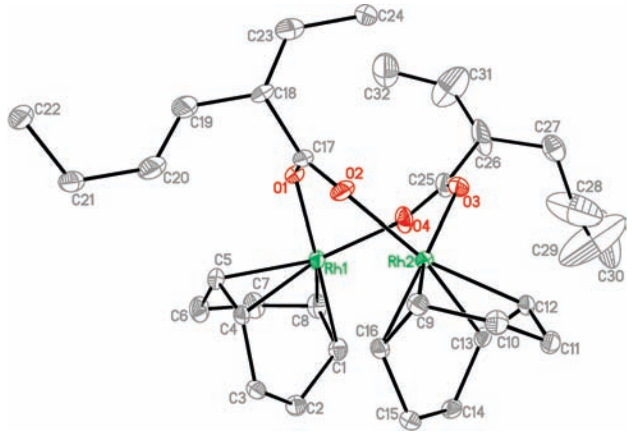

Figure 2. Single crystal X-ray diffraction structure and atomic numbering scheme for **2** with thermal ellipsoids at 30% probability. For the sake of clarity, hydrogen atoms are not shown.

atoms reveals square planar geometries expected for d^8 Ir(I) and Rh(I). However, in both complexes the square planes are imperfect: the metal atoms are displaced from their ligand planes by 0.1522 and 0.1328 Å for Ir1 and Ir2 respectively, and likewise, by 0.1293 and 0.1180 Å for Rh1 and Rh2, respectively, bringing the metal atoms closer together than they would otherwise be. Displacement from the ligand planes has been observed in similar complexes[34] and has been interpreted as evidence of M−M interaction.[42] The dihedral angle between the planes is 56.5° for **1** and 58.1° for **2**, close to angles observed in similar complexes,[42−44] some also with bridging carboxylates.[34,45] The dihedral angle is influenced by the metal atom, the terminal ligands, and the type of bridging ligands for complexes of this type.[46,47]

Table 1. Selected Bond Lengths (Å) for **1** and **2**

bond	**1**, M = Ir	**2**, M = Rh
M1−C8	2.086(5)	2.093(4)
M1−C4	2.086(3)	2.088(3)
M1−O4	2.087(3)	2.086(2)
M1−C5	2.097(4)	2.104(3)
M1−O1	2.097(3)	2.095(2)
M1−C1	2.103(4)	2.105(3)
M2−O2	2.082(3)	2.078(2)
M2−C9	2.084(4)	2.087(3)
M2−C13	2.089(3)	2.092(3)
M2−C12	2.093(4)	2.098(3)
M2−C16	2.094(3)	2.101(3)
M2−O3	2.101(3)	2.100(2)
O1−C17	1.262(6)	1.251(5)
O2−C17	1.261(5)	1.266(4)
O3−C25	1.260(7)	1.262(5)
O4−C25	1.254(7)	1.254(5)

In addition, torsion angles about the M−M axes are 20.4° and 22.0° in **1** and **2**, respectively, as determined using the [C1,C4,C5,C8] centroid-M1 and [C9,C12,C13,C16] centroid-M2 vectors. This leads to a staggering of the two 1,5-COD ligands consistent with similar established structures.[33,34,43,44,46]

Electron counting for complexes **1** and **2** gives formal 16 electron metal centers with no formal M−M bonds. The M−M distances of structures related to **1** and **2**, and what M−M interactions, if any, have been suggested for analogous complexes, can be found in Supporting Information, Table S2. The M−M distances in **1** and **2** of 3.2776(2) Å and 3.3390(4) Å,[48] respectively, agree well with precedent for those compounds in which some extent of weak M−M interaction is believed likely.[28,43b,49] Such axial M−M bonding interactions in dimeric, square planar, d^8−d^8 structures have been previously investigated,[47,50] with it now understood that bonding occurs as a result of donor−acceptor interactions between filled d_{z^2} and empty p_z orbitals.[47,50] Furthermore, bands in the UV−vis absorption spectra, at λ_{max} = 486 nm for **1**, and λ_{max} = 422 nm for **2** (Supporting Information, Figure S5), correspond to bands assigned to metal-centered $d\sigma^*$−$p\sigma$ transitions in the UV−vis spectra of similar compounds.[44,51,52]

Selected bond lengths and angles with estimated standard deviations are given in Tables 1 and 2, respectively, for both compounds. The average M−O distance for **1** is 2.092(6) Å while for **2** it is 2.090(4) Å, close to expected values.[30,34,45] The individual Ir−O distances in **1** are 2.097(3) and 2.082(3) Å for one 2-ethylhexanoate ligand and 2.087(3) and 2.101(3) Å for the other, each bound to Ir1 and Ir2, respectively. Likewise, the individual Rh−O distances in **2** are 2.095(2) and 2.078(2) Å for one 2-ethylhexanoate ligand, and 2.086(2) and 2.100(2) Å for the other, for Rh1 and Rh2, respectively. These distances indicate non-symmetrical bridging of the 2-ethylhexanoate ligands. Each metal center and each 2-eth-

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Table 2. Selected Bond Angles (deg) for **1** and **2**

bond	**1**, M = Ir	**2**, M = Rh
C8−M1−C4	99.17(17)	99.08(14)
C8−M1−O4	86.00(17)	86.09(13)
C4−M1−O4	166.32(14)	164.91(12)
C8−M1−C5	82.35(18)	82.55(15)
O4−M1−C5	153.88(15)	155.97(13)
C8−M1−O1	149.41(16)	150.61(13)
C4−M1−O1	91.47(13)	90.91(11)
O4−M1−O1	90.31(14)	91.36(11)
C5−M1−O1	87.98(15)	88.31(12)
C4−M1−C1	82.15(15)	82.42(13)
O4−M1−C1	94.26(16)	93.18(13)
C5−M1−C1	91.51(17)	91.18(14)
O1−M1−C1	170.54(14)	169.94(12)
O2−M2−C9	85.41(14)	85.51(12)
O2−M2−C13	166.05(15)	165.32(12)
C9−M2−C13	99.28(15)	99.02(12)
O2−M2−C12	154.13(15)	155.52(12)
C9−M2−C12	82.56(15)	82.60(13)
O2−M2−C16	93.49(13)	92.77(11)
C13−M2−C16	82.22(14)	82.44(12)
C12−M2−C16	91.69(15)	91.30(12)
O2−M2−O3	89.89(13)	90.55(10)
C9−M2−O3	151.15(15)	152.13(12)
C13−M2−O3	92.07(14)	91.72(11)
C12−M2−O3	89.72(14)	90.06(11)
C16−M2−O3	169.17(15)	168.87(12)
C17−O1−M1	130.9(3)	131.9(2)
C17−O2−M2	126.3(3)	126.5(2)
C25−O3−M2	128.7(3)	128.7(2)
C25−O4−M1	126.9(3)	127.8(3)
O2−C17−O1	125.6(4)	126.2(3)
O2−C17−C18	117.2(4)	116.5(4)
O1−C17−C18	117.2(4)	117.3(3)
O4−C25−O3	125.9(4)	125.8(3)
O4−C25−C26	118.6(6)	117.0(4)
O3−C25−C26	115.5(6)	117.2(4)

ylhexanoate has one M−O bond longer than the other, with an average difference of 0.015(6) Å in **1** and 0.015(4) Å in **2**. The average M−C distance is 2.09(1) in **1** and 2.096(9) Å in **2**. The average olefinic C═C bond lengths are 1.42(1) and 1.398(9) Å in **1** and **2**, respectively. The marginally longer C═C bond in **1** could be interpreted as the result of the more electron rich Ir(I) engaging in a greater degree of π-back-bonding than its Rh(I) counterpart. These values and interpretations are consistent with expectations based on similar structures.[33,34,43,46]

The α carbon of 2-ethylhexanoate is stereogenic. Complexes **1** and **2** crystallize with (R,R) and (S,S) enantiomers in a unit cell (centrosymmetric space group $P2_1/n$, $Z = 4$). The possibility exists, therefore, to prepare chiral analogues of **1** and **2** (i.e., using enantiopure 2-ethylhexanoate, or analogous chiral ligands) to effect asymmetric catalysis.

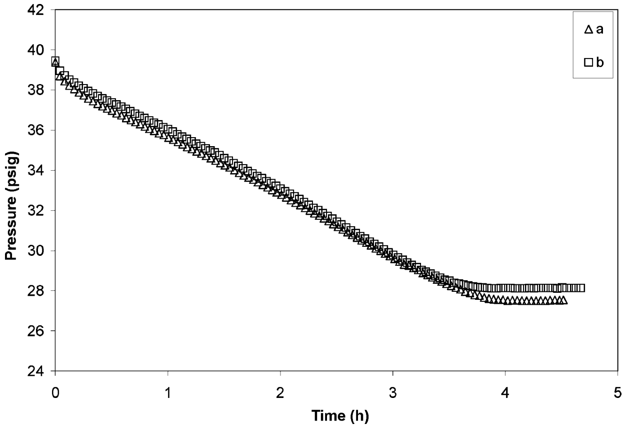

Figure 3. Two representative runs for the hydrogenation of cyclohexene using an Ir Ziegler-type hydrogenation catalyst formed upon combination of **1** and $AlEt_3$, Al/Ir = 1. Experimental conditions for all hydrogenations were solvent = cyclohexane, temp. = 22.0 °C, catalyst concentration = 1.2 mM in [Metal], initial cyclohexene concentration = 1.65 M, and stirring = 1000 rpm. For clarity, only every fifth data point collected of run "a" is displayed. The absence of an induction period shows that either an active catalyst was present from the start of the hydrogenation, or conceivably formed essentially immediately once H_2 was added. The change of the solution during the reaction to darker brown, and the subtle changes to the slope of these curves, suggest that further catalyst evolution is taking place during the hydrogenation.[17]

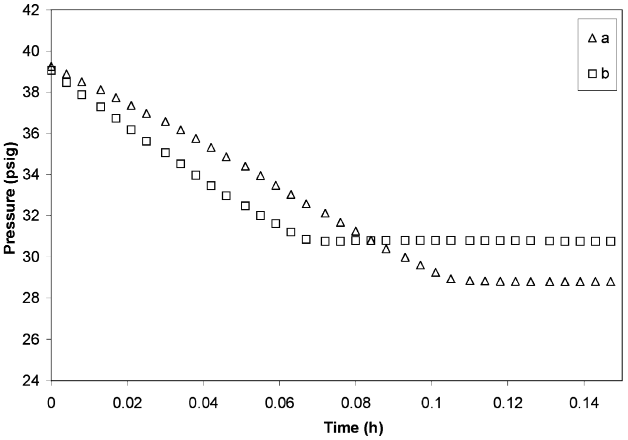

Figure 4. Two representative runs for the hydrogenation of cyclohexene using a Rh Ziegler-type hydrogenation catalyst formed upon combination **2** and $AlEt_3$, Al/Rh = 1. Again, the absence of an induction period demonstrates that either an active catalyst is present from the start of the hydrogenation, or forms essentially immediately once H_2 was added. The catalyst formed using Rh **2** is >30 fold more active than its Ir **1** counterpart. Because of this high activity, the reproducibility of the two hydrogenation curves shown here is sensitive to the reproducibility of the H_2 gas purge cycle, the start of data acquisition, and the precise stirring speed, as would be characteristic of reactions influenced by H_2 gas-to-solution MTL.[57]

Demonstration of Catalytic Hydrogenation Activity. It is important to demonstrate that **1** and **2** form Ziegler-type hydrogenation catalysts. This was accomplished by the addition of a cyclohexane solution of $AlEt_3$ to a cyclohexane solution of **1** or (separately) **2**, at an Al/M = 1 ratio; the result is an immediate change, from the orange solution of **1** to tawny yellow, or the yellow solution of **2** to clear brown. Representative cyclohexene hydrogenations are shown in Figures 3 and 4 for **1** and **2**, respectively. Active H_2 uptake begins immediately in both cases, suggesting that the products of the reaction between $AlEt_3$ and **1** or **2** have *preformed active Ziegler-type hydrogenation catalysts* (i.e., that the active catalysts are formed, at least in large part, from the addition of $AlEt_3$, rather than being solely reduced or activated solely by H_2). Catalyst formation from these systems is being optimized,[17] according to variables known to be important to Ziegler-type hydrogenation catalysts,[53−56] work that will be reported in due course.

The linear versus normally expected exponential shape of both the curves in Figures 3 and 4 is of interest. The Rh catalyst made from **2** is significantly more active for cyclohexene hydrogenation than the Ir catalyst made using **1** (>30 times according to linear fits to the portions of the curve during which pressure loss was occurring, Supporting Information, Figure S10 and Table S3. The rates of H_2

pressure loss in Figure 4 are close to the H_2 gas-to-solution MTL for the apparatus and conditions used,[17] which accounts for the observed linearity.[57] However, since the apparatus and conditions used are identical, the near-linearity of the >30-fold slower hydrogenation curves given by the catalyst made from **1**, shown in Figure 3, cannot also be explained by MTL effects. Close inspection of the hydrogenation curves for **1** reveals subtle changes in the rate of H_2 uptake during the hydrogenation. An additional point is that after all the cyclohexene had been consumed, the catalyst solutions appeared unchanged in the case of **2** (4−7 min), but had turned darker brown in the case of **1** (3.8 h). These observations imply that further catalyst development (i.e., in either consecutive or parallel reactions) is taking place as the cyclohexene hydrogenation proceeds in Figure 3. Detailed characterization studies using EXAFS, electron microscopy, and other methods are in progress,[17] now that **1** and **2** are available and shown to yield active Ziegler-type hydrogenation catalysts.

Control Experiments to Determine if $AlEt_3$ is Required to Form Active Catalysts. Since a fundamental characteristic of Ziegler-type hydrogenation catalysts is their "activation" by an organometallic cocatalyst, frequently AlR_3,[1,2] control experiments were performed to check the necessity of $AlEt_3$ in forming active hydrogenation catalysts from **1** and **2**. Hydrogenations were performed identically to those in Figures 3 and 4, but leaving out the $AlEt_3$ while substituting an equal volume of cyclohexane for the volume introduced by the $AlEt_3$ solution. The results, Supporting Information, Figure S9, reveal that active, though poorly stabilized, nanoparticle and/or bulk metal catalysts are formed following an induction period. These control experiments confirm the need for, and value of, $AlEt_3$ in producing *long-lived* hydrogenation catalysts from **1** and **2**.

Conclusions

The synthesis, unequivocal characterization, and utility as precursors of Zieger-type hydrogenation catalysts of $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ (**1**) and $[(1,5\text{-COD})Rh(\mu\text{-}O_2C_8H_{15})]_2$ (**2**) (COD = cyclohexadiene, $O_2C_8H_{15}$ = 2-ethylhexanoate) have been described herein. Compositional and structural characterization of these compounds was carried out by elemental analysis, FAB-MS, single crystal X-ray diffractometry, FT-IR, UV−vis, and NMR spectroscopy. X-ray crystallography showed that **1** and **2** are isostructural. The complexes are carboxylate-bridged dimers with terminal $\eta^{2:2}$-1,5-COD ligands. They have a bent geometry with dihedral angles of 56.5° and 58.1° for **1** and **2**, respectively, between the square ligand planes of the 4-coordinate M(I) centers. Formally non-bonding M−M distances of 3.2776(2) and 3.3390(4) Å for **1** and **2**, respectively, likely entail weak M−M bonding interactions.[28,42,43b,44,47,49,50]

Both **1** and **2** serve as effective precatalysts that, when combined with $AlEt_3$, form highly active Ziegler-type hydrogenation catalysts. The Rh catalyst formed from **2** is ≥30-fold more active than the Ir catalyst prepared from **1**. This suggests that it will prove useful to have both the Ir and Rh systems for comparison to industrial catalysts, commonly made from Ni or Co.[1,2] Control hydrogenations performed without $AlEt_3$ contained induction periods showing that **1** and **2** display a key feature of Ziegler-type hydrogenation catalysts by requiring "activation" by a cocatalyst, in this case $AlEt_3$.

Publication of our work on the characterization of the catalysts formed from **1** and **2** is forthcoming.[17] That work teaches that the use of well-defined, model second and third row, precatalysts **1** and **2** has been instrumental in elucidating further insights into Ziegler-type hydrogenation catalysts,[17] a ~40 year old problem left unanswered by studies using less well-defined, first row industrial precursors.

Experimental Section

Procedures, Materials, and Instrumentation. Unless indicated otherwise, all manipulations were performed either under N_2 in a Vacuum Atmospheres drybox or using air-free techniques on a Schlenk line. Oxygen levels were continuously maintained in the drybox at ≤5 ppm, monitored by a Vacuum Atmospheres O_2-level monitor. All glassware was oven-dried at 160 °C overnight before use and cooled either under vacuum or under N_2 in the drybox. Unless noted otherwise, all solvents, compounds, and other materials below were stored in the drybox. Cyclohexane was used as received (Sigma-Aldrich 99.5%, anhydrous: water <0.001%). Both cyclohexene (Aldrich, 99%) and tributylamine (J. T. Baker Chemicals) were distilled over sodium under an argon atmosphere before being transferred to the drybox. 2-Ethylhexanoic acid (Aldrich, 99+%) was purged with argon for 30 min. Prior to storage in the drybox, acetone (Burdick and Jackson, water content <0.5%) was purged with argon for 20 min. The complexes $[(1,5\text{-COD})M(\mu\text{-Cl})]_2$ (M = Ir, Rh), Ag(2-ethylhexanoate) (Strem, 99%), and Na(2-ethylhexanoate) (Aldrich, 97%) were used as received. KBr (Aldrich, 99+%, FT-IR grade) was oven-dried at 160 °C overnight before use. Filter paper (Whatman #4) was oven-dried at 160 °C for ≥1 h before use. Argon (General Air, 99.985%) was passed through oxygen and moisture traps consisting of activated carbon and molecular sieves prior to use. Hydrogen gas (General Air, 99.5%) was purified by passing through an indicating moisture trap (Scott Specialty Gas), a disposable O_2 cartridge (Trigon), and an indicating O_2 trap (Trigon). $AlEt_3$ was obtained (Aldrich, 93%) as the neat liquid and used as received. **Caution!** *Aluminum alkyls such as $AlEt_3$ are toxic and pyrophoric, and must be handled with extreme care using air and water-free techniques.*[58]

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Positive ion fast atom bombardment mass spectrometry (FAB-MS) data were acquired on a VG AutoSpec (Fisons Instruments). Nuclear magnetic resonance (NMR) spectra for ^1H and ^{13}C nuclei were obtained on a Varian Inova (JS-300) NMR spectrometer in CD_2Cl_2, CD_3COCD_3, or C_6D_6 (Cambridge Isotopes Laboratory). ^1H NMR spectra were referenced to the residual

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impurity in the deuterated solvents and manipulated by MestRec software after initial acquisition. Samples for Fourier transform infrared (FT-IR) spectroscopy were prepared as KBr discs using a KBr die and a Carver Laboratory Press. FT-IR spectra were obtained on a Nicolet Magna-IR 760 ESP IR spectrometer. Cyclohexane solution samples for UV−visible spectroscopy were prepared in the drybox in 1 cm glass cuvettes equipped with high vacuum stopcocks. Sample concentration was 0.218 and 0.196 (±0.001) mM for **1** and **2**, respectively. UV−visible spectra were obtained using a Hewlett-Packard 8452A diode-array spectrophotometer. Melting points were acquired using a Mel-Temp II melting point measurement apparatus. Sample preparations for X-ray crystallography, FT-IR, and melting points were performed in air where brief exposure of crystalline **1** and **2** to atmospheric oxygen occurred. No degradation of crystalline **1** or **2** was apparent from this treatment.

Synthesis of $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ (1) and $[(1,5\text{-COD})Rh(\mu\text{-}O_2C_8H_{15})]_2$ (2). Detailed accounts of the synthesis procedures are given in the Supporting Information. Briefly, for the synthesis of **1**, a stoichiometric amount of Bu_3NH(2-ethylhexanoate) made from combining Bu_3N and 2-ethyhexanoic acid in acetone was added to an acetone suspension of $[(1,5\text{-COD})Ir(\mu\text{-Cl})]_2$, causing the yellow/orange suspension to immediately turn to a deep-red solution. The product was then extracted into cyclohexane and washed several times with portions of degassed water to remove the residual $Bu_3NH^+Cl^-$. It was important to ensure both air-free conditions and a thorough hexane/H_2O extraction. The hexane was then removed in vacuo, and **1** was crystallized from an acetone solution by slowly cooling to −78 °C, 61% yield. Anal. Calcd for $C_{32}H_{54}Ir_2O_4$ (mol. wt. 887.15 g/mol): C, 43.32; H, 6.14; N, 0.0; O, 7.2%. Found: C, 43.32; H, 5.94; $N < 0.5$; O, 7.9%. m.p.: 67−68 °C. FAB-MS peaks >15% rel. intensity (*m*/*z*, rel. intensity, (estimated ion)$^+$): 886.6, base peak, $([(1,5\text{-COD})Ir(O_2C_8H_{15})]_2)^+$; 741.5, 71%, $(C_{24}H_{37}Ir_2O_2$ or $C_{22}H_{29}Ir_2O_4)^+$; 597.0, 27%, $(C_{11}H_{17}Ir_2O_4)^+$; 591.0, 76%, $(C_{13}H_{19}Ir_2O_2)^+$; 443.1, 92%, $((1,5\text{-COD})Ir(O_2C_8H_{15})\text{-}1)^+$; 297.0, 17%, $(C_8H_8Ir)^+$. A compelling match exists between the observed isotope distribution for the parent ion and one calculated for $[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$ (see Supporting Information, Figure S1). ^1H NMR in C_6D_6, (δ in ppm, multiplicity, no. of H): 4.13−4.23, m, 4; 3.85−3.93, m, 4; 2.35−2.45, m, 4; 1.95−2.15, m, 6; 1.48−1.55, m, 4; 1.00−1.32, m, 20; 0.67−0.81, m, 12. ^{13}C NMR in C_6D_6, (δ in ppm): 188.4s, 64.1m, 55.8m, 50.9s, 33.4s, 32.7s, 31.9m, 30.5s, 27.0s, 23.5s, 14.6s, 12.8s. IR bands >20% abs. (cm^{-1}): 3030−2760m, 1560s, 1457s, 1419s, 1321s.

The procedure was very similar for the synthesis of **2**. Differences were that a solution of Na(2-ethylhexanoate) was used and the resulting crude product solution was filtered before the air-free hexane/H_2O extraction. Crystals of **2** were obtained in an 86% yield. A recrystallization of a portion of the product **2** was required to produce larger, light orange, irregularly shaped single crystals suitable for X-ray diffractometry. Anal. Calcd for $C_{32}H_{54}O_4Rh_2$ (mol. wt. 708.57 g/mol): C, 54.24; H, 7.68; O, 9.0%; Na, 0 ppm. Found: C, 54.28; H, 7.87; O, 8.4%; Na <46 ppm. m.p.: 57−58 °C. FAB-MS peaks >15% rel. intensity (*m*/*z*, rel. intensity, (estimated ion)$^+$): 708.4, 65%, $([(1,5\text{-COD})Rh(O_2C_8H_{15})]_2)^+$; 565.0, 87%, $((1,5\text{-COD})_2Rh_2(O_2C_8H_{15}))^+$; 455.0, 55%, $(C_{16}H_{25}O_2Rh_2)^+$; 415.0, 19%, $((C_{11}H_{13}O_4Rh_2)^+$; 353.1, base peak, $((1,5\text{-COD})Rh(O_2C_8H_{15})-1)^+$; 309.9, 24%, $(C_{13}H_{19}O_2Rh)^+$; 211.0, 67%, $((1,5\text{-COD})Rh)^+$; 147.1, 16%, $(Rh(O_2C))^+$. ^1H NMR in C_6D_6, (δ in ppm, multiplicity, no. of H): 4.30−4.40, m, 4; 4.18−4.30, m, 4; 2.65−2.82, m, 4; 2.15−2.38, m, 6; 1.20−1.72, m, 24; 0.85−0.98, m, 12. ^{13}C NMR in C_6D_6, (δ in ppm): 187.8s, 80.8d, 74.0d, 50.9s, 33.4s, 31.9s, 31.0s, 30.6s, 27.1s, 23.6s, 14.7s, 12.9s. IR bands >20% abs. (cm^{-1}): 3040−2760m, 1567s, 1462s, 1415s, 1324s, 952s, 817s.

Table 3. Summary of Crystallographic Data and Refinement for Compounds **1** and **2**

compound	**1**	**2**
chemical formula	$C_{32}H_{54}Ir_2O_4$	$C_{32}H_{54}O_4Rh_2$
formula weight	887.15	708.57
T (K)	100(1)	100(1)
λ (Å)	0.71073	0.71073
space group	$P2_1/n$	$P2_1/n$
a (Å)	15.7748(5)	15.7608(4)
b (Å)	9.8962(3)	9.9032(3)
c (Å)	20.8847(7)	20.8259(5)
β (deg)	108.408(2)	108.527(1)
V (Å^3)	3093.50(17)	3082.09(14)
ρ_{calcd} (mg/m^3)	1.905	1.527
Z	4	4
μ (mm^{-1})	8.629	1.105
final R indices[a]	$R_1 = 0.0443$, $wR_2 = 0.0827$	$R_1 = 0.0504$, $wR_2 = 0.1260$

[a] R_1 is for $[I > 2\sigma(I)]$, wR_2 is for all data: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

X-ray Crystallographic Structure Determination and Refinement. X-ray diffraction data were collected on a Bruker Kappa APEXII X-ray diffractometer equipped with a beam monochromator. Corrections applied were Lorentz, polarization, and absorption (SADABS).[59] Data collection and cell refinement were accomplished using Bruker SMART software, and data reduction using Bruker SAINT. Both structures were solved by direct methods. Structure solution, structure refinement, and figure preparation were achieved using Bruker SHELXTL.[60] Refinements were accomplished by full-matrix weighted least-squares on F^2 for all reflections. Anisotropic displacement parameters were used for refinement of all non-hydrogen atoms. Hydrogen atoms were included at idealized positions in structure factor calculations. Experimental details for crystal data and structural refinement of **1** and **2** are displayed in Table 3.

Precatalyst and Catalyst Solution Preparation. The Ir and Rh precatalysts **1** and **2** were used in catalyst preparation by first making a stock solution of each in cyclohexane. Specifically, a stock solution of **1**, 7.20 mM in [Ir], was prepared by weighing out 0.0430 ± 0.0001 g (0.0485 mmol) of crystalline **1** and dissolving with 13.46 ± 0.01 mL of cyclohexane. A stock solution of **2**, 7.20 mM in [Rh] was prepared by weighing out 0.04337 ± 0.0001 g (0.0612 mmol) of crystalline **2**, and dissolving in 17.00 ± 0.01 mL of cyclohexane. $AlEt_3$ was used as a 36.0 mM stock solution in cyclohexane prepared by adding 50−70 mL of cyclohexane to a 100 mL volumetric flask, followed by 0.53 ± 0.01 mL of neat $AlEt_3$ measured out by syringe, and then diluting to the mark (this included a 7% correction factor to take into account the 93% purity of the $AlEt_3$, even though the impurities are primarily other aluminum alkyls).

Catalyst solutions were prepared individually, from the stock precatalyst and $AlEt_3$ cocatalyst solutions, in new 22 × 175 mm Pyrex borosilicate culture tubes containing new 5/8 × 5/16 in. Teflon-coated magnetic stirbars. Both culture tube and stirbar had been cleaned by rinsing three times with nanopure water prior to drying at 160 °C overnight and cooled either under vacuum or under N_2 in the drybox. Specifically, and using **1** as an example, a catalyst solution 1.2 mM in [Ir] was prepared individually, and in the drybox, by first adding 0.50 ± 0.01 mL of 7.2 mM **1** to a culture

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tube, followed by 1.90 ± 0.02 mL of cyclohexane (Sigma-Aldrich 99.5%, anhydrous: water <0.001%, used as received). The level of water present is a crucial variable for these $AlEt_3$-containing catalysts.[17,53] Next, 0.100 ± 0.001 mL of 36.0 mM $AlEt_3$ in cyclohexane was rapidly added via syringe, with stirring at 1.0×10^3 rpm (measured with a Monarch Instruments Pocket-Tachometer 100), to make an Al/Ir = 1 solution.

Catalytic Hydrogenation of Cyclohexene. The procedure and apparatus for hydrogenation have been described in detail elsewhere.[18a,61,62] Briefly, after a catalyst solution was prepared, 0.50 ± 0.01 mL of cyclohexene was added, and the culture tube was placed inside a Fisher−Porter (FP) bottle which was sealed, brought out of the drybox, placed in a temperature controlled bath set to 22.0 ± 0.1 °C, and connected to the hydrogenation line[18a,61,62] via TFE-sealed Swagelock Quick-Connects. Stirring of 1000 rpm powered by a Fauske Super magnetic stirplate was started. The use of this stirrer was important in ensuring continuous vortex stirring of the sample at a constant rate in an effort to diminish the influence of H_2 gas-to-solution mass-transfer limitations (MTL).[57] The FP bottle was then filled and purged with H_2 at 40 psig once every 15 s for three and a half-minutes for a total of 15 times. The pressure inside the FP bottle was set to 40 psig, and pressure data acquisition started at the interfaced computer,[18a,61,62] at a total elapsed time of 4 min after the first purge. Hydrogenation conditions: total solution volume was 3.0 mL, 1.2 mM in [M], initially 1.65 M in [cyclohexene], stirred at 1000 rpm, and maintained at 22.0 °C. Pressure data was collected from the FP bottle on the H_2 line by means of an Omega PX-621 pressure transducer interfaced to a PC running LabVIEW 7.0 and handled using Microsoft Excel.[18a,61,62] For control hydrogenations without added $AlEt_3$, hydrogen pressure data was converted to cyclohexene concentration using the known 1:1 H_2 to cyclohexene stoichoimetry.[18a,61] Fits to the data were obtained using Microcal Origin 7.0 according to the 2-step Finke−Watzky mechanism for nanocluster formation consisting of slow nucleation ($A \rightarrow B$, rate constant k_1) followed by fast autocatalytic surface growth ($A + B \rightarrow 2B$, rate constant k_2).[18a]

Acknowledgment. We thank Ms. Susie Miller for conducting the X-ray structure determinations and Prof. Oren Anderson for proofreading the X-ray structure descriptions. This work was supported by NSF Grant CHE-0611588.

Supporting Information Available: Tables with literature and references for previous syntheses of related Ir and Rh(1,5-COD)(μ-O_2CR)-type compounds, and compounds with similar structures. Detailed synthesis procedures and observations. FAB-MS images. Spectra and discussions thereof: FT-IR; UV−vis; and ^{1}H,^{13}C, and VT ^{1}H NMR. Hydrogenation kinetic curves including a control experiment without added $AlEt_3$, fits to the data, and a table of the fit results. A cif file containing the crystallographic data for both structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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