Direct Carbonylation of Indenyl Ligated Complexes $In(CO)_2FeCH(OR')R$ ($R = Ph$, $p\text{-}OCH_3Ph$, $R' = SiMe_3$; $R = Ph$, $R' = CH_3$) under Mild Reaction Conditions

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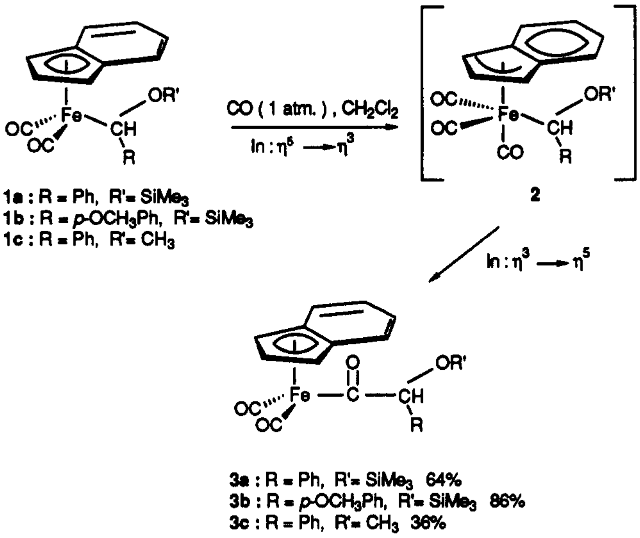
Direct carbonylation of (α-siloxybenzyl)iron complexes $In(CO)_2FeCH(OSiMe_3)R$ ($R = Ph$, $p\text{-}OCH_3Ph$) under mild reaction conditions (1 atm, ambient temperature) afforded the acyl compounds $In(CO)_2FeCOCH(OSiMe_3)R$ in very good yield. The (α-methoxybenzyl)iron complex $In(CO)_2FeCH(OCH_3)Ph$ was also carbonylated in fair yield. Carbon monoxide insertion was determined to be a function of the combined effects of the indenyl (In) ligand, a phenyl group, and an α-siloxy/alkoxy substituent. Proof of this was demonstrated by failure of the cyclopentadienyl (Cp) analog $Cp(CO)_2FeCH(OSiMe_3)Ph$, the methyl substituted complex $In(CO)_2FeCH(OSiMe_3)CH_3$, and the benzyl complex $In(CO)_2FeCH_2Ph$ to undergo carbonylation under similar reaction conditions.

Introduction

Our earlier interest in establishing novel methodologies for generating (α-oxyalkyl)iron-type complexes led us to a new procedure for the synthesis of cyclopentadienyl (Cp) dicarbonyl (α-siloxyalkyl)iron complexes.[1] This method was extended to the preparation of indenyl (In) ligated (α-siloxyalkyl)iron complexes.[2] Both the Cp and In ligated complexes have been successfully applied to cyclopropanation.[1,2]

To further extend the use of these complexes, we considered the carbonylation reaction for preparation of the acyl products. Cutler has utilized the alkoxymethyl complexes $Cp(CO)_2FeCH_2OR$ ($R = Me, Et$) in CO insertion reactions for conversion to C_2 and C_3 organic compounds.[3] However, direct carbonylation of these complexes to their alkoxyacetyl products $Cp(CO)_2FeCOCH_2OR$ was not possible;[4] instead ligand promotion (PPh_3, $P(OMe)_3$) under forced reaction conditions (refluxing CH_3CN, 4-10 days) was required.[3a] Conversely, the related α-siloxy manganese complex, $(CO)_5MnCH(OSiMe)_3Ph$ does undergo direct carbonylation but under a high carbon monoxide pressure (2000 psi).[5] Recently, Cutler developed an indirect method for carbonylation of the indenyl ligated alkoxymethyl complexes $In(CO)_2FeCH_2OR$ ($R = Me, Et$) and the ethoxyethyl complex $In(CO)_2FeCH(OEt)CH_3$ with the $In(CO)_2Fe$ anion to promote CO insertion by forming a bimetallic intermediate.[6] Here we wish to report a simple, direct carbonylation of indenyl dicarbonyl (α-oxyalkyl)-iron complexes under mild reaction conditions (1 atm, 6-16 h).

Scheme 1



1a: R = Ph, R' = $SiMe_3$
1b: R = $p\text{-}OCH_3Ph$, R' = $SiMe_3$
1c: R = Ph, R' = CH_3

3a: R = Ph, R' = $SiMe_3$ 64%
3b: R = $p\text{-}OCH_3Ph$, R' = $SiMe_3$ 86%
3c: R = Ph, R' = CH_3 36%

Results and Discussion

Direct carbonylation of the (α-siloxybenzyl)iron complexes $In(CO)_2FeCH(OSiMe_3)R$ ($R = Ph, p\text{-}OCH_3Ph$)[2] was achieved in very good yield by blanketing a CH_2Cl_2 solution of the α-siloxybenzyl complexes **1a,b** with 1 atm of CO gas at room temperature (20 °C) (Scheme 1). The ν(CO) frequencies of the terminal carbonyls and acyl were monitored by FTIR. Three emerging peaks at ca. 2018, 1963, and 1634 cm^{-1} indicated the progress of the reaction. The reaction was determined to be complete after 6-12 h. Separation by column chromatography on alumina resulted in isolated yields of 64-86% for the acyl products as light yellow-orange solids. Characterization by spectroscopic methods identified the products as the α-siloxyacyl complexes. The only apparent competing reactions were decomposition of the starting materials to pinacol silyl ethers $[RCH(OSiMe_3)]_2$[7] and the iron dimer $[In(CO)_2Fe]_2$.[8]

These carbonylation reactions of the indenyl-based complexes were surprisingly simple. No methods of

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[1] Vargas, R. M.; Theys, R. D.; Hossain, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 777.

[2] Details related to the synthesis of these (α-siloxybenzyl)iron complexes **1a,b** and their use in cyclopropanation will be forthcoming in a later publication.

[3] (a) Bodnar, T.; Coman, G.; LaCroce, S.; Lambert, C.; Menard, K.; Cutler, A. *J. Am. Chem. Soc.* **1981**, *103*, 2471. (b) Bodnar, T. W.; Crawford, E. J.; Cutler, A. R. *Organometallics* **1986**, *5*, 947.

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promotion were necessary, and the conditions were extremely mild. Only 1 atm of CO gas at ambient temperature (20 °C) was required to give very good yields of the acyl complexes **3** after 6–12 h.[9] Carbonylation of the related manganese complex $(CO)_5MnCH(OSiMe_3)Ph$ required 2000 psi of CO gas at 25 °C in THF to achieve a 50% conversion to the silyloxyacyl complex.[5]

The ease with which **1a,b** undergo carbonylation is apparently related in part to the indenyl ligand. Cutler had previously "observed that substitution of η^5-In for η^5-Cp on iron alkyl complexes greatly facilitates their carbonylation".[10] This was attributed to a reversible slippage from η^5 to η^3 with the indenyl ligand, opening up a coordination site for CO. We presume that the carbonylation of **1** is also facilitated by η^5 to η^3 ring slippage through the plausible intermediate **2**. To prove that the indenyl ligand was necessary, we attempted to carbonylate the cyclopentadienyl (Cp) analog of **1a**, $Cp(CO)_2FeCH(OSiMe_3)Ph$.[1]

Attempted carbonylation of $Cp(CO)_2FeCH(OSiMe_3)Ph$ under 1 atm of CO pressure in CH_2Cl_2 at room temperature was unsuccessful. Only starting material and a small concentration of the decomposition products, $[Cp(CO)_2Fe]_2$ and $[PhCH(OSiMe_3)]_2$,[7] were detected by FTIR. Furthermore, addition of $AgBF_4$ as an oxidation promoter failed to give any of the desired carbonylation product. These results and the successful carbonylations of **1a,b** clearly demonstrate that the indenyl ligand is one requirement for CO incorporation. To further understand the effects of the siloxy and phenyl substituents in this reaction, carbonylation of three other complexes were evaluated. The tendency of the complexes $In(CO)_2FeCH(X)R$ ($X = OSiMe_3$, $R = CH_3$; X = H, R = Ph; $X = OCH_3$, R = Ph) to undergo carbonylation was assessed.

The (siloxymethyl)methyliron complex $In(CO)_2FeCH(OSiMe_3)CH_3$ was treated similarly to **1a,b** with 1 atm of CO gas. This complex proved to be inert under these reaction conditions, demonstrating that in addition to the indenyl ligand, the phenyl group also plays a role in carbonylation.[11] However, how the phenyl group facilitates carbonylation is not known.[12]

To determine whether the phenyl group and the indenyl ligand could activate CO insertion without the siloxy substituent, the benzyl complex $In(CO)_2FeCH_2Ph$ was synthesized and submitted to the carbonylation reaction. Reaction of a CH_2Cl_2 solution of the benzyliron complex $In(CO)_2FeCH_2Ph$ with 1 atm of CO gas was found to be inert to carbonylation at room temperature after 41 h. This clearly shows that an α-siloxy group is also necessary for carbonylation of these indenyl ligated and phenyl substituted iron complexes. Treatment of an α-alkoxy substituted complex such as $In(CO)_2FeCH(OCH_3)Ph$ would further indicate whether another α-oxy substituent will promote carbonylation.

Direct carbonylation of the (α-methoxybenzyl)iron complex $In(CO)_2FeCH(OCH_3)Ph$ (**1c**) was achieved in fair yield by blanketing a CH_2Cl_2 solution of the complex with 1 atm of CO gas at ambient temperature. The ν(CO) frequencies of the terminal carbonyls and acyl were monitored by FTIR. Three emerging peaks at 2018, 1962, and 1637 cm^{-1} indicated the progress of the reaction. The reaction was determined to be complete after 16 h. Separation by column chromatography on alumina resulted in a ^1H NMR determined yield of 36% for the yellow-orange acyl oil **3c** (Scheme 1).[13] Characterization by spectroscopic methods identified the product as the α-methoxyacyl complex, $In(CO)_2FeCOCH(OCH_3)Ph$. A complex mixture of byproducts in the crude reaction mixture resulted. One significant competing reaction included decomposition of starting material to the pinacol methyl ether $[PhCH(OCH_3)]_2$[14] and the indenyl dimer $[In(CO)_2Fe]_2$. It is apparent from these results that an α-methoxy substituent can also be used to facilitate carbonylation of the indenyl ligated and phenyl substituted iron complex. However, the reaction time is extended and carbonylation is not as clean as its siloxy analog.

The role of the α-oxy group in enhancing carbonylation is not known. However, it may involve an intramolecular interaction of the acyl oxygen in the transition state with the electropositive group (CH_3, $SiMe_3$) on the α-oxy substituent. This hypothesis would parallel that put forth by Gladysz to explain carbonylation enhancement of $(CO)_5MnCH_2(OSiMe_3)$.[15]

Conclusion

The indenyl ligated (α-siloxybenzyl)iron complexes **1a,b** were shown to undergo simple and efficient carbonylation to form their acyl analogs **3a,b**. The corresponding (α-methoxybenzyl)iron complex also undergoes carbonylation but the process is complicated by side reactions. Together these reactions represent the first examples of direct, unpromoted carbonylation of cyclopentadienyl or indenyl ligated iron-type α-siloxy/alkoxy complexes under mild reaction conditions. These carbonylation reactions are apparently a function of the combined effects of an indenyl ligand, a phenyl group, and an α-siloxy/alkoxy substituent. Further studies on extending this carbonylation to a greater variety of phenyl substituted complexes and to different siloxy complexes are planned to elucidate the importance of the phenyl and α-siloxy groups. Moreover, use of the α-siloxyacyl complexes **3** for synthetic applications is underway.

Experimental Section

General Data. All reactions and chromatographic separations of air-sensitive materials were performed under a nitrogen atmosphere employing standard Schlenk-type techniques unless otherwise stated. Ether and dichloromethane (CH_2Cl_2) were freshly distilled under nitrogen from sodium benzophenone ketyl and phosphorus pentoxide, respectively. Pentane was distilled from Na under an atmosphere of nitrogen. $CDCl_3$ was dried over phosphorus pentoxide, degassed three times, and distilled via bulb to bulb distillation under vacuum into a capped Schlenk tube and stored for later use.

Infrared spectra were recorded on a Nicolet MX-1 FTIR spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained at 250 and 62.9 MHz, respectively, on a Bruker NMR spectrometer.

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[9] Interestingly, no carbonylation product from **1a** was detected by FTIR over 5 h while the reaction flask was submerged in an ice bath, indicating a temperature dependence.

[10] Forschner, T. C.; Cutler, A. R.; Kullnig, R. K. *Organometallics* **1987**, *6*, 889.

[11] Cutler established that $In(CO)_2FeCH(OSiMe_2Ph)CH_3$ was also inert to CO (80 psig, CH_2Cl_2). A. Cutler, personal communication.

[12] The role of the phenyl substituent in facilitating carbonylation is currently under investigation.

[13] ^1H NMR indicated a small amount of rearranged product was present.

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Starting Materials. The indenyl ligated (α-siloxyalkyl)iron complexes $In(CO)_2FeCH(OSiMe_3)R$ (R = Ph, *p*-OMePh, CH_3) were synthesized by reaction of $In(CO)_2FeNa$[8] and the corresponding aldehyde followed by treatment with $ClSiMe_3$.[1] Likewise, the cyclopentadienyl ligated (α-siloxybenzyl)iron complex was synthesized in the same manner but by replacing the indenyl ligated anion with $Cp(CO)_2Fe^-$.[1] The benzyl complex $In(CO)_2FeCH_2Ph$ was synthesized from $In(CO)_2FeNa$ and $ClCH_2Ph$.[16] The (α-methoxybenzyl)iron complex $In(CO)_2FeCH(OCH_3)Ph$ was synthesized by reaction between $In(CO)_2FeNa$ and the carboxonium salt $PhCH{=}OCH_3BF_4$.[17]

Carbonylation of $In(CO)_2FeCH(OSiMe_3)Ph$. A 275-mg (0.677-mmol) sample of $In(CO)_2FeCH(OSiMe_3)Ph$ was dissolved in 10 mL of CH_2Cl_2 in a side-arm flask and degassed twice by the freeze–pump–thaw method. The orange solution was treated at ambient temperature with 1 atm of carbon monoxide gas and vigorously stirred. The ν(CO) frequencies of the terminal carbonyls and acyl were monitored by FTIR. The reaction was judged to be complete after 12 h. The solvent was removed from the maroon colored solution under reduced pressure and the residue dissolved in a 5% ether–pentane mixture and transferred via canula to a water-jacketed chromatography column containing neutral activity IV alumina. A very pale yellow band was eluted as the first fraction with a 1–2% ether–pentane mixture. The ^1H NMR of this fraction identified it as the pinacol silyl ether, $[PhCH(OSiMe_3)]_2$.[7] A bright yellow band **3a** was eluted as the second fraction with a 2–5% ether–pentane mixture in 64% yield. A brown dimer $[In(CO)_2Fe]_2$ band was eluted just behind the product band with a 5–10% ether–pentane mixture. The light orange-yellow solid **3a** was characterized by spectroscopic methods as the siloxyacyl product $In(CO)_2FeCOCH(OSiMe_3)Ph$. IR ($CH_2Cl_2$): 2018, 1964, 1633 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz, −20 °C): δ 0.05 (s, 9H, $OSi(CH_3)_3$), 4.63 (s, 1H, FeCOCH), 4.65 (t, J = 2.9 Hz, 1H, In H_2), 5.11 (br s, 1H, In H_{1or3}), 5.32 (br s, 1H, In H_{3or1}), 7.13–7.37 (m, 9H, In and Ph). ^{13}C NMR ($CDCl_3$, 62.9 MHz, −20 °C): δ −0.2 ($OSi(CH_3)_3$), 72.6, 72.9 (In $C_{1,3}$), 88.5 (FeCO*C*H), 103.0 (In C_2), 104.6, 106.5, (In $C_{3a,7a}$), 123.8, 124.2, 126.5, 127.1, 127.2, 127.4, 128.0 (In benzo C's and Ph), 138.5 (C_{ipso}), 214.2, 215.2 ($C\equiv O$), 262.2 ($C{=}O$). Anal. Calcd for $C_{22}H_{22}FeO_4Si$: C, 60.84; H, 5.10. Found: C, 61.20; H, 5.14.

Carbonylation of $In(CO)_2FeCH(OSiMe_3)(p\text{-}OCH_3Ph)$. A 95.5-mg (0.219-mmol) sample of $In(CO)_2FeCH(OSiMe_3)(p\text{-}OCH_3Ph)$ was dissolved in 4 mL of CH_2Cl_2 and treated as described above. The carbonylation reaction was judged to be complete by FTIR after 6 h. The solvent was removed under reduced pressure and the residue dissolved in a 10% CH_2Cl_2–pentane mixture and transferred via canula to a water-jacketed chromatography column containing neutral activity III alumina. A very pale yellow band was eluted as the first fraction with a 1–2% CH_2Cl_2–pentane mixture. This fraction was identified by its ^1H NMR as the pinacol silyl ether, $[(p\text{-}OCH_3Ph)CH(OSiMe_3)]_2$.[7] A brown dimer $[In(CO)_2Fe]_2$ band was eluted as the second fraction with a 10–20% CH_2Cl_2–pentane mixture. A bright yellow band **3b** was eluted as the third fraction with a 30–50% mixture of CH_2Cl_2–pentane in 86% yield. The light orange-yellow solid **3b** was characterized by spectroscopic methods as the siloxyacyl product $In(CO)_2FeCOCH(OSiMe_3)(p\text{-}OCH_3Ph)$. IR ($CH_2Cl_2$): 2017, 1962, 1635 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz, −20 °C): δ 0.04 (s, 9H, $OSi(CH_3)_3$), 3.80 (s, 3H, OCH_3), 4.61 (s, 1H, FeCOCH), 4.68 (t, J = 2.9 Hz, 1H, In H_2), 5.18 (br s, 1H, In H_{1or3}), 5.32 (br s, 1H, In H_{3or1}), 6.87 (d, J = 8.6 Hz, 2H, Ph), 7.12 (m, 2H, In benzo), 7.29 (d, J = 8.6 Hz, 2H, Ph), 7.38 (m, 2H, In benzo). ^{13}C NMR ($CDCl_3$, 62.9 MHz, −20 °C): δ −0.2 ($OSi(CH_3)_3$), 55.2 (OCH_3), 72.6, 72.9 (In $C_{1,3}$), 88.3 (FeCO*C*H), 103.2 (In C_2), 104.7, 106.5 (In $C_{3a,7a}$), 113.3, 123.9, 124.2, 127.1, 127.2, 127.8 (In benzo C's and Ph), 130.6 (C_{ipso}), 158.6 (C_{para}), 214.3, 215.1 ($C\equiv O$), 262.2 ($C{=}O$). Anal. Calcd for $C_{23}H_{24}FeO_5Si$: C, 59.49; H, 5.21. Found: C, 59.61; H, 5.18.

Carbonylation of $In(CO)_2FeCH(OCH_3)Ph$. A 55.7-mg (0.160-mmol) sample of $In(CO)_2FeCH(OCH_3)Ph$ was dissolved in 4 mL of CH_2Cl_2 and treated as previously described. The carbonylation reaction was judged to be complete by FTIR after 16 h. The solvent was removed under reduced pressure, the residue dissolved in a 25% CH_2Cl_2–pentane mixture and transferred via canula to a water-jacketed chromatography column containing neutral activity IV alumina. A very pale yellow band was eluted as the first fraction with a 10–25% CH_2Cl_2–pentane mixture. This fraction was identified by its IR spectrum and ^1H NMR as pinacol methyl ether, $[PhCH(OCH_3)]_2$.[14] A brown dimer $[In(CO)_2Fe]_2$ band was eluted as the second fraction with a 50% CH_2Cl_2– pentane mixture. A yellow-orange oil **3c** was eluted as the third fraction with a 75% mixture of CH_2Cl_2–pentane in 36% yield, as determined by ^1H NMR.[13] The light orange-yellow oil **3c** was characterized by spectroscopic methods as the methoxyacyl product $In(CO)_2FeCOCH(OCH_3)Ph$.[18] IR (CH_2Cl_2): 2018, 1962, 1637 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz, −20 °C): δ 3.28 (s, 3H, OCH_3), 4.45 (s, 1H, FeCOCH), 4.62 (t, J = 2.9 Hz, 1H, In H_2), 5.05 (br s, 1H, In H_{1or3}), 5.31 (br s, 1H, In H_{3or1}), 7.11–7.21, 7.28–7.44 (m, 9H, In and Ph). ^{13}C NMR ($CDCl_3$, 62.9 MHz, −20 °C): δ 57.0 (OCH_3), 72.5, 73.0 (In $C_{1,3}$), 99.0 (FeCO*C*H), 102.0 (In C_2), 105.5, 106.0 (In $C_{3a,7a}$), 123.9, 127.2, 127.8, 128.0, 128.4 (In benzo C's and Ph), 135.4 (C_{ipso}), 213.7, 214.4 ($C\equiv O$), 258.7 ($C{=}O$).

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(18) We were unable to obtain a pure sample for CH analysis.