ORGANOMETALLICS Article

Kinetics and Mechanism of Indene C−H Bond Activation by $[(COD)Ir(\mu_2\text{-}OH)]_2$

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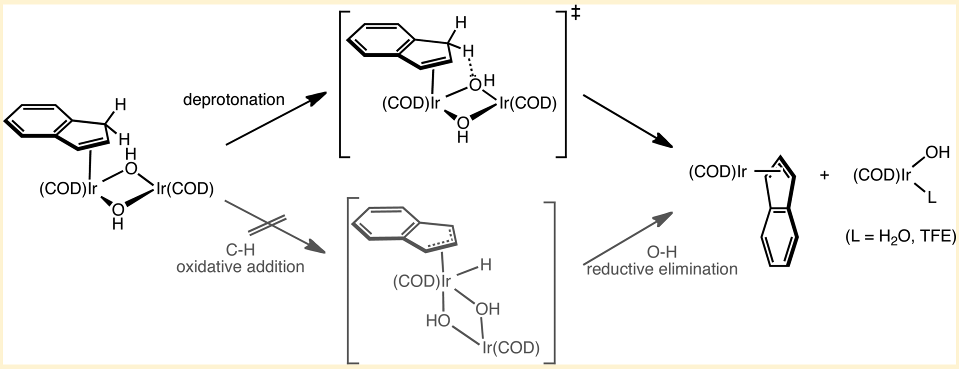
Supporting Information



ABSTRACT: The hydroxy-bridged dimer $[(COD)Ir(\mu_2\text{-}OH)]_2$ (COD = 1,5-cyclooctadiene) cleanly cleaves C−H bonds in indene and cyclopentadiene to produce (COD)Ir(η^3-indenyl) and (COD)Ir(η^5-C_5H_5), respectively. The kinetics of the formation of (COD)Ir(η^3-indenyl) are consistent with a mechanism that involves coordination of indene to $[(COD)Ir(\mu_2\text{-}OH)]_2$ followed by rate-determining C−H activation from the iridium dimer−indene unit. Transition-state analysis of the Ir and Rh hydroxy dimers indicates that the C−H activation proceeds through a direct deprotonation of indene by the M−OH unit rather than a stepwise oxidative addition/reductive elimination mechanism. The crystal structure of $[(COD)Ir]_5(\mu_4\text{-}O)(\mu_3\text{-}O)(\mu_2\text{-}OH)$, a dehydration product of $[(COD)Ir(\mu_2\text{-}OH)]_2$, is presented.

INTRODUCTION

Efficient and selective oxidative functionalization of the C−H bonds of hydrocarbons and other substrates could have a major impact on the development of catalysts for producing value-added fuels, commodity chemicals, and pharmaceuticals.[1] Many transition metal complexes capable of C−H activation are unstable or unreactive in the presence of water, which represents a significant obstacle because water is a potential byproduct of oxidative C−H functionalizations utilizing O_2. Additionally, many model systems for electrophilic C−H activation require making a new C−H bond (e.g., with formation of methane) as the target C−H bond is broken.[2] In consideration of these issues, C−H bond activation using metal alkoxy and hydroxy complexes in the presence of water and alcohols has been the focus of recent studies.[3−5]

Our group has recently found that the air- and water-stable hydroxy-bridged dimers $[(\text{diimine})M(\mu_2\text{-}OH)]_2^{2+}$ and the bis(aquo) dications $[(\text{diimine})M(OH_2)_2]^{2+}$ (M = Pd, Pt) are capable of activating C−H bonds of arenes and allylic positions of olefins.[6] Kinetic studies of these reactions revealed that Pd dimers dissociate to $[(\text{diimine})PdOH(\text{solv})]^+$ monomers in the presence of weakly coordinating solvents prior to reaction with indene, whereas the Pt dimers require acid assistance to generate $[(\text{diimine})Pt(OH_2)_2]^{2+}$, which undergoes faster reaction with indene as compared to the hydroxy-bridged dimer. In both cases, the rate-limiting step was the displacement of the coordinated solvent or water ligand by indene. We also explored the related dimer $[(COD)Rh(\mu_2\text{-}OH)]_2$, anticipating that solvent displacement from a neutral (COD)-Rh(OH)(solv) species would be faster than from the cationic group 10 analogues.[7] The hydroxy-bridged dimer $[(COD)Rh(\mu_2\text{-}OH)]_2$ was found to react with indene directly via the dimer, and the rate-limiting step was found to be C−H activation rather than ligand displacement. Furthermore, the Rh dimer reacts with indene more slowly than do the group 10 dimers. Thus, we have turned our attention to the Ir congener $[(COD)Ir(\mu_2\text{-}OH)]_2$, anticipating that it may undergo C−H activation more rapidly than $[(COD)Rh(\mu_2\text{-}OH)]_2$. Herein we report activation of C−H bonds of indene and cyclopentadiene by the iridium dimer, together with the results of kinetics studies of the mechanisms of these reactions.

RESULTS AND DISCUSSION

$[(COD)Ir(\mu_2\text{-}OH)]_2$ (**1**; COD = 1,5-cyclooctadiene) reacts with 2 equivalents of indene to quantitatively (by NMR)

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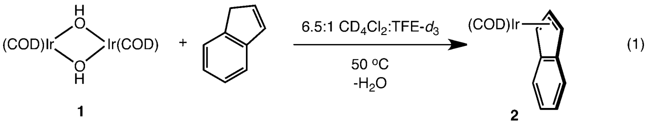
generate (COD)Ir(η^3-indenyl), **2**, with release of water (eq 1). The hydroxy-bridged iridium dimer is only slightly soluble in neat DCE-d_4 (DCE = 1,2-dichloroethane), so solvent mixtures of TFE-d_3 (TFE = 2,2,2-trifluoroethanol) and DCE-d_4 were utilized in the studies discussed below.

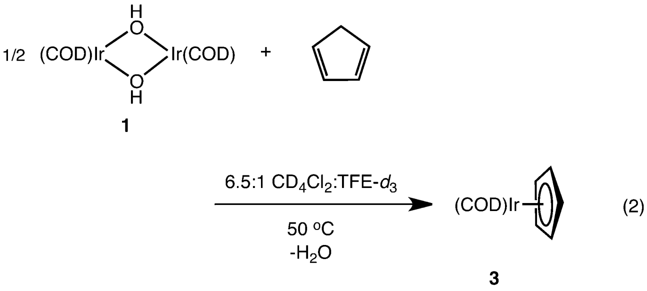


The reaction kinetics were followed under the conditions shown in eq 1, with varying concentrations of indene and TFE-d_3. Dimer **1** and product **2**, but no intermediates, were observed by ^{1}H NMR spectroscopy. Kinetic runs at varying [indene] (see Supporting Information (SI), Figures S1 and S2) indicate that the reaction is first order with respect to both indene and **1**. Similar to C−H activation with [(COD)Rh(μ_2-OH)]$_2$, there is a dependence on [TFE] that is consistent with a two-term rate law, wherein one pathway has a first-order dependence on [TFE] and the other is independent of [TFE] (see SI, Figure S3). C−H activation is strongly implicated as rate-determining by comparing the rates of reaction of **1** with indene and with 1,1,3-trideuteroindene, k_H/k_D = 3.1(1) (see SI, Figure S4). An Eyring analysis of the temperature dependence of reaction rate from 300 to 333 K indicates activation parameters $\Delta H^\ddagger$ = 20.9(1) kcal·mol^{-1} and $\Delta S^\ddagger$ = −12.7(1) eu, the latter consistent with coordination of indene to **1** in the transition state.

These kinetic data suggest a mechanism similar to that for reaction of indene with [(COD)Rh(μ_2-OH)]$_2$ (Scheme 1). The first-order dependence on [indene] indicates its pre-equilibrium coordination to **1** affording adduct **A**, with the equilibrium strongly favoring **1** because no intermediates are detected by ^{1}H NMR. In accord with the kinetics, the rate-determining step, likely C−H bond activation based on the KIE, occurs from a dimeric Ir species **A** generating 1 equivalent each of **2** and [(COD)Ir(OH)(solv)], **C**. Monomer **C** then reacts rapidly with another equivalent of indene to generate a second equivalent of **2**. The [TFE-d_3] dependence may indicate competitive precoordination of TFE to generate **B**, which can undergo C−H activation in a similar manner to generate **2** and **C**. Alternatively, the rate dependence on [TFE-d_3] could be a result of a change in solvent polarity; TFE-d_3 constitutes greater than 10% of solvent by volume.

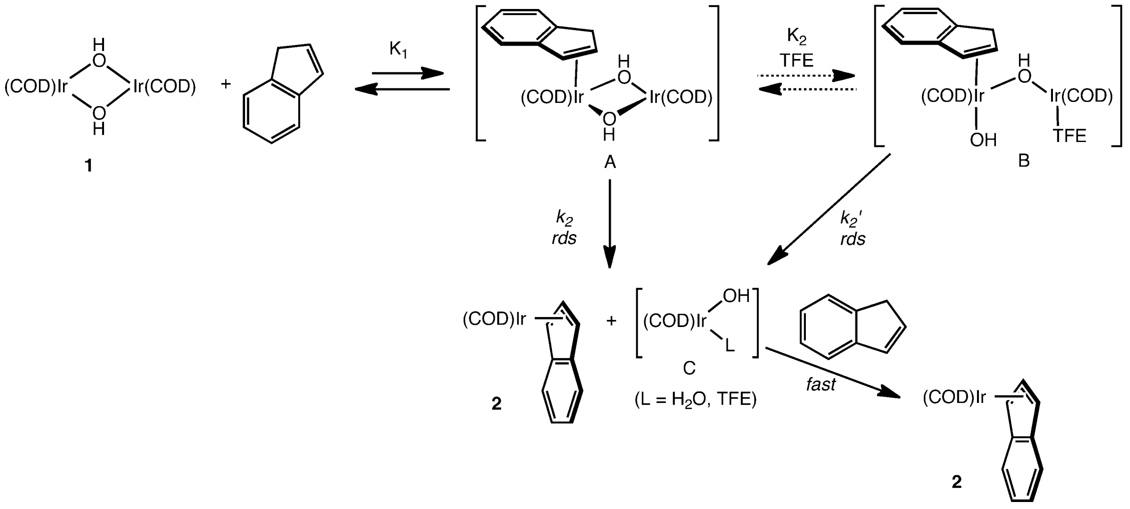
Compared to indene C−H activation with [(COD)Rh(μ_2-OH)]$_2$, the reaction of indene with **1** proceeds at roughly the same rate and through a similar mechanism. The enthalpy of activation is larger for the Ir system (20.9(1) kcal·mol^{-1} for Ir vs 16.6(1) kcal·mol^{-1} for Rh), but is partially offset by a less negative entropy of activation (−12.7 eu for Ir vs −21.7 eu for Rh). A possible explanation for the differences in $\Delta H^\ddagger$ could be differences in M−OH bond strength; if the transition state of C−H activation involves significant M−OH bond breakage, a stronger Ir−OH bond would lead to a larger $\Delta H^\ddagger$ than the corresponding Rh analogue. Since oxidation of Ir^{I} to Ir^{III} should be more facile than for Rh^{I} to Rh^{III}, which would result in a smaller $\Delta H^\ddagger$ in contradiction to the observations, we tentatively favor direct attack on the coordinated indene C−H bond by hydroxide rather than oxidative addition of the C−H bond followed by reductive elimination of water (Scheme 2).

Hydroxy-bridged dimer **1** does not activate the C−H bonds of cyclopentene, cyclohexene, or other substrates having stronger C−H bonds. However, **1** does rapidly react with the C−H bond of cyclopentadiene to produce (COD)Ir(η^5-C$_5$H$_5$), **3** (eq 2).

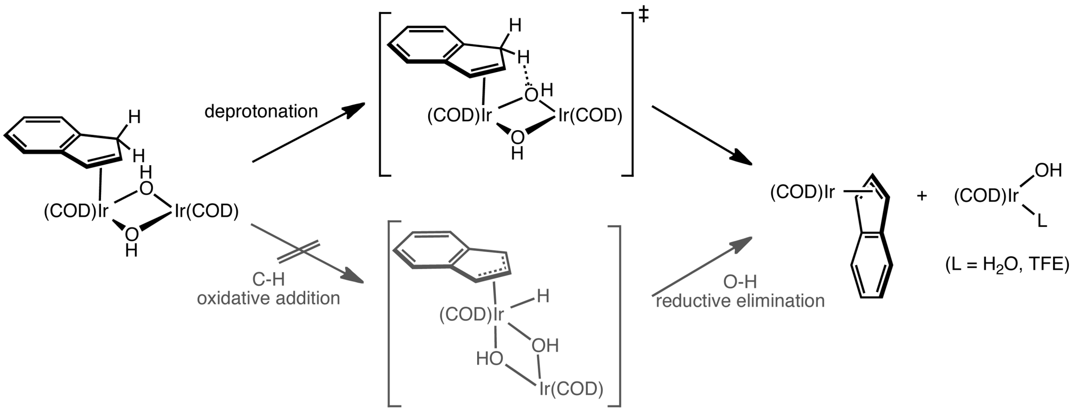


Interestingly, **1** is stable in dichloromethane that has not been dried, but it is unstable in dry dichloromethane. When yellow **1** was dissolved in dichloromethane-d_2 either dried over CaH$_2$ or passed through an activated alumina column, the solution turned a deep orange color over the course of a few hours. After standing overnight, the solution had precipitated needle-shaped, dark red crystals. An X-ray diffraction analysis of

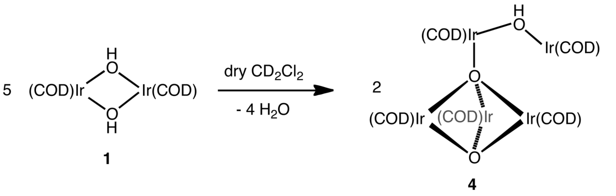
Scheme 1



Scheme 2



the red crystalline material revealed it to be a product of **1** resulting from loss of water, $[(COD)Ir^I]_5(\mu_4\text{-}O)(\mu_3\text{-}O)(\mu_2\text{-}OH)$, **4** (eq 3, Figure 1). Pentamer **4** contains a trinuclear Ir_3 core capped by two oxo ligands, similar to a trinuclear cluster prepared by Cotton, $[(COD)Ir^{II}]_3(\mu_3\text{-}O)_2(\mu_2\text{-}I)$.[8] The reaction is apparently driven by the expulsion of H_2O from **1** into dry methylene chloride and by the insolubility of **4**. The reaction does not appear to be reversible; addition of H_2O to a solution of **4** does not regenerate **1**.



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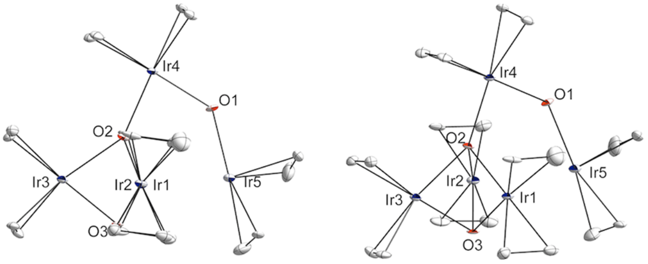

Figure 1. ORTEP drawings of **4** with 50% thermal ellipsoids (two views: side-on, left, and offset, right). Selected bond distances (Å): Ir1−O2 2.102(1); Ir2−O2 2.0885(1); Ir3−O2 2.1409(1); Ir4−O2 2.0827(1); Ir1−O3 2.0225(1); Ir2−O3 2.0467(1); Ir3−O3 2.0536(1); Ir4−O1 2.0361(1); Ir5−O1 2.0906(1). Intermetallic distances (Å): Ir1−Ir2 3.0443(1); Ir1−Ir3 2.7610(1); Ir1−Ir5 2.8632(2); Ir2−Ir3 2.7292(2); Ir2−Ir5 3.0890(2). H atoms and methylene groups of the COD ligands have been removed for clarity.

4 likely forms by initial dehydration of **1** to produce a bridging Ir oxo complex, [(COD)IrOIr(COD)], which proceeds to dimerize to form a tetranuclear Ir_4O_2 core, followed by reaction with an additional half-equivalent of **1**. The net result of the reaction is the spontaneous intramolecular deprotonation of a hydroxyl group to generate a bridging Ir^I oxo species. This transformation is unprecedented on Ir^I, and complex **4** appears to represent the first crystallographically characterized example of a formal Ir^I species containing bridging oxo ligands.

■ CONCLUSIONS

$[(COD)Ir(\mu_2\text{-}OH)]_2$ activates both indene and cyclopentadiene C−H bonds to produce $(COD)Ir(\eta^3\text{-indenyl})$ (**2**) and $(COD)Ir(\eta^5\text{-}C_5H_5)$ (**3**), respectively. The kinetic isotope effect and rate law reveal that **1** reacts directly from the substrate/dimer adduct and that C−H bond activation is rate-limiting. These features are similar to those for the rhodium analogue, $[(COD)Rh(\mu_2\text{-}OH)]_2$. Comparisons of the activation enthalpies for reaction of indene with **1** vs $[(COD)Rh(\mu_2\text{-}OH)]_2$ suggest that the mechanism of C−H activation by $[(COD)M(\mu_2\text{-}OH)]_2$ (M = Rh, Ir) is likely intramolecular deprotonation, rather than oxidative addition of the C−H bond to the metal center to produce Ir^{III} hydride followed by reductive elimination of water. Hydroxy-bridged dimer **1** spontaneously dehydrates in dry solvents to produce a pentameric Ir^I oxo-bridged complex, **4**, which may be of interest to water oxidation schemes.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out in a glovebox under a nitrogen atmosphere. $[(COD)Ir(\mu_2\text{-}OH)]_2$[9] and 1,1,3-trideuteroindene[10] were prepared according to literature procedures. Indene and dicyclopentadiene were reagent-grade commercial samples purchased from Sigma-Aldrich. Dicyclopentadiene was freshly cracked prior to use. 1,2-Dichloroethane-d_4 and trifluoroethanol-d_3 were purchased from Cambridge Isotopes and degassed prior to use. For some experiments, methylene chloride was dried via the method of Grubbs.[11] ^1H NMR spectra were recorded using a Varian INOVA 500 MHz spectrometer. X-ray crystallographic data collection was carried out on a Bruker KAPPA APEX II diffractometer with a 0.71073 Å Mo Kα source. Crystals were removed from a scintillation vial to a microscope slide coated with Paratone N oil. Samples were selected and mounted on a glass fiber with Paratone N oil. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. Details regarding refined data and cell parameters are displayed in Table 1.

Synthesis of (COD)Ir(η^3-indenyl) (2). A 5.0 mg amount of **1** (0.0079 mmol, 1 equiv) was dissolved in 650 μL of DCE-d_4 and 100 μL of TFE-d_3 in a J-Young NMR tube. Then 9.2 μL of indene (0.080 mmol, 10 equiv) was added to the solution, and the tube sealed and heated to 50 °C. The progression of the reaction was followed by NMR, with complete conversion occurring after 4 h. The identity of the product was confirmed by comparing the ^1H NMR spectrum to that of an authentic sample of **2** purchased from Strem.

Synthesis of (COD)Ir(η^5-C_5H_5) (3). A similar preparation to that used to produce **2** was used, substituting freshly cracked cyclopentadiene for indene. The reaction was followed by ^1H NMR, and complete conversion to product (by NMR) occurred within 30 min. The identity of **3** was confirmed by comparing the ^1H NMR spectrum

Table 1. Crystal and Refinement Data for Complex 4

CCDC number	885854
empirical formula	$C_{40}H_{60}O_3Ir_5{\cdot}CH_2Cl_2$
fw	1635.93
T (K)	100(2)
a, Å	10.3282(4)
b, Å	22.4057(9)
c, Å	12239(7)
α, deg	90
β, deg	92.280(2)
γ, deg	90
volume, Å^3	3982.6(3)
Z	4
cryst syst	monoclinic
space group	$P2_1/n$
d_{calc}, g/cm^3	2.726
range, deg	2.17 to 32.63
μ, mm^{-1}	16.819
abs correction	semiempirical
GOF	1.436
R_1[a]	R1 = 0.0236
wR_2[b] [$I > 2\sigma(I)$]	wR2 = 0.0381

[a]$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b]$wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

to a sample prepared via salt metathesis of $[(COD)Ir(\mu_2\text{-}Cl)]_2$ with NaCp following a literature procedure.[12]

Synthesis of $[(COD)Ir]_5(\mu_4\text{-}O)(\mu_3\text{-}O)(\mu_2\text{-}OH)$ (4). A 10 mg (0.016 mmol) portion of **1** was suspended in 2 mL of dry, degassed methylene chloride-d_2 in a J-Young NMR tube. The tube was sealed, and the suspension was refluxed in an oil bath for 1 h to give an orange solution with a small amount of **1** undissolved at the bottom. The solution was cooled to room temperature and left to stand overnight, during which time small red crystals of **4** formed. After 12 h, near quantitative formation of **4** occurred. **4** was identified via X-ray crystallography since it was insoluble in all solvents tested. The formation of **4** could also be achieved without heating the suspension, but the general insolubility of **1** resulted in this method being slower and lower yielding. For comparison purposes, **1** was dissolved in "wet" methylene chloride-d_2. However, **1** remained intact and did not produce $[(COD)Ir]_5(\mu_4\text{-}O)(\mu_3\text{-}O)(\mu_2\text{-}OH)$.

Standard Reaction Protocol for Kinetics Experiments. A 750 μL sample of a 6.5:1 DCE-d_4/TFE-d_3 stock solution containing 0.010 M **1** (5 mg, 0.0079 mmol) and 5 μL of TMS_2O (as a standard) was syringed into a J-Young NMR tube inside a glovebox. The sample was cooled to 0 °C, and the desired amount of a 1.575 M stock solution of indene in DCE-d_4 was added to the reaction (50, 100, or 200 μL) via syringe. An additional amount of DCE-d_4 was added to reactions that contained less than 200 μL of the indene stock solution to give all reactions a total volume of 0.95 mL. The reactions were then inserted into the preheated NMR probe, and the temperature was allowed to equilibrate for 5 min before locking and shimming the instrument. An additional 5 min was utilized for locking and shimming before finally starting data collection 10 min after initial sample insertion. Single spectra were collected every 5 min until the starting material was completely consumed. The spectra were processed using the MestReNova software package, and the starting material and product peaks were integrated against the internal TMS_2O standard. The two peaks used for all kinetic determinations were the vinylic COD peak in **1** (Figure 2, 3.68 ppm) and the 2-position of the η^3-indenyl in **2** (Figure 2, 6.04 ppm). In all cases, disappearance of the starting material was directly correlated to appearance of product. Several of the reactions were run in duplicate or triplicate to confirm reproducibility. The KIE experiments were carried out in a similar manner, utilizing 1,1,3-trideuteroindene in place of normal indene.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Log plots and Eyring plots for all kinetic analyses. Tables of bond lengths, angles, and anisotropic displacement parameters for **4**. X-ray crystallographic data file (CIF) for **4**. The crystallographic data for **4** have been deposited with the Cambridge Crystallographic Data Center and can be obtained by requesting the deposition number. This material is available free of charge via the Internet at http://pubs.acs.org.

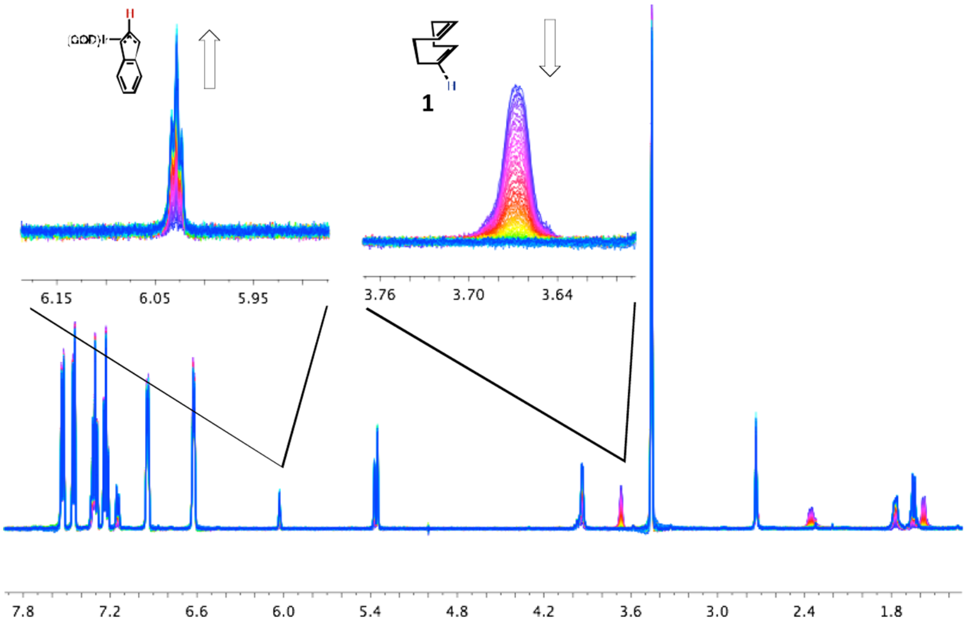

Figure 2. Example spectral array for a kinetic run of **1** with 10 equivalents of indene at 50 °C. The peaks that were integrated were the vinylic COD protons on the starting material **1** and the 2-H position on the product **2**.

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Notes

The authors declare no competing financial interest.

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