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Preliminary communication

Interconversion of acetyl- and terminal-carbonyl groups on labeled (η^5-indenyl)$(CO)_2Fe^{13}C(O)CH_3$

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Abstract

The ^{13}C-labeled (95–99%) acetyl complex $(\eta^5\text{-In})(CO)_3Fe^{13}C(O)CH_3$ (**8**) (In = indenyl) has been prepared by acylating $In(CO)_2Fe^- Na^+$ (**1**) with $CH_3{}^{13}C(O)Cl$. All of the starting **1** must be consumed in this reaction (at −78°C), or 45% of the product results as $In(CO)(^{13}CO)FeC(O)CH_3$ (**9**). Once isolated, neither **8** nor mixtures of **8** and **9** further redistribute or lose this label after pressurizing under 800 atm CO, or after heating in heptane, THF, or acetonitrile solution. Treating **8** with even trace amounts of **1** or of $Cp(CO)_2Fe^- Na^+$ (**5**) rapidly interconverts the acetyl and terminal carbonyls, thus transforming **8** into mixtures of **8** and **9**. A mechanism is proposed that involves a labile metalla-β-diketonate $In(CO)Fe(Fp\text{-}CO)(CH_3{}^{13}CO)^- Na^+$.

The η^5-indenyl ligand (In) through reversible η^5–η^3 ring slippage potentially makes available an additional metal coordination site for ligand associative reactions [1]. We previously had used the fully characterized η^3-indenyliron carbonylate **2** in a carbonylation sequence giving the acetyl complex **4** (eq. 1) [2]. In a related study, we also have treated a nucleophilic iron metalate Fp^- (**5**) with the methyl complex $In(CO)_2FeCH_3$ (**6**) and formed the fully characterized bimetallic acetyl compound *cis*-**7** [3]. Bimetallic **7** exists as an equilibrating mixture of **7a** and **7b** (eq. 2) that, however, crystallizes as **7b** (as determined by X-ray crystallography). Both reactions (eq. 1 and 2) have in common a proposed η^3–η^5 indenyl ring shift [4] attendant with methyl-CO migratory-insertion [5] that affords the acetyl ligand.

We now report preparative and novel reaction chemistry of $In(CO)_2Fe^{13}C(O)CH_3$ (**8**) that engenders shuttling of the ^{13}C-labeled CO between the acetyl and terminal carbonyl ligand positions. Reactions described herein do not occur with the readily accessible Cp-analog of **8**, $Cp(CO)_2Fe^{13}C(O)CH_3$ [6*], as determined by the results of parallel experiments.

Special precautions are required to prepare **8** by acylating 99% ^{13}C-1 acetyl chloride (Kor Isotopes) with $In(CO)_2Fe^- Na^+$ (**1**). Standard procedures used in

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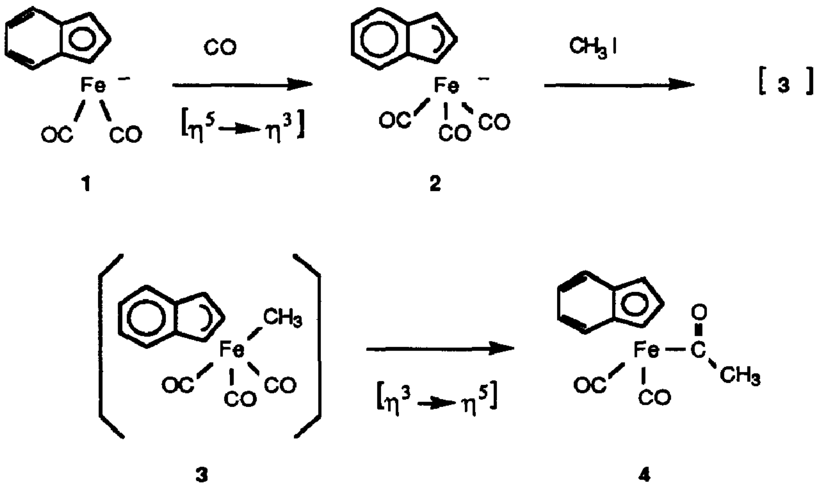
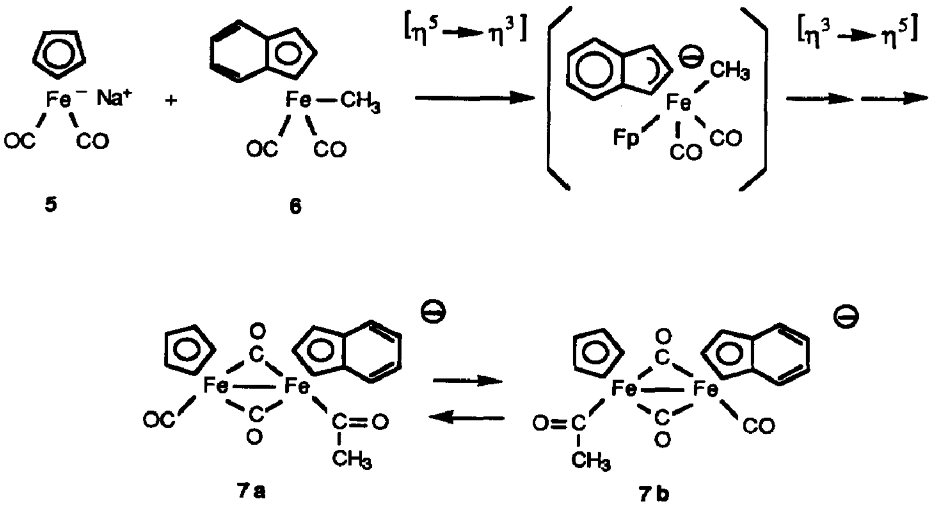
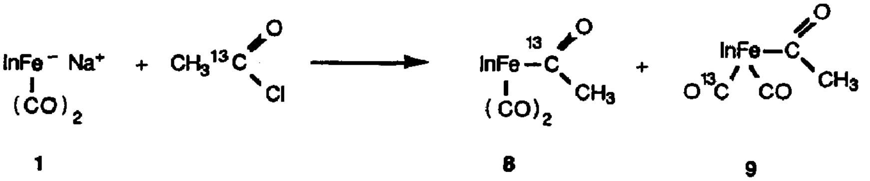


(1)



(2)

synthesizing unlabeled **4** from acetyl chloride plus **1** [7] inevitably give mixtures containing variable proportions of **8** and 30–45% **9** (eq. 3) [8*].



[3]

Mixtures containing predominantly **8** (95–99%), however, result from adding the $CH_3{}^{13}C(O)Cl$ to a cold (−78° C) THF solution of the metalate **1**, and after 0.25 h,

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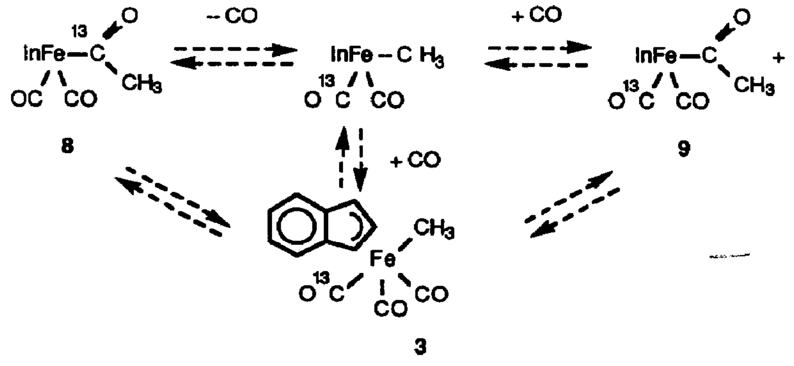
* Reference numbers with asterisks indicate notes in the list of references.



(4)

quenching the reaction mixture with MeI (0.2 equiv.). Isolation of the product (52–71% yields) entails warming to room temperature, extracting and then precipitating impurities from CH_2Cl_2/excess pentane (repeated several times), and crystallizing from heptane (−78 ° C).

Once isolated and purified, both **8** and mixtures of **8** and **9** are surprising nonlabile towards altering the ^{13}CO label distribution. Pressurization of CH_2Cl_2 solutions of either under CO (1.0 to 80 atm, 24 h) effected no change; ^{13}CO label neither washed out of the acetyl complexes nor distributed between acetyl and terminal CO positions. Heating solutions containing **8** in heptane (85 ° C, 3 h), in THF (87 ° C, 3 h), or in acetonitrile (110 ° C, 7.5 h) likewise had no effect on the IR spectra. Taken together, these results precluded uncatalyzed CO deinsertion–reinsertion equilibria (eq. 4) contributing to the label redistribution that is observed under preparative conditions [9].

In the presence of even trace amounts (1–10%) of either In- or Cp-bearing metalate **1** or **5**, however, the shuttling of labeled CO between acetyl and terminal CO positions is rapid at room temperature. Figure 1 illustrates the results of IR spectral monitoring (over 12 min) of THF solutions initially containing 6.67×10^{-2} *M* **8** (99% ^{13}C-acetyl) and 7.0×10^{-4} or 4.0×10^{-3} *M* **1**. The lower energy acetyl for $\nu(CO)$ for **8** clearly diminishes in intensity as the higher energy $\nu(CO)$ for **9** increases. Maintaining these reagents at −78 ° C (1 h) prevents this label redistribution; adding MeI to the cold reaction mixture before warming efficiently traps **1** (or **5**) and returns unchanged **8**.

Attempts to detect intermediates in this redistribution reaction by treating stoichiometric amounts of **8** or **4** with metalates **1**, **5**, FpLi [10,11], or Fp_2Mg [11,12] were unsuccessful. During the first few minutes label shuttling between acetyl and terminal carbonyl positions of **8** was evident, but the only additional IR spectral absorptions corresponded to those of Fp_2 increasing in intensity. This degradation of metalate to dimer was especially pronounced when using FpLi and Fp_2Mg. The reaction between $Fp^- Na^+$ (**5**) and $In(CO)_2FeCOCH_3$ (**4**) for 1.5 h was quenched with MeI and worked up by column chromatography. Three bands eluted, although much decomposition residue also was evident. These bands corresponded to (1) a mixture of the methyl complexes $FpCH_3$ (19%) and $In(CO)_2FeCH_3$ (**6**) (12%), (2) Fp_2 (65%), and (3) $In(CO)_2FeCOCH_3$ (36% recovery). $FpCOCH_3$ (which is inert towards **5**) was not detected.

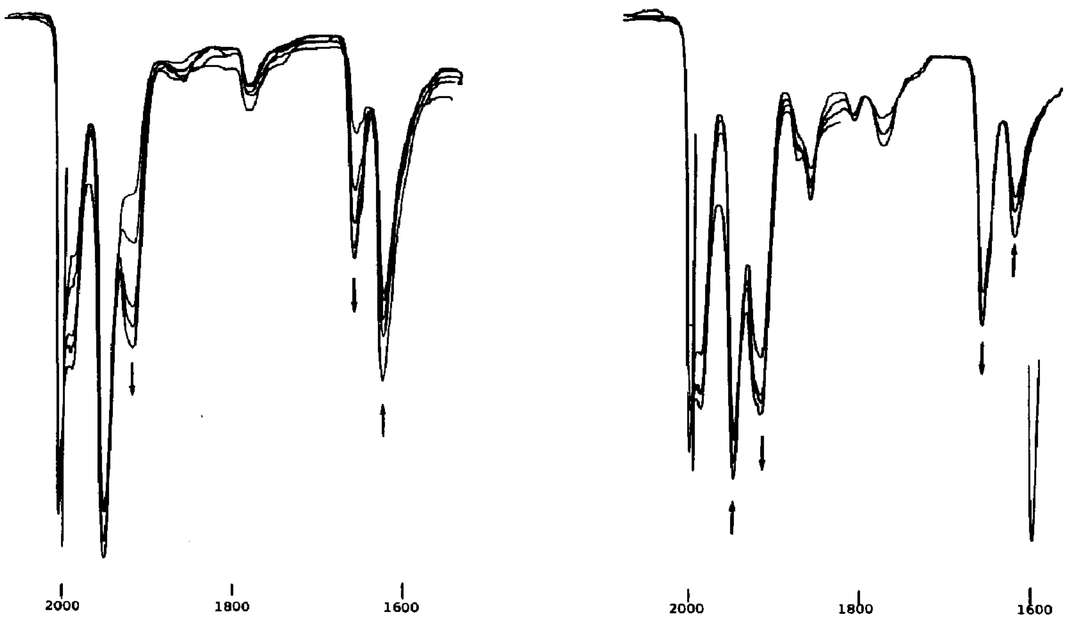


Fig. 1. In(CO)$_2$Fe^{13}C(O)CH$_3$ (**8**), 6.67×10^{-2} *M* in THF, treated with In(CO)$_2$Fe$^-$ Na$^+$ (**5**): (A) 7.0×10^{-4} *M*; (B) 4.0×10^{-3} *M*. IR spectral scans over 12 min.

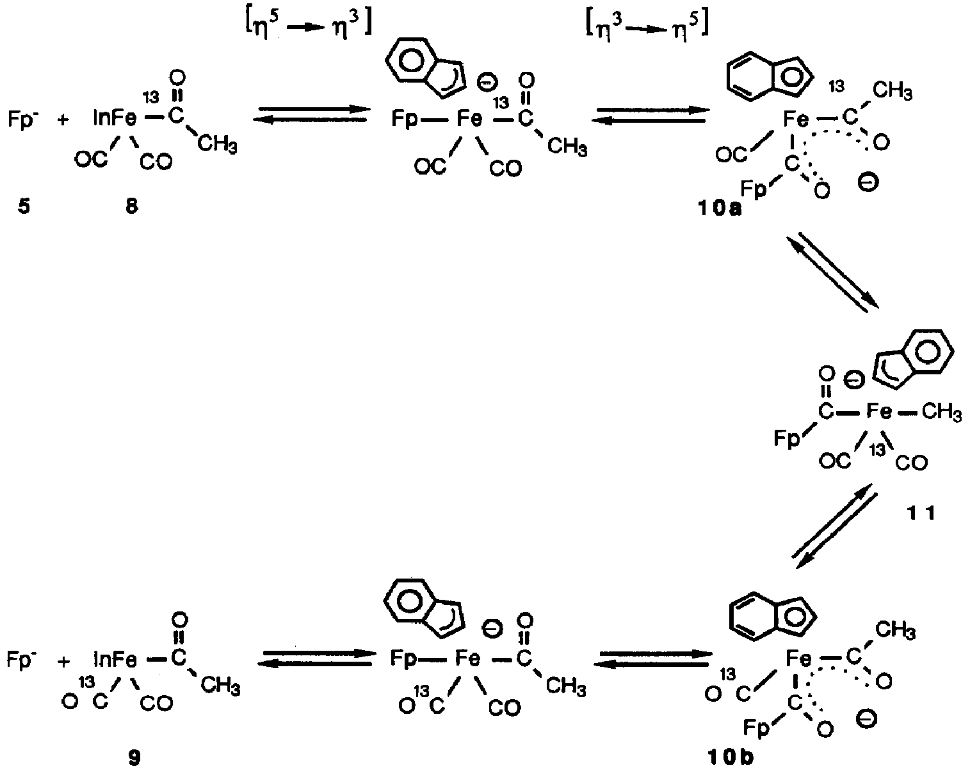


Fig. 2.

In Fig. 2, an admittedly speculative mechanistic scheme accounts for at least the early stages of the reaction between **5** and **8**. Key steps include nucleophilic attack of **5** at the iron center of **8** (cf., eq. 2) and subsequent Fp-to-CO migration to afford a metalla-β-diketonate derivative [13] **10a**.

In principle, **10a** also could result from direct nucleophilic addition of **5** to a terminal carbonyl and thus bypass the proposed η^5–η^3 In ligand shifts. Indenyl ring slippage nevertheless must be involved in rationalizing the isomerization of **10a** to **10b** and for the inability of $Fp^{13}C(O)CH_3$ to redistribute labeled ^{13}CO in the presence of Fp^- Na^+ (**5**). We resist invoking $(\eta^3\text{-In})(CO)_2(^{13}CO)FeCH_3$ (obtained through loss of Fp^- from **11**) as an active participant, since the unlabeled analog **3** (eq. 1) preferentially decarbonylates to the methyl complex **6** in the absence of exogenous CO. Studies in progress will continue probing synthetic and mechanistic consequences of using the η^5-Indenyl ligand to generate a labile metal center.

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8 $In(CO)_2FeC(O)CH_3$ (**4**); IR (C_6H_{12}): 2019, 1963, 1669 cm^{-1}; (THF): 2015, 1953, 1663 cm^{-1}; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 253.8 ($COCH_3$), 213.7 ($C\equiv O$), 72.6 (CH_3); MS (CI) m/z 270 (M^+). $In(CO)_2Fe^{13}C(O)CH_3$ (**8**) (99%, ^{13}C): IR (C_6H_{12}): 2020, 1963, 1635 cm^{-1}; (THF): 2018, 1956, 1627 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.43 (d, J 4.9 Hz, CH_3); $13C\{^1H\}$ NMR ($CDCl_3$): δ 252.6 ($COCH_3$, intense), 214.3 ($C\equiv O$), 72.0 (d, J 23 Hz, $COCH_3$); MS (CI): m/z 271($M+1$). $In(CO)(^{13}CO)FeC(O)CH_3$ (**9**): IR (C_6H_{12}): 1999, 1929, 1670 cm^{-1}; (THF) 1996, 1924, 1664 cm^{-1}; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 253.5 ($COCH_3$), 212.0 ($C\equiv O$, intense); MS (CI): m/z 271($M+1$). IR spectra of **4**, **8**, and **9** closely match those of their Cp analogs.

9 Carbonylation of **6** under unusually mild conditions (1–4.5 atm CO in CH_2Cl_2) also may involve transience of $(\eta^3\text{-In})(CO)_3FeCH_3$ (**3**); T.C. Forschner and A.R. Cutler, Organometallics, 4 (1985) 1247; manuscript in preparation.

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