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Preliminary communication

Bimetallic acetyl complexes: $(\eta^5\text{-indenyl})_2(CO)_3Fe_2(COCH_3)^-$ and $(\eta^5\text{-indenyl})(\eta^5\text{-Cp})(CO)_3Fe_2(COCH_3)^-$: their role in a novel carbonylation reaction

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Abstract

Treating alkyl(η^5-indenyl) iron complexes $In(CO)_2FeR$ ($R = CH_3$, CH_2OCH_3) with either nucleophilic metalate $Cp(CO)_2Fe^-Na^+$ ($Cp = \eta^5\text{-}C_5H_5$) or $In(CO)_2Fe^-Na^+$ affords stable bimetallic complexes $In(CO)Fe(\mu\text{-}CO)_2Fe(In)(COCH_3)^-Na^+$ (**3**) and $(In)(Cp)(CO)_3Fe_2(COR)^-Na^+$ (**4**, $R = CH_3$; **9**, $R = CH_2OCH_3$). The fully characterized PPN^+ salts **3** and **4** ($PPN = Ph_3P{=}N{=}PPh_3$) both retain *cis*-structures having terminal (η^1) acyl ligands. Compound **4** exists as a 1/1 mixture of isomers corresponding to the acetyl group at alternate iron centers: results of ^1H NMR magnetization transfer experiments further established that these isomers slowly equilibrate at room temperature. X-ray structural determination of $\mathbf{4}PPN^+$ showed that it crystallizes as the isomer having the acetyl coordinated on the CpFe end. These binuclear acyl products readily fragment (1 atm CO, R′X) into mononuclear acyl products, $Cp(CO)_2FeCOCH_3$ and $Cp(CO)_2FeCOCH_2OCH_3$ from **4** and **9**, respectively, and $In(CO)_2FeCOCH_3$ from **3**. By-products include $In(CO)_2FeR'$ ($R' = CH_3$, CH_3CH_2, Ph_3Sn) and, depending on the reaction conditions, binuclear vinylidene compounds. A reaction pathway is proposed that accounts (by invoking reversible η^5/η^3-In ligand shifts) for the regioselective cleavage and carbonylation of **4** and **9** to their mononuclear $Cp(CO)_2Fe$-acyl products.

Carbonylating organoiron alkyl complexes FpR ($Fp = (\eta^5\text{-}C_5H_5)(CO)_2Fe$; $R = CH_3$, CH_2CH_3) to their acyl derivatives FpC(O)R requires forcing conditions [1]. The necessary alkyl-CO migratory-insertion step [2] must be promoted by adding

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Lewis or proton acids [3], by incorporating electron-transfer chain catalysis [4], or by substituting η^5-indenyl (In) for Cp or PPh_3 for ligated CO [1a]. Similar attempts at carbonylating $FpCH_2OCH_3$ or $In(CO)(L)FeCH_2OCH_3$ (L = CO, PPh_3) (up to 80 atm CO) failed [4,5], further demonstrating that the alkoxymethyl ligand does not migrate as readily to an ancillary carbonyl [6]. The desired alkoxyacetyl derivatives, available from other synthetic routes, provide templates for converting CO into C_2 (or larger) oxygenated organic molecules [7].

We now report a new procedure for carbonylating iron alkyl complexes $In(CO)_2FeR$, (**1**, R = CH_3; **2**, R = CH_2OCH_3) that involves, (i) a stable bimetallic acyl intermediate resulting from metalate-induced alkyl-CO migration [8*], (ii) the presence of at least one η^5-In ligand on this intermediate, and (iii) its regioselective cleavage (1 atm CO) to mononuclear acyl compounds.

Methyl complex $In(CO)_2FeCH_3$ (**1**) [9] reacts with either nucleophilic metalate $In(CO)_2Fe^-Na^+$ or $Cp(CO)_2Fe^-Na^+$ in THF solution (1 h) and gives bimetallic acetyl complexes **3** and **4** (eqs. 1 and 2) (85%, by IR spectral monitoring). Metathesis of the resulting yellow-brown solutions with PPN^+Cl^- ($PPN^+ = Ph_3{=}N{=}PPh_3^+$) afforded the fully characterized salts **3**PPN$^+$ and **4**PPN$^+$ (isolated yields 52 and 78%, respectively) **. Both PPN$^+$ salts are stable in CH_2Cl_2 or THF solutions, and no reaction occurs with CO (5 atm, 8 h) [10*].

IR spectra of **3**PPN$^+$ and **4**PPN$^+$ are similar: strong ν(CO) absorptions occur for the terminal (1906 cm^{-1}), bridging (1702 cm^{-1}), and acetyl (1568 cm^{-1}) carbonyl groups. Counterion dependency of the latter absorption, in particular, is consistent with ion-pairing to a terminal acetyl group [8a,11*]. Both ^1H and ^{13}C NMR spectra of **3**PPN$^+$, each having two sets of non-equivalent In ring absorptions, further indicate the presence of one isomer in solution. NMR spectra of **4**PPN$^+$, however, exhibit two sets of In, Cp, and acetyl absorptions that indicate two isomers in 1/1 ratio. These isomers equilibrate slowly on the NMR time scale as determined by results of a ^1H NMR magnetization (spin saturation) transfer experiment [12*]. An X-ray crystallographic structure determination of **4**PPN$^+$ (Fig. 1) * further demonstrates that it crystallizes as the *cis*-structure having a planar (η^5-In)Fe group, although the terminal acetyl group [13] coordinates to the CpFe end. Taken

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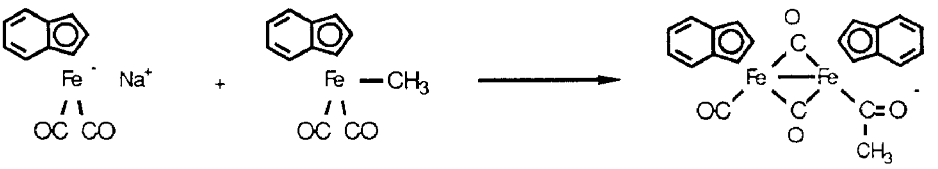
* Reference numbers with asterisks indicate notes in the list of references.

** Data for **3**PPN$^+$: ^1H NMR (CD_2Cl_2) δ 7.76–7.10 (m, 36H, PPN + *In*(CO)Fe: benzo + *In*(Ac)Fe: benzo), 6.87 (AA′BB′, 2H, *In*(Ac)Fe: benzo), 5.10 (d, *J* 2.8 Hz, 2H, *In*(CO)Fe: H(1,3)), 5.03 (t, *J* 2.8 Hz, 1H, *In*(CO)Fe: H(2)), 4.96 (t, *J* 2.8 Hz, 1H, *In*(Ac)Fe: H(2)), 4.23 (d, *J* 2.8, 2H, *In*(Ac)Fe: H(1,3)), 1.78 (s, 3H, CH_3). {^1H}^{13}C NMR (CD_2Cl_2) δ 285.7 ($COCH_3$), 277.1 (μ-CO), 216.3 (FeCO), 123.5, 122.4, 122.3, 122.0 (*In*: benzoCH), 108.4 (*In*$FeCOCH_3$: C(3a,7a)), 105.3 (*In*FeCO: C(3a,7a)), 97.6 (*In*$FeCOCH_3$: C(2)), 96.4 (*In*FeCO: C(2)), 78.8 (*In*FeCO: C(1,3)), 71.8 (*In*-$FeCOCH_3$: C(1,3)), 42.7 (CH_3). Anal. Found: C, 70.11; H, 5.43. **3PPN$^+$·THF** (1/1) calcd.: C, 70.27; H, 5.14%. Data for **4a**PPN$^+$ + **4b**PPN$^+$ (1/1): ^1H NMR (CD_2Cl_2) δ: 7.48–7.40 (m, 34H, PPN + In AA′BB **4a**/**4b**), 7.25 (AA′BB′, 2H, In **4b**), 6.81 (AA′BB′, 2H, In **4a**), 5.24 (t, *J* 2.6 Hz, In: H(2) **4b**), 4.75 (t, *J* 2.6, In: H(2) **4a**), 4.64 (d, *J* 2.6 Hz, In: H(1,3) **4b**), 4.41 (s, Cp **4a**), 4.27 (s, Cp **4b**), 4.25 (d, *J* 2.6 Hz, In: H(1,3) **4a**), 1.92 (s, CH_3 **4b**), 1.82 (s, CH_3 **4a**). {^1H}^{13}C NMR (CD_2Cl_2) **4a**PPN$^+$ + **4b**PPN$^+$ (1/1): δ 278.8 (μ-CO, **4a**/**4b**), 123.7, 123.4, 122.5, 122.3 (In: benzoCH **4a**/**4b**), 289.5 ($COCH_3$, **4b**), 284.1 ($COCH_3$, **4a**), 217.8 (FeCO, **4a**), 216.2 (FeCO, **4b**),107.8 (In: C(3a,7a) **4a**), 105.4 (In: C(3a,7a) **4b**), 94.8 (In: C(2) **4b**), 87.8 (In: C(2) **4b**), 87.2 Cp (**4a**), 84.5 (Cp **4b**), 79.5 (In: C(1,3), **4b**), 75.0 (In: C(1,3) **4a**), 44.7 (CH_3 **4b**), 43.0 (CH_3 **4a**). Anal. Found: C, 68.65; H, 5.36. **4**PPN$^+$·THF (1/1) calcd.: C, 68.82; H, 5.18%.



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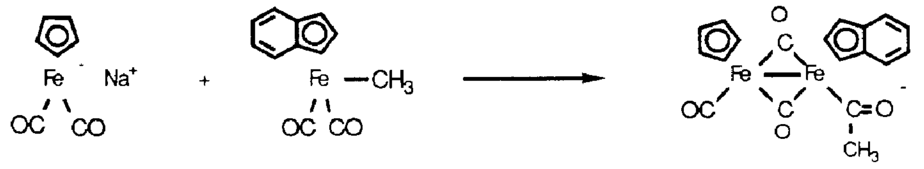

1 4 (2)

together, these data are consistent with *cis* structures [14*] for **3** and **4** that have the acetyl ligand shuttling between the two iron ends [15*,16*]. A μ-oxyethylidene compound (e.g., **5** from **4**) is a plausible intermediate [8d–f,18]; its existence also is implicated as a result of derivitization studies.

Fragmenting the binuclear acetyl compounds **3** and **4** into mononuclear acetyl complexes with 1 atm CO and Ph_3SnCl or MeI completes the carbonylation

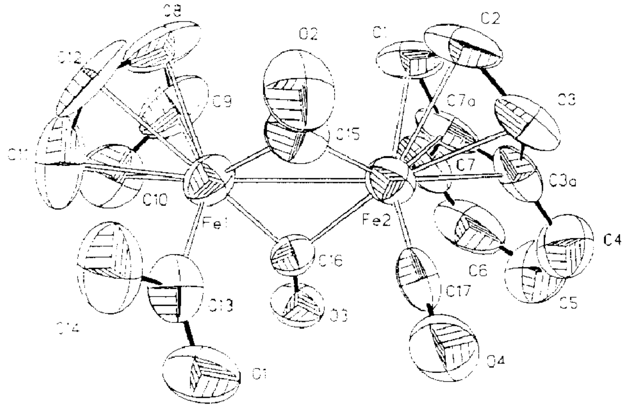

Fig. 1. ORTEP diagram of **4bPPN**$^{+}$* drawn with 50% probability thermal ellipsoids. The [PPN^{+}] counterion and hydrogen atoms are not shown. Selected structural parameters: Fe(1)–Fe(2) 2.513(2) Å; Fe(1)–C(13) 1.935(13) Å; C(13)–C(14) 1.516(20) Å; C(13)–O(1) 1.218(17) Å; fold angle 158.3°, Fe(1)–C(15)–Fe(2)/Fe(1)–C(16)–Fe(2); fold angle 174.8°, C(1)–iC(2)–C(3)/C(3)–C(3a)–C(4)–C(5)–C(6)–C(7a)–C(1).

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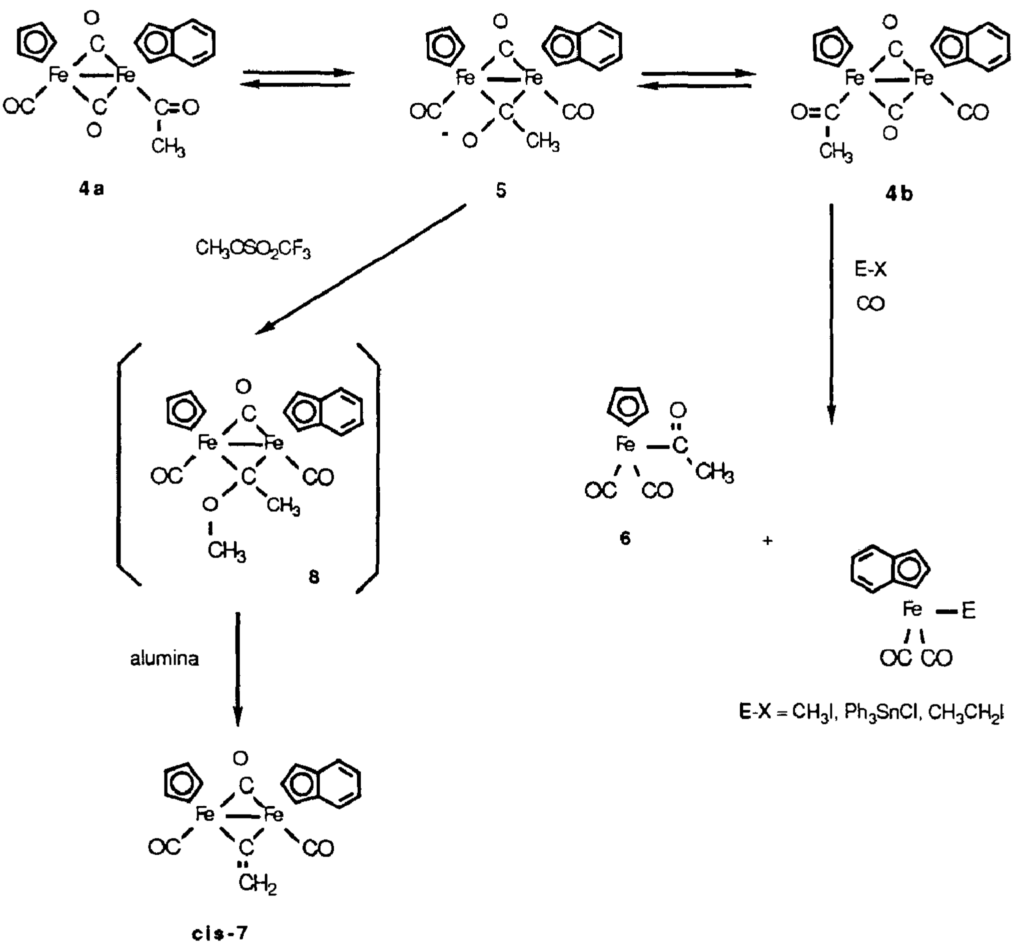
* Crystal data for $InCp(CO)_3Fe_2COCH_3 \cdot PPN^+ \cdot OC_4H_8$ (**4bPPN**$^+$): as brown plates by slow cooling of the THF/ether solution; 0.21×0.03×0.65 mm, orthorhombic $P2_12_12_1$ (No. 19): a 10.836(2) Å, b 13.161(2) Å, c 35.140(7) Å; V 5011(1) Å^3; $Z = 4$; ρ(calcd) = 1.36 g cm^{-3}; Nicolet R_{3m} diffractometer; μ 57.4 cm^{-1}; $\lambda(\text{Cu-}K_\alpha)$ 1.54178 Å; $2\theta_{max} = 110°$: $N_{refl} = 3077$, $(I > 3\sigma(I)) = 2356$; $R = 6.51$, $R_w = 0.0542$; heavy-atom solution, blocked cascade refinement, all non-hydrogen atoms anisotropic, all hydrogen atoms as idealized isotropic contributions; SHELXTL (Rev. 5.1) computer programs (Nicolet Corp., Madison, WI).



Scheme 1.

procedure. The regiochemistry further observed in cleaving the CpIn dimer **4** into Cp(CO)$_2$FeCOCH$_3$ (**6**) is especially noteworthy (Scheme 1) *. Treating **4**PPN$^+$ and Ph$_3$SnCl in CH$_2$Cl$_2$ or THF solution (1 atm CO, 2 h) thus provides **6** and In(CO)$_2$FeSnPh$_3$ [19] (75–85% yields after column chromatography) as the only organometallic products. Similar work-up of the MeI reactions with **4**PPN$^+$ in CH$_2$Cl$_2$ solution (1 atm CO, 12 h) gives **6** (53% yield), In(CO)$_2$FeCH$_3$ (**1**) (61%), *cis*-μ-ethenylidene dimer Cp(CO)Fe(μ-CO)(μ-C=CH$_2$)Fe(CO)In (*cis*-**7**) (50%), and *trans*-**7** (3%). Spectroscopic assignments of fully characterized *cis*-**7** and *trans*-**7** match those for analogous bis-(CpFe)-μ-vinylidene compounds [Cp(CO)Fe]$_2$(μ-CO)(μ-C=CH$_2$) [18]. In the absence of a CO atmosphere, **4**PPN$^+$ reacts with MeOSO$_2$CF$_3$ or acetyl chloride to produce only μ-vinylidene complexes (85%, as 22/1 *cis*-**7** and *trans*-**7**) after column chromatography. Binuclear acetyl compounds **3** and **4** therefore can be converted selectively into either mononuclear acetyl

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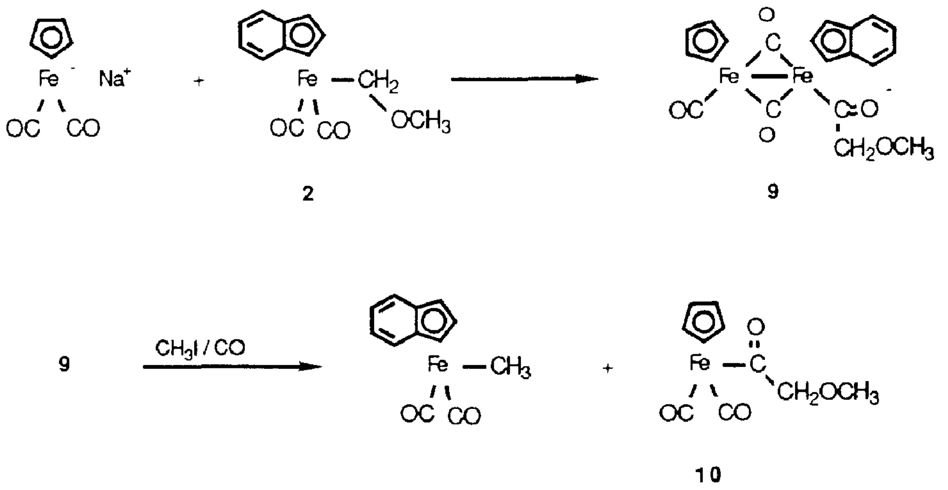
* Reactions between **3**PPN$^+$ and MeI or Ph$_3$SnCl (1 atm CO) produce similar products. Thus, **3**PPN$^+$ and either MeI in THF or Ph$_3$SnCl in THF or CH$_2$Cl$_2$ solutions afford In(CO)$_2$FeCOCH$_3$ [9b] (87–94% isolated yields) and either **1** or In(CO)$_2$FeSnPh$_3$ (86–94%). In CH$_2$Cl$_2$ solution, **3**PPN$^+$ and MeI (1 atm CO, 7 h), gives **1** (38% isolated yield), In(CO)$_2$FeCOCH$_3$ (39%), and the fully characterized [In(CO)Fe]$_2$(μ_2-CO)(μ-C=CH$_2$) as only its *cis* isomer (56%).



(3)

complexes or dinuclear ethenylidene compounds (Scheme 1) by manipulating the reaction conditions.

This carbonylation procedure is noteworthy also for carbonylating the alkoxymethyl ligand (eq. 3). Treating $In(CO)_2FeCH_2OMe$ (**2**) in THF solution with $Cp(CO)_2Fe^-Na^+$ and then with MeI/1 atm CO (5 h) affords $FpCOCH_2OMe$ (**10**) (43% yield after chromatography) as the only acyl complex.

Studies in progress further address the role of the indenyl ligand in the two-step carbonylation procedure: metalate promoted alkyl-CO insertion and subsequent cleavage of the bimetallic acyl intermediate * to mononuclear acyl product.

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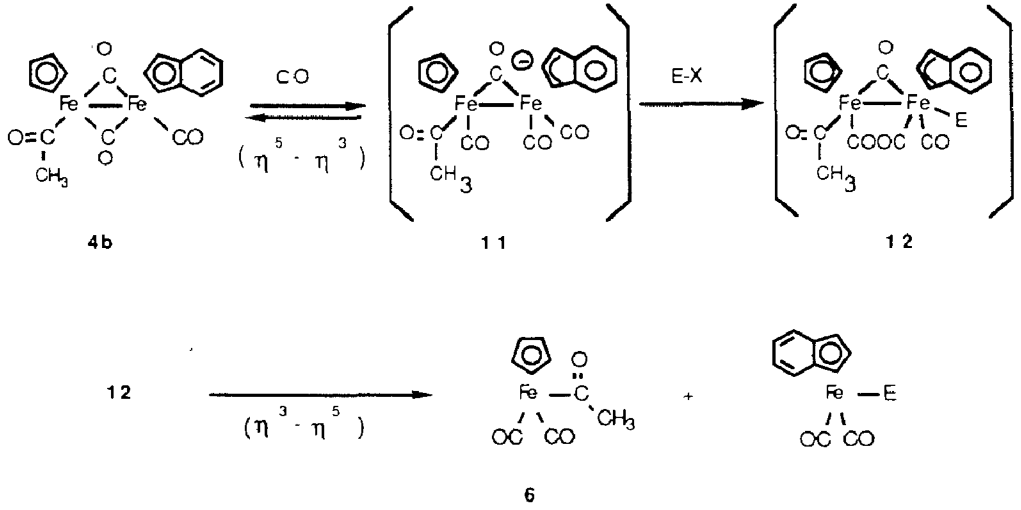
* Proposed mechanism for regioselective alkylation of $CpIn(CO)_3Fe_2(COCH_3)^-$ (**4**). Regioselective cleavage of **4** to **6** is consistent with **4b** (Scheme 1) selectively ligating CO and giving **11**. This (η^3-In) intermediate, analogous to (η^3-In)$Fe(CO)_3^-$ [10], then alkylates at iron and gives **12**. Indenyl-ligand ring slippage back to the thermodynamically favored η^5-Indenyl [17] and dimer fragmentation afford the observed products. The precise timing of the carbonylation, the indenyl ring slippage, and the alkylation (with E–X) steps remain to be determined.



E-X = CH_3I, Ph_3SnCl, CH_3CH_2I

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16 Postulated mechanism for generating **3** or **4** entails nucleophilic attack of Fp^- or $In(CO)_2Fe^-$ at the iron center of $In(CO)_2Fe\text{-}CH_3$ (**1**) coincident with η^5/η^3 In ligand slippage [17]. Subsequent methyl-CO migration (with η^3/η^5 In tautomerization) and collapse to a bridging CO dimer affords the terminal acetyl dimers. Neither Fp^- nor $In(CO)_2Fe^-$ (as Li^+, Na^+, and PPN^+ salts), however, react with $Cp(CO)_2FeCH_3$ (8 h).

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