# Preparation and Reaction Chemistry of ($\eta^5$-Indenyl) Iron Alkyl Complexes

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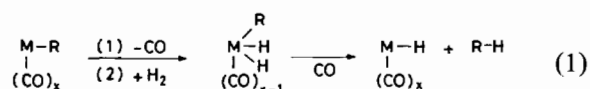
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## Abstract

The four methyl and acetyl complexes In(CO)-(L)FeR (L = CO, $PPh_3$; R = $CH_3$, $COCH_3$) have been synthesized and characterized as $\eta^5$-indenyl (In) complexes. These were prepared in an attempt at using the indenyl ligand to generate a vacant coordination site, through its $\eta^5/\eta^3$ tautomerization, and hence promote hydrogenation of the methyl or acetyl ligand. These complexes, however, remain inert towards $H_2$ under generally mild conditions: to 50 °C/1200 psig $H_2$ in 1,2-dichloroethane solution. When the temperature is raised to 100 °C these complexes degrade, with no evidence for acetaldehyde/ethanol production.

## Introduction

The ($\eta^5$-$C_5H_5$)(CO)(L)Fe—R series of $\eta^1$-alkyl and -acyl complexes have been a mainstay of transition organometallic chemistry, a great deal being known about both synthetic nuances and mechanistic details involving the chemistry of the Fe—C $\sigma$-bond [1]. Yet hydrogenation of these complexes with hydrogenolysis [2] of the alkyl or acyl ligand has not been realized [2]. In contrast, hydrogenation of analogous $(CO)_5Mn$—R [2, 3] and $(CO)_4Co$—R [4] compounds cleaves the metal—R bond [eqn. (1)] and extrudes R—H. Such reactivity derives from the well-established CO-lability of these Mn and Co complexes; the plausible reaction sequence** entails first CO dissociation, then oxidative addition of $H_2$ to the now coordinatively unsaturated metal center, reductive elimination

$$M-R \xrightarrow[\text{(2) } +H_2]{\text{(1) } -CO} \underset{(CO)_{x-1}}{M\overset{R}{\underset{H}{\diagup}}} \xrightarrow{CO} \underset{(CO)_x}{M-H} + R-H \quad (1)$$

of RH, and reassociation of CO. A similar hydrogenation mechanism is less likely for the CpFe series of alkyl/acyl complexes due to the relative non-lability of its CO ligands (under thermal conditions). This non-lability undoubtedly originates in the presence of the Cp ligand (a potent forward-donor of electron density of the metal)*** which enhances the metal-to-CO back-bonding.

In recent reports we have used the Cp(CO)(L)Fe system [L = CO, $PPh_3$, $P(OCH_3)_3$] to support the coordinated-ligand chemistry that transpires in

$$CpFe^+ \longrightarrow \longrightarrow Fe-C\overset{O}{\underset{CH_2OR}{\diagup}} \quad Fe-CH\overset{OR}{\underset{CH_2OR}{\diagup}} \quad Fe-CH_2\overset{}{\underset{COR}{\diagdown}} \quad Fe-CH_2\overset{}{\underset{CH}{\diagdown}} \quad Fe-CH\overset{OR}{\underset{CH}{\diagup}}$$

$$Fe = Cp(CO)(L)Fe \qquad (2)$$

converting two carbonyls to $C_2$-ligands and subsequently to their $C_2$-organics [9]. Thus, starting with $Cp(CO)_3Fe^+$ two CO groups have been selectively converted [eqn. (2)] to the $C_2$-oxygenated ligands alkoxyacetyl, $\alpha,\beta$-dialkoxyethyl, carboalkoxymethyl, formylmethyl and $\alpha$-alkoxyformylmethyl. Protonolysis of the latter three using strong acid then released free alkyl acetate, acetaldehyde, and glycolaldehyde ether, respectively. We are now interested in designing related alkyl iron complexes and devising reaction conditions for hydrogenating these $C_2$-ligands and releasing the free organic molecules.

Our approach to hydrogenating organoiron alkyl complexes entails supplanting the $\eta^5$-Cp ligand by $\eta^5$-indenyl (*i.e.*, In)† and in so doing attempt to promote an associative mode of reactivity between In(CO)(L)Fe—R complexes (1–4) and $H_2$ [eqn. (3)].
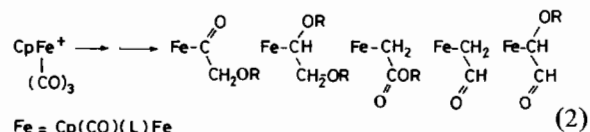
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**This mechanism obviously has many features in common with that for homogeneous hydrogenation of alkenes [5a]. Heterolytic cleavage of $H_2$ by the alkyl metal complex appears not to be important with Gr 8 metals [5b]. Molecular $H_2$ need not be the actual reductant [eqn. (1)] as sufficient precedent exists for hydride complexes M—H (procured with $H_2$) also causing the net hydrogenolysis of M—R under certain conditions. Plausible mechanisms include: (1) oxidative addition of M—H to the alkyl complex (*e.g.*, eqn. (1) with M—H in place of $H_2$) [6] (2) free-radical chain reactions, and (3) binuclear reductive elimination [7].

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***For theoretical treatment of bonding in $Cp(CO)_2Fe$ system see ref. [8b].

†Unless otherwise noted, the In descriptor refers to $\eta^5$-indenyl complexation through the fused 5-member ring. $\eta^3$-In designates metal bonding via $\eta^3$-allylic complexation of the same ring, but using the benzenoid-allyl tautomer. Only $\eta^5$-In complexes have been detected in our studies. Also, we have not detected any haptotropic rearrangement processes in which metal center migrates across the fused $C_9H_7$ ring system [10].

$$\text{Fe-R} \longrightarrow \text{Fe} \cdots \text{H} \longrightarrow \text{Fe-H} + \text{R-H} \quad (3)$$

1 L = CO; R = CH$_3$     3 L = PPh$_3$; R = CH$_3$

2 L = CO; R = COCH$_3$     4 L = PPh$_3$; R = COCH$_3$
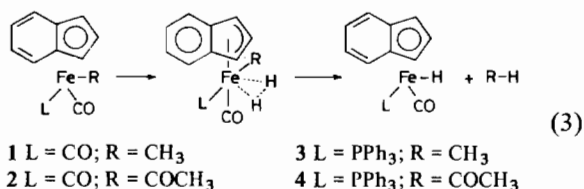
Driving force for this associative mechanism in binding H$_2$ results from availability of the $\eta^3$-In tautomer, which affords a coordinatively unsaturated metal center. Transience of this tautomer presumably derives from benzenoid resonance stabilization of the ene-$\eta^3$-allyl intermediate. The overall $\eta^5$-In/$\eta^3$-In transformation therefore could generate a vacant coordination site on Fe for binding H$_2$ (oxidative addition*) without having to dissociate a CO ligand. Subsequent reaction between ligated H$_2$ and the coordinated alkyl or acyl group— reductive elimination of RH—may be further induced as the $\eta^3$-In 'snaps-back' to its thermodynamically favored $\eta^5$-tautomer. In this paper we report on full synthetic details for the In(CO)(L)FeR complexes 1—4 and on their attempted hydrogenation reactions.

## Experimental

All synthetic manipulations were performed under a nitrogen atmosphere using standard syringe/septum and Schlenk-type bench-top techniques for handling moderately air-sensitive organometallics [11]. Solvents for synthetic work and for recording spectral data were deoxygenated by bubbling nitrogen through for ~20 minutes. Camag alumina (neutral, activity 3) was used in column chromatography. Hydrogenation studies were carried out under conditions of vigorous stirring using a Parr Instrument Company Mini-Reactor fitted with an overhead stirrer and a glass liner. Heating of pressurized reactions was accomplished with an automatic temperature regulator.

Infrared spectra were taken of CH$_2$Cl$_2$ solutions (0.10 mmol/1.5 ml) in a NaCl amalgam-spaced (0.10 mm) solution cell and were recorded on a Perkin-Elmer Model 297 spectrophotometer. The $\nu$(CO) frequencies (2200—1450 cm$^{-1}$) were calibrated against the polystyrene 1601 cm$^{-1}$ absorption; they are accurate to ±2 cm$^{-1}$ below and ±5 cm$^{-1}$ above 2000 cm$^{-1}$. IR spectra of the methyl and acetyl complexes used in this study exhibited straight-line Beer's law behavior in CH$_2$Cl$_2$

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*We use the three-center transition state formulation:

$$\text{Fe} \overset{\text{H}}{\underset{\text{H}}{\cdots}}$$

to denote H$_2$ interacting at and perhaps oxidatively adding to a vacant coordination site.

solution. $^1$H NMR spectra were taken of concentrated CDCl$_3$ solution after centrifuging trace amounts of insoluble residues. Varian models T-60 and XL-200 NMR spectrometers supplied the NMR spectra, which are reported as $\delta$ values in ppm downfield from internal (CH$_3$)$_4$Si. GLC analyses were performed by using a Gow-Mac Model 505 instrument equipped with 4 ft. by 1/4 in. stainless-steel column packed with Carbowax 20 M (20%) on Chromosorb P (80/100 mesh) (He carrier, column temperature 150 °C). Combustion microanalyses were performed by Baron Consulting Co., Orange, Connecticut and by Mic Anal, Tucson, Arizona.

Organic reagents were procured commercially and used as received. Tetrahydrofuran was additionally distilled under nitrogen from sodium benzophenone ketyl. Methylene chloride and 1,2-dichloroethane were distilled under nitrogen from P$_2$O$_5$, and nitromethane was dried by storing (under nitrogen) over freshly activated 4 Å molecular sieves. Authentic samples of [Cp(CO)$_2$Fe]$_2$, Cp(CO)$_2$FeCH$_3$ [11], Cp(CO)$_2$FeCOCH$_3$ [12], Cp(CO)(PPh$_3$)FeCH$_3$ [13], and Cp(CO)(PPh$_3$)FeCOCH$_3$ [13] were available from previous studies for direct spectroscopic comparison.

*Preparation of [In(CO)$_2$Fe]$_2$, 7*

This procedure is an adaptation of that by Hallam and Pauson [14]. A 1 l, three-necked flask equipped with an overhead stirrer, a Friedrichs condenser (connected to an oil-filled glass bubbler/N$_2$ inlet), and a stopper was charged with indene (400 ml, 3.44 mol) and iron pentacarbonyl (40 ml, 0.304 mol). (The Fe(CO)$_5$ had been pre-filtered through glass wool/sand.) As the yellow-brown solution heated at 145 °C (oil bath) both 5 h, a reddish-purple suspension and much gas (CO) evolution resulted. An additional 40 ml of Fe(CO)$_5$ was added and the mixture was heated for another 8 h, or until the yellow Fe(CO)$_5$ condensate was no longer detected. The reaction was cooled to room temperature, diluted with 400 ml pentane, cooled to 0 °C for 1 h, and filtered. The crude black solid, after washing with 3 × 50 ml pentane, was extracted with acetone (8 × 100 ml); and these extracts were filtered through a 4 cm layer of alumina (using a coarse-porosity sintered-glass filter funnel, 6.5 in. I.D.). **Caution: The crude reaction residues were pyrophoric.** The acetone filtrates were evaporated, and the product was extracted with CH$_2$Cl$_2$ (7 × 80 ml). Filtration of the combined CH$_2$Cl$_2$ extracts through alumina (4 cm), concentration to 200 ml, dilution with 90 ml heptane, and further concentration (to ~100 ml) on a Buchi rotovaporator slowly deposited reddish-brown crystals of [In(CO)$_2$Fe]$_2$, 7 [14]. These were filtered, washed with pentane (3 × 25 ml) and vacuum dried. Yield 24.36 g (18%) of spectroscopically pure 7. IR (CH$_2$Cl$_2$) 1991,

1949 cm$^{-1}$ (C≡O), 1881 cm$^{-1}$ (C=O); NMR (CDCl$_3$) $\delta$ 7.16 (m, 4 H, benzo), 5.22 (m, 1 H, C$_2$H), 4.95 (m, 2 H, C$_{1,3}$H).

### Preparation of In(CO)$_2$FeCH$_3$, 1

To a nitrogen-flushed three-necked 500 ml amalgam flask, fitted with a nitrogen inlet-adapter and overhead stirrer, was added 350 ml of de-oxygenated THF, excess of 1% sodium amalgam (70 ml, freshly decanted), and [In(CO)$_2$Fe]$_2$ (15.00 g, 33.03 mmol). The mixture was stirred vigorously in the presence of a slightly positive nitrogen atmosphere for 45 min. The solution turned from dark red-brown to red-orange. Excess sodium amalgam was drained carefully through the bottom stopcock, after allowing the mixture to settle ($\sim$0.5 h). Treatment of the remaining In(CO)$_2$-Fe$^-$Na$^+$ solution with CH$_3$I (4.3 ml, 69.5 mmol) (dropwise addition via syringe into the gently stirred mixture) afforded a yellow-brown suspension. This was evaporated and extracted with pentane (8 × 40 ml), and the combined extracts were percolated through a 3 cm bed of alumina (Schlenk filter). All yellow material was eluted from the alumina with pentane, before solvent was evaporated from the combined pentane fractions. A dark yellow-brown oil remained after vacuum drying ($10^{-2}$, 1 h) that corresponded to spectroscopically pure In(CO)$_2$FeCH$_3$ 1 [15] (15.32 g, 95%). IR (CH$_2$Cl$_2$) 2003, 1948 cm$^{-1}$ (C≡O); NMR (CDCl$_3$) $\delta$ 6.95 (m, 4 H, In-benzo), 5.10 (d, J = 2.4 Hz, 2 H, In-C$_{1,3}$H), 4.61 (t, J = 2.4 Hz, 1 H, In-C$_2$H), −0.45 (s, 3 H, FeCH$_3$).

### Preparation of In(CO)$_2$FeCOCH$_3$, 2

A THF solution (300 ml) containing In(CO)$_2$-Fe$^-$Na$^+$ was prepared from [In(CO)$_2$Fe]$_2$, 7, (9.00 g, 19.82 mmol) as described above. Remaining amalgam was drained, and the anion solution was transferred via 16 ga stainless-steel double-ended needle and nitrogen pressure to a second reaction flask. This reaction flask, a 500 ml one-necked round-bottom with a magnetic stirring bar and a nitrogen inlet-adapter fused to the side, containing the anion solution was gently stirred as acetyl chloride (4.5 ml, 63 mmol) was injected. After 5 min the resulting yellow suspension was evaporated, extracted with CH$_2$Cl$_2$ (7 × 40 ml), the extracts were filtered through 5 cm of alumina. The combined extracts then were concentrated to 100 ml, diluted with 75 ml heptane, and concentrated again (to $\sim$75 ml) on a Buchi rotovaporator. Some golden-brown solid appeared, although crystallization was completed only after cooling the mixture to −80 °C (0.5 h). Solvent was then removed using a stainless steel-needle (18 ga) (fitted with 5 mm sintered-glass dispersion tube) and nitrogen pressure. Two washings of the resulting yellow-brown crystals

with pentane (40 ml each, −80 °C) and vacuum drying ($10^{-2}$ mm, 2 h at 22 °C) left 9.26 g (86%) of In(CO)$_2$FeCOCH$_3$, 2 as yellow-brown crystals, mp 66.0−67.5 °C. IR (CH$_2$Cl$_2$) 2019, 1959 cm$^{-1}$ (C≡O), 1664 cm$^{-1}$ (C=O); NMR (CDCl$_3$) $\delta$ 7.42, 7.18 (A$_2$B$_2$ mults, 4 H, In-benzo) 5.58 (d, J = 2.9 Hz, 2 H, In-C$_{1,3}$H), 4.99 (t, J = 2.9 Hz, 1 H, In-C$_2$H), 2.49 (s, 3 H, COCH$_3$).

*Anal.* Calcd. for C$_{13}$H$_{10}$O$_3$Fe: C, 57.80; H, 3.73. Found: C, 58.07; H, 3.70.

### Preparation of In(CO)(PPh$_3$)FeCH$_3$, 3

A CH$_2$Cl$_2$/hexane solution (150/150 ml) containing PPh$_3$ (7.59 g, 28.9 mmol) and In(CO)$_2$-FeCH$_3$, 1, (5.40 g, 22.3 mmol) was photolyzed in an Ace Glass Co. photochemical reactor (quartz probe) and a 450-W Hanovia high-pressure mercury-arc lamp. During photolysis the solution was magnetically stirred, gently purged with nitrogen, and cooled with circulating cold tap water. The initially yellow-brown solution turned red-brown (with only a trace of sediment) as the reaction neared completion (8 h). Progress of this reaction was monitored also by IR spectral examination of aliquotes.

Removal of solvent under reduced pressure provided a reddish-brown oil. Methylene chloride/hexane (1:3) extracts (8 × 40 ml, combined) of the residue were passed through a 5 cm column of alumina (3.5 cm O.D. Schlenk filter). This procedure separated In(CO)(PPh$_3$)FeCOCH$_3$, 4, which remained as an orange band at the top of the alumina, from In(CO)(PPh$_3$)FeCH$_3$ 3 as the mobile reddish-brown band. (CH$_2$Cl$_2$ development of the column later eluted 4, 620 mg.) The CH$_2$Cl$_2$/hexane eluate was concentrated, diluted with ethanol, cooled, and filtered. Reddish-brown crystals remained after washing with ethanol (3 × 10 ml) and vacuum drying ($10^{-2}$ mm, 3 h). Yield In(CO)(PPh$_3$)FeCH$_3$, 3, 7.83 g (74%), mp 133−134 °C. IR (CH$_2$Cl$_2$) 1905 cm$^{-1}$ (CO); NMR (CDCl$_3$) $\delta$ 7.6−6.8 (complex mult, 19 H, PPh$_3$ + In-benzo), 4.78 (m, 1 H, In-C$_2$H), 4.62 (m, 2 H, In-C$_{1,3}$H), −0.78 (d, J = 7.0 Hz, 3 H, FeCH$_3$).

*Anal.* Calcd. for C$_{29}$H$_{25}$OPFe: C, 73.12; H, 5.28. Found: C, 73.28; H, 5.31.

### Preparation of In(CO)(PPh$_3$)FeCOCH$_3$, 4

A yellow-brown nitromethane solution (125 ml) of In(CO)FeCH$_3$, 1, (2.56 g, 10.6 mmol) and PPh$_3$ (3.89 g, 14.8 mmol) was heated at 50 °C (using an oil bath) for 24 h. This produced a reddish-brown solution, which was evaporated to a gummy red residue. A 4:1 heptane/CH$_2$Cl$_2$ mixture (20 ml) was used to dissolve and to add this residue to a chromatography column containing 8 cm activity 3 alumina/pentane. Development of this column with pentane (100 ml) eluted PPh$_3$ and trace amounts

of unreacted **1**; $CH_2Cl_2$ workup (250 ml) then cleanly removed the acetyl **4** as a red-orange band, which was collected, concentrated (to 150 ml), and diluted with 60 ml of heptane. Further concentration under reduced pressure produced a small amount of oil. A minimum volume of $CH_2Cl_2$ ($\sim$5 ml) then was added to redissolve this oil, and the flask was cooled first at $-20\,^{\circ}C$ (5 h) and then to $-80\,^{\circ}C$. The red crystals, which started coming out at $-20\,^{\circ}C$, were retained after the solvent was transferred out via a double-ended transfer needle/sintered-glass frit. Pentane washing (3 × 25 ml) of the retained crystals at room temperature left 3.33 g (62%) $In(CO)(PPh_3)FeCOCH_3$, **4**, as red crystals.

A second crop of red crystals was obtained after further concentrating the combined filtrates to 20 ml and then cooling ($-80\,^{\circ}C$). The product, after isolating as indicated above, supplied another 1.14 g of **4**; total yield 93%, mp 166–169 $^{\circ}C$. IR ($CH_2Cl_2$) 1914 cm$^{-1}$ (C≡O), 1608 (C=O); NMR ($CDCl_3$) $\delta$ 7.6–6.2 (complex mult, 19 H, $PPh_3$ + In–benzo), 5.08 (br s, 1 H, In–$C_{1\,or\,3}$H), 4.91 (t, J = 7 Hz, 1 H, In–$C_2$H), 4.56 (br s, 1 H, In–$C_{3\,or\,1}$H), 2.26 (s, 3 H, $CH_3$).

*Anal.* Calcd. for $C_{30}H_{25}O_2PFe$: C, 71.44; H, 4.99. Found: C, 71.12; H, 4.93.

### *Attempted Hydrogenation of In(CO)$_2$FeCH$_3$, 1*

A 1,2-dichloroethane solution (30 ml) of $In(CO)_2$-$FeCH_3$, **1**, (485 mg, 2.0 mmol) was pressurized at 800 psig $H_2$ and vented for a total of five cycles before pressurizing again at 1175 psig $H_2$. This pressure was maintained as the reaction was stirred at 50 $^{\circ}C$ for 15 h. After cooling to room temperature, the reaction then was vented and the yellow solution (containing only a trace of sediment) was examined by IR spectroscopy. Over 90% of the starting **1** was recovered, with no other detectable organometallics.

This reaction was repeated, but at 1210 psig $H_2$ and 100 $^{\circ}C$ for 16 h. After breakdown of the reaction no starting **1** or any other metal carbonyl was evident by IR spectroscopy; and insoluble brown residue was recovered. Through GLC analysis of the supernatant it was confirmed that neither acetaldehyde nor ethanol were present.

### *Attempted Hydrogenation of In(CO)(PPh$_3$)FeCH$_3$, 3*

The methyl complex $In(CO)(PPh_3)FeCH_3$, **3**, (300 mg, 0.63 mmol) was a dark red-brown 1,2-dichloroethane solution (25 ml) and was pressurized at 1220 psig $H_2$/100 $^{\circ}C$/10 h. The reactor then was cooled first to room temperature then to $-80\,^{\circ}C$ prior to releasing the pressure. This cooling had the effect of distilling most of the solvent out of the liner into the bottom of the stainless-steel reactor. Through IR spectral and GLC analyses of this clear solution neither acetaldehyde nor ethanol were detected. The residue remaining inside the

glass insert consisted of insoluble precipitate and a 2:1 mixture of $In(CO)(PPh_3)FeCOCH_3$, **4**, and starting **3** in $\sim$5% yield, as determined by IR spectroscopy.

A similar reaction but in 1:1 $CH_2Cl_2$–$CF_3CH_2$-OH at 1000 psig $H_2$/room temperature for 10 h afforded only unreacted **3**. By quantitative IR spectral analysis, over 95% of **3** was recovered.

A control reaction also was run in order to test the detection limits of our GLC analytic procedure. The dark red-brown 1,2-dichloroethane solution (20 ml) containing $In(CO)(PPh_3)FeCH_3$, **3**, (125 mg, 0.26 mmol), ethanol (7.4 $\mu$, 0.13 mmol), and acetaldehyde (7.4 $\mu$l, 0.13 mmol) was added under nitrogen to the nitrogen-flushed pressure reactor. The reactor was briefly flushed with $H_2$, and then it was pressurized to 1100 psig $H_2$, while heating at 100 $^{\circ}C$ (9 h). Cooling of the reactor to 0 $^{\circ}C$ distilled most of the solvent (14.8 ml) into the reactor before the pressure was released. GLC analysis of this clear solution and quantification using the absolute calibration plot procedure easily and quantitatively accounted for both the acetaldehyde and ethanol. Identity of the acetaldehyde also confirmed by IR spectroscopy, $\nu$(C=O) 1722 cm$^{-1}$. Taken together, these results indicate that both potential products acetaldehyde and ethanol would have been detected if they had formed in 1–5% yield during any of our hydrogenation studies.

### *Attempted Hydrogenation of In(CO)$_2$FeCOCH$_3$, 2*

A yellow 1,2-dichloroethane solution (20 ml) of $In(CO)_2FeCOCH_3$, **2**, (250 mg, 0.92 mmol) was pressurized with $H_2$ (1175 psig) at 100 $^{\circ}C$ for 12 h. The reactor after cooling to 0 $^{\circ}C$ contained most of the solvent outside of the glass insert; IR spectral and GLC analysis of this clear solution failed to detect any acetaldehyde or ethanol. Yellow-brown residues in the glass insert contained starting **2** as the only organometallic species (IR spectral examination), which was recovered (153 mg) in 61% yield after extraction and column chromatography.

### *Attempted Hydrogenation of In(CO)(PPh$_3$FeCOCH$_3$, 4*

A solution of $In(CO)(PPh_3)FeCOCH_3$, **4**, (300 mg, 0.59 mmol) in 1,2-dichloroethane (20 ml) was pressurized under 1100 psig $H_2$ at 50 $^{\circ}C$ for 10 h. IR spectral examination of the unchanged reddish solution was consistent with quantitative recovery of **4**. The reaction was therefore repeated, but using 1270 psig $H_2$ at 120 $^{\circ}C$ for 7 h. Then the reactor was cooled first to room temperature then to $-80\,^{\circ}C$ before venting the pressure. IR spectral and GLC analyses of the clear condensate (14 ml) that had collected outside of the glass insert indicated the absence of acetaldehyde and

ethanol. The material remaining inside the insert contained much brown precipitate and by IR spectral examination only a trace of undecomposed **4** in the supernatant.

Similar results were obtained when hydrogenation of **4** was attempted in nitromethane: 1200 psig $H_2/$ 100 °C/18 h. Attempted hydrogenation in $CF_3CH_2$-OH using only 88 psig $H_2$ at room temperature (12 h) returned unchanged **4** in quantitative yield.

## Results and Discussion

Impetus for using $In(CO)(L)Fe$ methyl and acetyl complexes **1−4** in this hydrogenation study follows from our recent results [16] on carbonylating a number of Fe and Ru methyl complexes, including $Cp(CO)(L)FeCH_3$ (L = CO, $PPh_3$) and **1** and **3**. $\eta^5$-Indenyl in place of the Cp ligand greatly enhances the ease with which the methyl complexes carbonylate [eqn. (4)]. For example, both **1** and **3** readily carbonylate in $CH_2Cl_2$ with 80 psig CO (room temperature)—**3** even with 1 atm of CO—whereas the Cp-containing methyl complexes require acidic solvents (*e.g.*, $CF_3CH_2OH$) and/or acid catalysts ($HBF_4$) for similar reactivity. We attribute this enhanced carbonylation reactivity of **1** and **3** to the operation of an associative carbonylation mechanism [eqn. (4)]: the facile $\eta^5$-to-$\eta^3$ shift of the



(4)
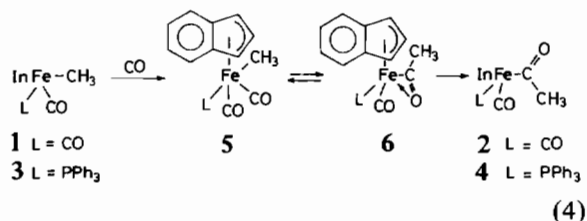
indenyl ligand opens up a coordination site and shuttles a CO onto the iron, giving **5**. Subsequent methyl-CO migratory-insertion[††] (*i.e.*, **6**) and regeneration of the thermodynamically favored $\eta^5$-In gives the acetyl products[§]. This proposed mechanism is merely another manifestation of the indenyl-effect.

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[††]In most examples, the migratory-insertion step (generating the acyl ligand) preceeds association of the new CO ligands [17].

[§]That these hypothesized $\eta^3$-In intermediates **5** and **6** are viable is in accord with the results of a $^{13}$C-labeling study on **2**. Thus $In(CO)_2Fe^{13}COCH_3$ (prepared by acylating $In(CO)_2Fe^-Na^+$ with 90%-$^{13}$C-acetyl chloride) upon warming to room temperature rapidly equilibrates its acetyl $^{13}$CO into terminal CO positions without any net loss of label:

$$In(CO)_2Fe^{13}COCH_3 \rightleftharpoons In(CO)(^{13}CO)FeCOCH_3$$
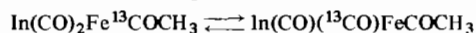
The facility of this reversible shuttling of $^{13}$CO between acetyl and terminal CO positions is best accommodated by transience of the aforementioned $\eta^3$-indenyl intermediates. For comparison, this behavior is not observed with the similarly labeled Cp analog $Cp(CO)_2Fe^{13}COCH_3$ [18].

$\eta^5$-Indenyl complexes generally exhibit substantially increased rates over those observed with their analogous $\eta^5$-Cp complexes for CO ligand replacement by phosphines or phosphites—a phenomenon referred to as the indenyl effect [19]. Kinetic studies for these replacement reactions are generally in accord with an associative mode of reactivity at the metal center, involving either a $S_N2$ process [eqn. (5)] or a rapid preequilibrium with a coordinatively unsaturated $\eta^3$-In intermediate [eqn. (6)] [19, 20]. $In(CO)_3Mo$ alkyl complexes also exhibit pronounced tendencies to undergo associative reactions with two-electron donor ligands, as exemplified by phosphine-induced CO insertion on the methyl



(5)

(6)
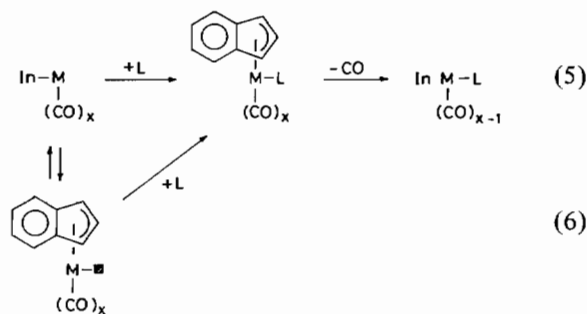
complex [21] and by unusually facile decarbonylation reactions during certain coordinated ligand transformations [15].

We are not aware of any examples whereby $\eta^5/\eta^3$-indenyl ligand tautomerization, by creating a new coordination site [eqn. (7)], promotes oxidative addition of $H_2$ and subsequent hydrogenation of substrate (S) bound as another ancillary ligand. Such an agenda, however, is followed during homogeneous hydrogenation of (bound) alkenes using certain $\eta^3$-allyl [22] and methyl carbonyl [23] complexes as the catalyst precursors. An $\eta^3$-$\eta^1$ interconversion [eqn. (8)] or a methyl-CO migratory insertion [eqn. (9)] frees up the coordination site that is needed for oxidative addition of $H_2$ to these metal centers. It should be noted that operation of these catalytic cycles entails reductive elimination of RH (R being derived from the bound alkene); this is precisely the net reaction that we are probing with $In(CO)(L)Fe-R$ (**1−4**) complexes [eqn. (3)].



(7)

(8)

(9)
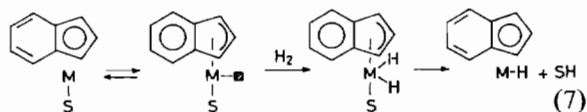
The four methyl and acetyl complexes required for this study were synthesized using standard organometallic procedures that have been developed for their Cp analogs [11–13]. Figure 1 summarizes this preparative chemistry. The experimental section provides details for high-yield syntheses of 1–4 starting with the known dimer [In(CO)$_2$Fe]$_2$, 7 [14] and its nucleophilic reduction product In(CO)$_2$-Fe$^-$Na$^+$ [15]. Indeed, the parent methyl complex 1 already had been reported [15, 24]. All four complexes closely resemble their Cp-containing analogs in terms of physical appearance, stability, solubility, chromatographability, and spectral attributes.
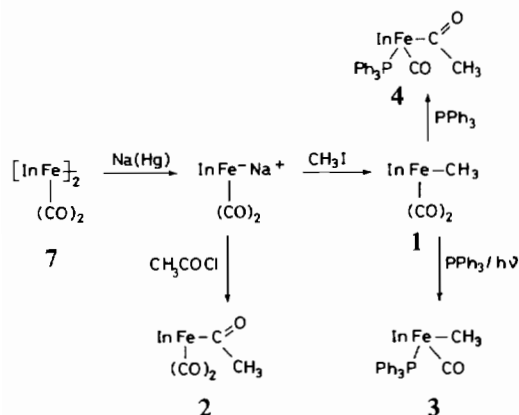


Fig. 1. Synthesis of $\eta^5$-In(CO)(L)FeR complexes.

The IR and $^1$H NMR spectra of the indenyl iron methyl and acetyl complexes 1–4 are symmarized in Table I, along with similar data for their Cp-containing analogs. Inspection of this data certainly reinforces the overall resemblance of the electronic environment at the iron center for corresponding $\eta^5$-In– and Cp–iron complexes. One noteworthy difference is the slight upfield shift in the $^1$H NMR spectrum of the methyl complexes 1 and 3 vs. their

CpFe analogs. This shift can be accounted for, however, by magnetic anisotropy of the benzo ring, which through rotation about the $\eta^5$-In—Fe bonding axis will pass over the methyl ligand. A similar mechanism for the $\eta^5$-indenyl group influencing $^1$H NMR chemical shifts of proximate protons on coordinated ligands has been advanced by Faller and co-workers [25] in assigning the exo- and endo-isomers of $\eta^3$-allyl ligand on In(CO)$_2$-Mo(CH$_2$CRCH) complexes.

In Fig. 2 we present, as a working hypothesis, plausible pathways for hydrogenating the methyl and acetyl complexes In(CO)(L)FeR (1–4). With both methyl or acetyl complexes, the primal step would be oxidative addition of H$_2$ to the $\eta^3$-In complex, followed by reductive elimination of product. The methyl complexes, moreover, could produce either methane or commensurate with the CO-methyl insertion step acetaldehyde. Considering results of other hydrogenation studies with carbonylmetalate methyl (or other alkyl) complexes [2–4], we anticipated that acetaldehyde and ethanol would be the major products of hydrogenating 1–4. (The ethanol would arise from further reduction of acetaldehyde.) Accordingly, our experiments were designed so that attempted hydrogenation of 1–4 would be followed IR spectral and GLC analyses for (1) acetaldehyde and ethanol and (2) recovered organoiron complexes.
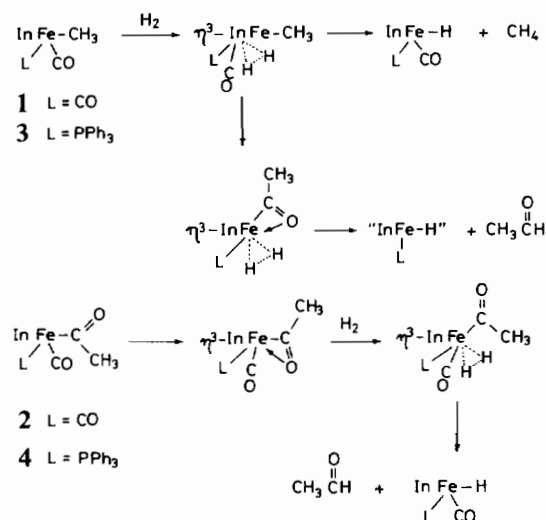


Fig. 2. Postulated hydrogenation pathways for In(CO)-(PPh$_3$)FeR methyl and acetyl complexes.

The results of our attempted hydrogenation of the In(CO)(L)FeR complexes 1–4 were uniformly negative. All four complexes in 1,2-dichloroethane are untouched by 1000–1200 psig H$_2$ up to ~50 °C. When these reactions were reexamined at 100–120 °C, the starting methyl or acetyl complex

TABLE I. Spectral Data for In and Cp Iron Methyl and Acetyl Complexes.

| | IR$^a$ | | NMR$^b$ |
|---|---|---|---|
| | $\nu$(C$\equiv$O) | $\nu$(C=O) | $\delta$(CH$_3$) |
| Cp(CO)$_2$Fe–CH$_3$ | 2003, 1948 | – | +0.15 |
| In(CO)$_2$Fe–CH$_3$ | 2003, 1948 | – | –0.45 |
| Cp(CO)(PPh$_3$)Fe–CH$_3$ | 1900 | – | –0.18 |
| In(CO)(PPh$_3$)Fe–COCH$_3$ | 1905 | – | –0.78 |
| Cp(CO)$_2$Fe–COCH$_3$ | 2020, 1960 | 1645 | +2.57 |
| In(CO)$_2$Fe–COCH$_3$ | 2019, 1959 | 1651 | 2.45 |
| Cp(CO)(PPh$_3$Fe–COCH$_3$ | 1915 | 1600 | 2.25 |
| In(CO)(PPh$_3$)Fe–COCH$_3$ | 1914 | 1608 | 2.26 |

$^a$cm$^{-1}$ in CH$_2$Cl$_2$.   $^b$ppm in CDCl$_3$.

had degraded and no acetaldehyde or ethanol were detected. We rule out some unspecified decomposition of either acetaldehyde or ethanol on the basis of results from a control experiment. Both potential products are recovered after cooking (100 °C) under 1100 psig $H_2$ and in the presence of $In(CO)(PPh_3)$-$FeCH_3$, 3. In all pressurized reactions above 100 °C no discernible (by IR spectroscopy) organometallic products were found—not even the thermally stable and thermodynamically favored dimer [In-$(CO)_2Fe]_2$, 7.

## Conclusion

The four methyl and acetyl complexes In(CO)-(L)Fe–R (L = CO, PPh$_3$; R = CH$_3$, COCH$_3$) have been characterized as being readily available, stable and non-labile $\eta^5$-indenyl complexes. Attempts at using the indenyl ligand to generate a vacant coordination site and hence promote hydrogenation of the methyl or acetyl ligand failed. This failure contravenes the precedents for indenyl ligands, through their $\eta^5/\eta^3$ tautomerization, enforcing associative reactions with potential ligands (e.g., CO with methyl complexes 1 and 3). Further discussion on why hydrogen apparently does not add to or otherwise react with 1–4 must await the results of continuing studies on hydrogenating other $\eta^5$-indenyl-containing alkyl complexes.

## Acknowledgment

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