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(Cyclopentadienone)iron Shvo Complexes: Synthesis and Applications to Hydrogen Transfer Reactions

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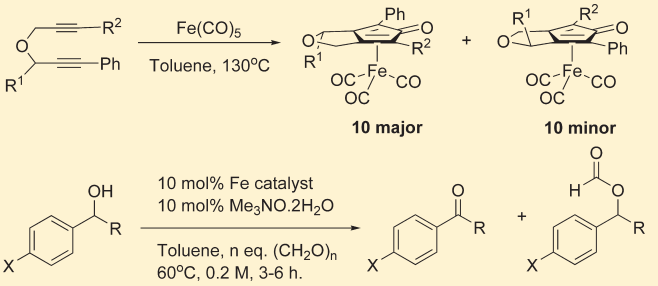
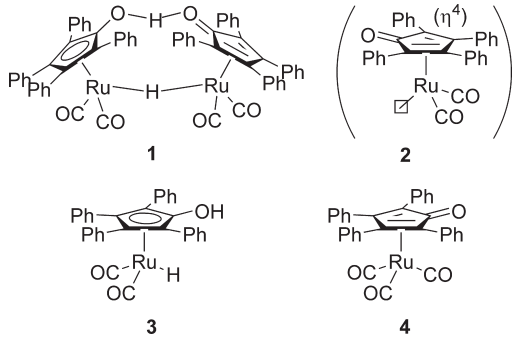
Supporting Information

ABSTRACT: A series of (cyclopendienone)iron tricarbonyl complexes were prepared using an intramolecular cyclization strategy. These were applied to the catalysis of the oxidation of alcohols to aldehydes and ketones. When paraformaldehyde was used as the hydrogen acceptor, formate esters were obtained as coproducts and, in several cases, the major products.



INTRODUCTION

The ruthenium dimer **1** is widely employed as a reagent for the transfer of pairs of hydrogen atoms between alcohols and ketones/aldehydes.[1−4] Catalyst **1** splits into two monometallic complexes, **2** and **3**, which are oxidized and reduced versions of each other; complex **2** removes two hydrogen atoms from an alcohol via a cyclic transition state (Figure 1), while complex **3** transfers two hydrogen atoms to a ketone or aldehyde via the same mechanism.[4] Coupling this process to an enantioselective esterification process has been employed in efficient dynamic kinetic resolution of alcohols and amines.[2,3] Dimer **1** is prepared from the tricarbonylruthenium complex **4**, by refluxing in isopropyl alcohol,[1] and can be converted fully to **3** using hydrogen gas or by transfer hydrogenation, e.g. from formic acid, and thus act as a ketone or imine reduction catalyst.



We are interested in the development of catalysts for the transfer of hydrogen atoms between organic molecules, in order to produce a convenient liquid fuel from alcohols available in biomass residues (e.g., glycerol from biodiesel production, carbohydrates from starch and cellulose, etc.). The use of precious-metal complexes for this purpose is well established but is problematic due to their high cost and toxic properties.[5] For these reasons we have recently investigated the use of iron-based complexes for organic transformations and, in particular, (cyclopentadienone)iron complexes[6−10] for hydrogen transfer processes. Several examples of the synthesis and applications of such complexes to alcohol oxidation[10] and ketone reduction[6] have been disclosed in the recent literature. The use of a number of other iron complexes for reduction of ketones, including asymmetric variants, has also recently been reported.[11]

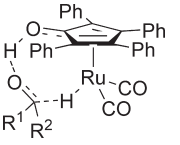


Figure 1. Mechanism of hydrogen transfer to C═O bonds: concerted "outer sphere" process.

In previously reported work in this area, Casey and Guan reported on the synthesis and applications of the related iron hydride complex **5** to ketone hydrogenation and transfer hydrogenation.[6a−c] Hydride **5** was formed from the tricarbonyliron precursor **6**, using a process reported by Knölker.[6d] (Cyclopentadienone)iron complexes of this type have been known for some time,[7] having been prepared by the reaction of iron carbonyl complexes $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ with diphenylacetylene in 1959 by Schrauzer.[7a] The intramolecular variation of this cyclization was used in the synthesis of **6**[8] by Pearson et al., who also

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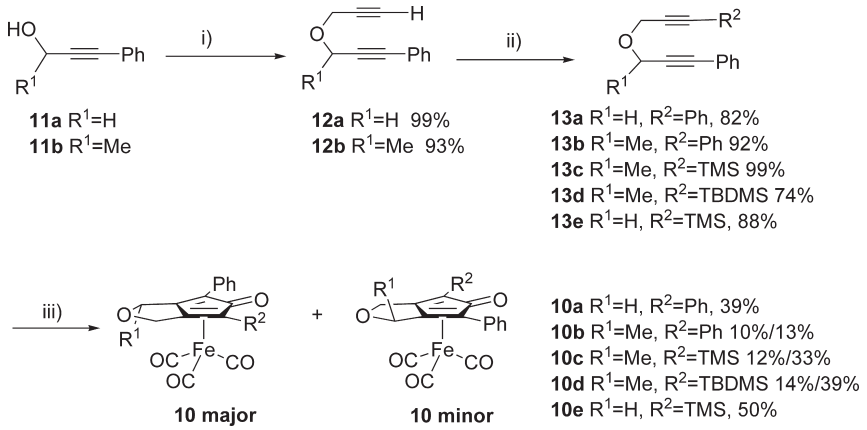
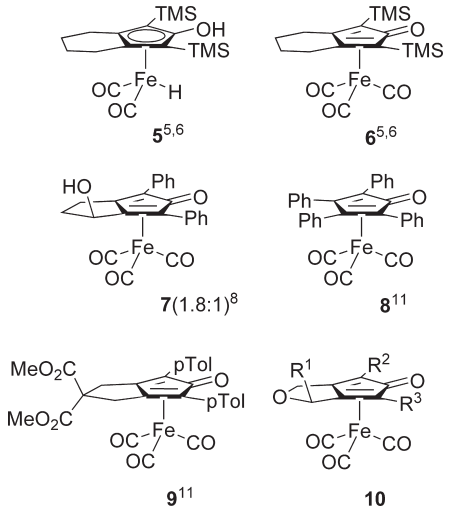
Scheme 1. Synthesis of (Cyclopentadienone)iron Complexes[a]



[a] Reagents and conditions: (i) $BrCH_2CCH$, NaH, THF, 0 °C. (ii) for **13c**−**e**, *n*BuLi, THF, −78 °C then R_3SiCl, −78 °C to room temperature, for **13a,b**, PhI, $PdCl_2(PPh_3)_2$, CuI, NEt_3, 72 h; (iii) $Fe(CO)_5$, toluene, 130 °C, 24 h.

noted that it was an effective method for the formation of derivatives **7** containing a chiral center (diastereomeric ratio 1.8:1).[8] Iron hydride complexes similar to **5** have been reported and studied by Baird et al.,[9] and recently both Guan[10a] and Funk[10b] reported on the use of **5** in the oxidation reactions of alcohols, using acetone as an acceptor, while Williams reported a similar application of the iron derivatives **8** and **9**.[10c] In this paper, we describe the synthesis, and applications to transfer hydrogenation, of a series of (cyclopentadienone)iron complexes.



RESULTS AND DISCUSSION

Earlier reports on the use of (cyclopentadienone)iron complexes for hydrogen transfer reactions suggested that a higher catalyst loading was generally needed in comparison to the case for the analogous ruthenium catalysts. We therefore selected a catalyst design (**10**) which would permit the relatively simple introduction of variable groups at three positions, providing scope to adjust the steric hindrance and electronic properties of the complexes. The approach to the catalysts is summarized in Scheme 1 and began from the alcohols **11a,b**, which were first

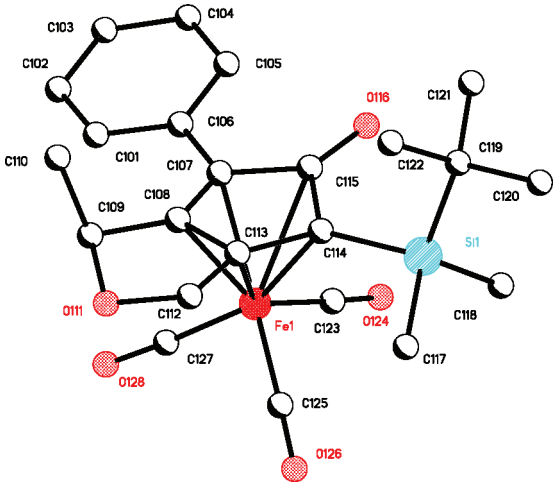


Figure 2. X-ray crystallographic structure of the minor isomer of complex **10d**,[12] showing one of two crystallographically independent but chemically identical enantiomeric molecules in the X-ray crystallographic structure.

alkylated using propargyl bromide to the diynes **12a,b**, respectively. In the next step, either a trialkylsilyl or a phenyl group was introduced. The resulting diynes that were prepared were then cyclized using $Fe(CO)_5$ to give the complexes shown. In the case of **10b**−**d** an unequal mixture of two separable diastereoisomers was formed. The structure of the minor diastereoisomer of complex **10d** was obtained by X-ray crystallography (Figure 2)[12] and proved to be that in which the methyl group on the dihydrofuran ring was trans to the iron tricarbonyl group. The relative stereochemistry in **10b,c** has been assigned by analogy with that found for **10d**. If $Fe_3(CO)_{12}$ was used in the complexation, a quantity of an unwanted diiron complex was also formed; this class of product has previously been identified and characterized in diyne cyclizations with iron carbonyl reagents.[7] The separated diastereoisomers, where appropriate, were tested separately in the subsequent hydrogen transfer reactions.

In addition, the nitrogen-bridged derivative **14** was prepared by a similar intramolecular cyclization of **15** (25% yield). An attempt was made to form complexes in which R^2 = H, by cyclization of **12a,b**; however, these were formed in low yields

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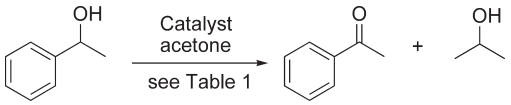
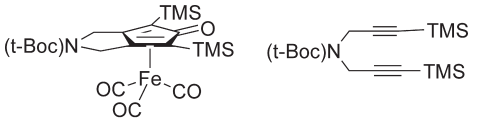
Table 1. Hydrogen Transfer from 1-Phenylethanol to Acetone: Initial Tests[a]



entry	complex	cat. (mol %)	[ketone] (mol dm^{-3})[b]	added H_2O[c]	T (°C)	time (days)	conversn to ketone (%)
1	**6**	10	0.24	yes	60	2	trace
2	**6**	10	0.59	yes	80	2	trace
3	**8**	10	0.19	no	60	4	29
4	**8**	5	0.38	no	60	4	29
5	**8**	10	0.19	no	80	4	63
6	**8**	5	0.38	no	80	4	45
7	**8**	10	0.19	yes	60	4	82
8	**8**	5	0.38	yes	60	4	67
9	**8**	10	0.19	yes	80	4	95
10	**8**	5	0.38	yes	80	4	92
11	**8**	10	0.19	10 mol %	60	2	85
12	**14**	10	0.19	yes	60	2	trace
13	**10a**	10	0.17	yes	60	2	trace
14	**10b** (major)	10	0.59	yes	80	2	trace
15	**10c** (major)	10	0.21	yes	60	2	trace
16	**10c** (major)	10	0.59	yes	80	2	trace
17	**14**	10	0.59	yes	80	2	trace

[a] Reactions were followed by ^{1}H NMR. [b] Acetone was used as solvent. [c] Added water refers to addition of ca. 35 mg of water to the reaction, except for entry 11.

and were contaminated by side products; therefore, these could not be tested in hydrogen transfer reactions.



14 **15**

For comparative purposes, samples of the tetraphenyl complex **8** and the *n*-butyl-bridged complex **6** were also prepared, following literature methods. Complex **6** was prepared by cyclization of the diyne precursor with iron pentacarbonyl (67%),[6] while **8** was made by direct complexation of 2,3,4,5-tetraphenylcyclopentadienone with triiron dodecacarbonyl in 91% yield.

The new catalysts were tested in the oxidation of 1-phenylethanol using a series of ketones and aldehydes as the hydrogen acceptors. Initial tests with acetone were conducted without prior formation or isolation of the corresponding iron hydride complex: i.e., the objective was to form this in situ. These reactions were initially followed by ^{1}H NMR or by gas chromatography (GC); however, the ^{1}H NMR method was prone to errors due to the volatility of the reagents, and hence GC analysis represents the preferred technique and was used throughout the rest of our studies. The results for the acetone-promoted oxidation are shown in Table 1. Adding a small amount of water to the system gave higher conversions, perhaps serving to hydrolyze one of the CO ligands to form the active species, in agreement with results published by Williams.[10c] While good conversions of alcohol to ketone could be obtained using the tetraphenyl-substituted "iron-Shvo" catalyst **8**, only traces of product were obtained with the other catalysts, even at higher concentrations and after heating for several days.

In view of the low conversions, efforts were made to synthesize hydroxycyclopentadienyl iron hydrides;[6] the hydride derived from **6** has been shown to be a very effective alcohol oxidation catalyst by Guan et al.[10a] The methods previously discussed for complex **6** involving base hydrolysis[6] were, however, found to be unsuccessful in our hands when applied to complex **8**, although an impure iron hydride complex could be observed by ^{1}H NMR when **6** was used as the starting material (see the Supporting Information). Guan et al. have reported[10a] that attempts to isolate iron hydride derivatives of closely analogous complexes bearing phenyl rings adjacent to the OH group on the cyclopentadienyl ring resulted in decomposition, which they speculated to proceed via a dimeric complex. In contrast, hydride **5** appears to be more stable due to the steric effects of the bulky trimethylsilyl substituents, which prevent a detrimental dimer formation.[10a] There is precedent for the use of $KBEt_3H$ to produce a ruthenium formyl complex from a tolyl analogue of **8** which converted to the hydride upon raising the temperature.[4a] Attempts in our hands to reproduce the procedure on complex **8**, however, failed to produce any observable hydride or formyl proton signals in the ^{1}H NMR spectrum.

A similar approach by analogy with a communication by Ogoshi[13] involved using borane to donate a hydride to one of the CO ligands or directly to the metal center via a ring-slip mechanism. This method enjoyed limited success using the *ruthenium* analogue of **8**, i.e. **4**; weak hydride signals were observed in the ^{1}H NMR spectrum at −9.86 and −18.37 ppm, indicating the presence of monomeric and dimeric hydride

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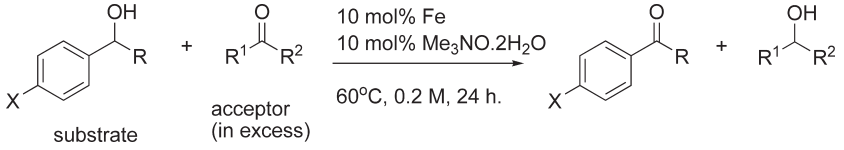
Table 2. Oxidation of 1-Phenylethanol and Derivatives Catalyzed by Iron Complexes Activated in Situ by TMANO[a]



entry	R	X	R^1	R^2	cat.	conversn (%)
1	Me	H	Me	Me	**6**	61
2	Me	H	Me	Me	**8**	99
3	Me	H	Me	Me	**10a**	15
4	Me	H	Me	Me	**10b** (major)	14
5	Me	H	Me	Me	**10b** (minor)	2
6	Me	H	Me	Me	**10c** (major)	11
7	Me	H	Me	Me	**10c** (minor)	34
8	Me	H	Me	Me	**10d** (major)	11
9	Me	H	Me	Me	**10d** (minor)	63
10	Me	H	Me	Me	**14**	17
11	Me	OMe	Me	Me	**8**	100 (6 h)
12	H	OMe	Me	Me	**8**	88 (5 h)[b]
13	Me	Cl	Me	Me	**8**	48
14	c-C_6H_{11}CH(OH)Me		Me	Me	**8**	86
15	Me	H	Me	H	**8**	43[b]
16	Me	H	Et	H	**8**	24[b]
17	Me	H	n-Pr	H	**8**	34[b]
18	Me	OMe	n-Pr	H	**8**	63[b]
19	H	OMe	n-Pr	H	**8**	15[b]
20	Me	Cl	n-Pr	H	**8**	27[b]
21	c-C_6H_{11}COMe		n-Pr	H	**8**	22[b]

[a] When acetone was the oxidant, it was used as the solvent. When an aldehyde was the oxidant, 5 equiv was used and toluene was employed as solvent. In all cases, [ketone] = 0.2 M. [b] Trace or no formation of ester.

complexes, respectively.[4a] Using this method with the iron complex **8**, a broad signal was observed at 13.81 ppm, falling near the expected range for metal formyl protons,[14] which could indicate the presence of an iron formyl complex.

Following unsuccessful attempts to form hydroxycyclopentadienyl hydride complexes, and with a view to develop a practical process, our efforts were instead focused on in situ activation. Trimethylamine *N*-oxide (TMANO) is a known reagent for the decarbonylation of metal carbonyl complexes[15] which has been used to mediate ligand substitution reactions of cyclopentadienone carbonyl complexes[16] and demetalation to form the free cyclopentadienone.[17] Since we started this project, Funk et al. reported the use of this method for activation of complex **6** toward the alcohol oxidation process and disclosed extensive applications and mechanistic details.[10b] It was found that a vented vessel was required for best results: i.e., to release the trimethylamine and carbon dioxide which is likely formed upon reaction of Me_3NO with a carbonyl ligand of the complex, thereby rendering the decarbonylation irreversible.

Using 1 molar equiv of TMANO per mole of complex, improved in situ activation of iron cyclopentadienone complexes toward hydrogen transfer was achieved using standard conditions of heating at 60 °C for 24 h in the presence of an excess of the acceptor (Table 2). When acetone was used as the acceptor, complex **8** again gave the highest conversion (99%) out of the catalysts tested, followed by complex **10d** (minor) (63%). Using complexes **10b**−**d**, there was a pronounced difference in reactivity between diastereoisomers of the same complex. An electron-rich substrate was more readily oxidized than an electron-poor one, and a corresponding primary alcohol proved to be more resistant to oxidation, giving a product in lower conversion in agreement with related published results.[10] Acetylcyclohexane formation (entry 14) could be achieved in good conversion under the standard conditions, indicating that the reaction is not limited to the preparation of acetophenone derivatives.

Some relatively volatile aldehydes were tested as acceptors for the reaction—in this case using a 5-fold excess of aldehyde in toluene solution. While the results were positive, the conversions remained below those obtained using acetone. Although there is potential for formation of esters under these conditions, these were not observed.

When the complexes were tested using paraformaldehyde as an acceptor with toluene as the solvent, an unexpected observation was made: the formation of acetophenone was achieved but the major product of the reaction in most cases was 1-phenylethyl formate (Table 3). Although complex **8** again gave the most consistently high conversions of 1-phenylethanol, both isomers of **10c** and the nonchiral **10e** also gave products in good conversions under the standard conditions listed. Several complexes showed increased selectivity for 1-phenylethyl formate over the ketone product. The use of more paraformaldehyde resulted in increased levels of formation of the formate, although

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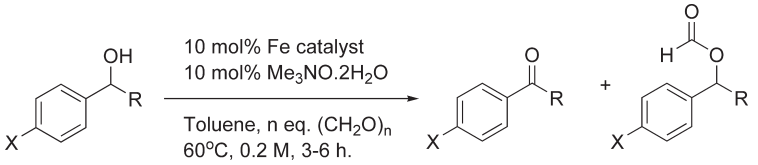
Table 3. Reaction of 1-Phenylethanol in the Presence of Paraformaldehyde with Iron Complexes[a]



						selectivity	
entry	complex[b]	X	R	*n*	total conversn (%) (time (h))[c]	ketone	formate
1	**6**	H	Me	5	67 (6)	26	74
2	**8**	H	Me	5	88 (6)	56	44
3	**10a**	H	Me	5	30 (6)	26	74
4	**10b** (major)	H	Me	5	24 (6)	29	71
5	**10b** (minor)	H	Me	5	7 (6)	39	61
6	**10c** (major)	H	Me	5	98 (6)	52	48
7	**10c** (minor)	H	Me	5	85 (6)	22	78
8	**10d** (major)	H	Me	5	34 (6)	41	59
9	**10d** (minor)	H	Me	5	71 (6)	22	78
10	**10e**	H	Me	5	96 (5)	32	68
11	**14**	H	Me	5	78 (6)	42	58
12	**10e**	H	Me	10	94 (5)	19	81
13	**10e**	H	Me	15	99 (4)	15	85
14	**10e**	H	Me	25	80 (6)	14	86
15	**8**	OMe	Me	5	93 (6)	70	30
16	**8**	OMe	H	5	97 (3)	55	45
17	**8**	Cl	Me	5	94 (3)	65	35
18	**10e**	OMe	Me	5	96 (6)	50	50
19	**10e**	OMe	H	5	99 (3)	19	81
20	**10e**	Cl	Me	5	91 (6)	24	76

[a] In all cases, [ketone] = 0.2 M; in cases where the reaction time is 24 h, a further 5 equiv of paraformaldehyde was added after 4 h. [b] A control reaction with no catalyst resulted in no formation of product. [c] Unless otherwise stated, the reaction time was 24 h.

the ratio appeared to remain unchanged at ca. 15:85 (entries 12−14), even when a large excess was used. At these high loadings of paraformaldehyde, the conversion decreased, possibly due to catalyst inhibition. The promising results obtained with **8** and **10e** prompted us to conduct further tests on extended substrates (entries 14−19). Similar results were obtained to those observed with acetone, with electron-rich substrates being more quickly oxidized in higher conversions. We are not aware of a similar transformation using an iron-based catalyst.

The formate may be formed by trapping the alcohol with a molecule of formaldehyde and subsequent hydride transfer (Scheme 2). The hydride transfer step would be required to take place via a $\eta^5-\eta^3$ slippage of the cyclopentadienyl ring, as has been proposed for related systems.[4] Alternatively, a hemiacetal may be lost and subsequently oxidized through a Tishchenko-type mechanism, catalyzed by the complex.[18a] Subsequent to the completion of this series of experiments, a report on the formylation of amines with paraformaldehyde using iridium complexes was published,[18b] the mechanism of which may have features in common with that shown in Scheme 2.

In summary, a series of novel (cyclopentadienyl)iron tricarbonyl complexes were prepared and tested, alongside closely related but known complexes, as catalysts for the oxidation of alcohols by a transfer hydrogenation mechanism. Of the series that were examined, under conditions of in situ activation, the (tetraphenylcyclopentadienone)iron catalyst **8** proved to be the most active for oxidation using acetone as an acceptor, although several catalysts exhibited a similar activity for hydrogen transfer with paraformaldehyde as an acceptor, resulting in an unexpected competing formylation reaction. To our knowledge, the paraformaldehyde−formate conversion has not previously been reported using any iron-based catalyst and may have some value as a potential "green" transformation given the relatively low toxicity of iron compared to that of more commonly used precious-metal catalysts.

EXPERIMENTAL SECTION

Solvents and reagents for the synthesis of complexes and catalytic reactions were degassed prior to use, and all reactions were carried out under either a nitrogen or argon atmosphere. All heated experiments were conducted using thermostatically controlled oil baths. Reactions were monitored by TLC using aluminum-backed silica gel 60 (F254) plates and visualized using UV 254 nm or phosphomolybdic acid (PMA), ninhydrin, potassium permanganate, and vanillin dips as appropriate. Flash column chromatography was carried out routinely using 60 Å silica gel (Merck). Reagents were used as received from commercial sources unless otherwise stated. ^{1}H NMR spectra were recorded on a Bruker DPX (300 or 400 MHz) spectrometer. Chemical shifts are reported in δ units, parts per million relative to the singlet at 7.26 ppm for

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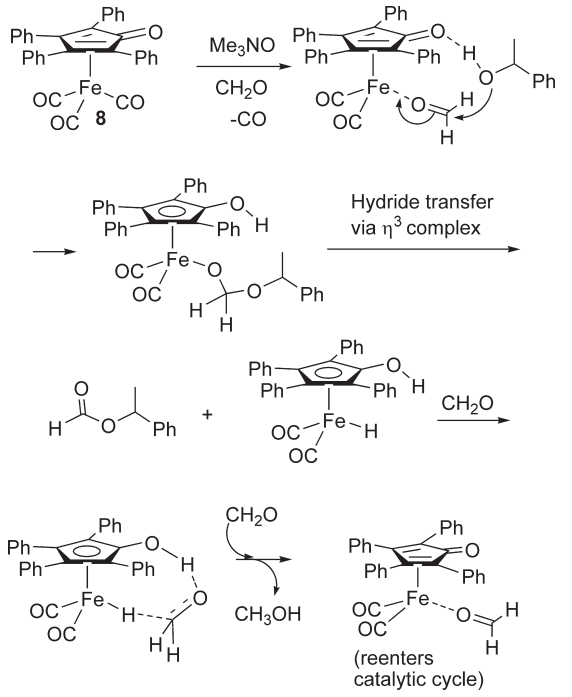
Scheme 2. Proposed Mechanism for Formation of Formate



chloroform. Coupling constants (J) are measured in hertz. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR Golden Gate instrument. Mass spectra were recorded on a Bruker Esquire2000 or a Bruker MicroTOF mass spectrometer. Melting points were recorded on a Stuart Scientific SMP 1 instrument and are uncorrected. GC analysis was performed using a Hewlett-Packard 5890 instrument. Dry solvents were purchased and used as received. The following compounds are known and have been fully characterized: *N-tert*-butoxycarbonyldipropargylamine,[19] 1,8-bis(trimethylsilyl)-1,7-octadiyne,[20] 4-phenyl-3-butyn-2-yloxy(prop-2-yne) (**12b**),[21] 3-phenyl-2-propyn-1-yloxy(prop-2-yne) (**12a**),[22] 3-phenyl-2-propyn-1-yloxy(3-phenylprop-2-yne) (**13a**),[23] 4-phenyl-3-butyn-2-yloxy(3-phenylprop-2-yne) (**13b**),[21] and tricarbonyl(2,4-bis(trimethylsilyl)bicyclo[4.3.0]nona-1,4-dien-3-one)iron (**6**).[8]

1,7-Bis(trimethylsilyl)-*N*-*tert*-butoxycarbonyldipropargylamine (15). *N-tert*-Butoxycarbonyldipropargylamine[19] (1.50 g, 7.78 mmol) was dissolved in dry THF (50 mL) and cooled to −78 °C. *n*-Butyllithium in hexanes (1.6 M, 10.0 mL, 16.0 mmol) was added dropwise, and the mixture was stirred for 2 h, after which time chlorotrimethylsilane (2.00 mL, 15.6 mmol) was added and the solution was warmed to room temperature. The reaction was quenched after 45 h with saturated NH_4Cl solution (50 mL), and the product was extracted into Et_2O (3 × 50 mL), dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The product **15** was purified by column chromatography on silica with a gradient elution from 100% hexane to 80/20 hexane/ethyl acetate to give a pale yellow liquid (1.34 g, 3.97 mmol, 51%). ESI MS: m/z found M^+ + Na 360.1802, calcd for $C_{17}H_{31}NNaO_2Si_2$ 360.1791. IR: ν_{max} 1703, 1444, 1400, 1365, 1240, 1162, 1006, 837, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.14 (broad s, 4H, CH_2), 1.47 (s, 9H, $(CH_3)_3CCO_2N$), 0.16 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.49, 154.40, 100.86, 80.77, 36.00, 28.29, −0.11. ESMS+: m/z 360 $[M + Na]^+$.

4-Phenyl-3-butyn-2-yloxy(3-(trimethylsilyl)prop-2-yne) (13c). 4-Phenyl-3-butyn-2-yloxy(prop-2-yne) (**12b**; 1.00 g, 5.45 mmol) was dissolved in dry THF (15 mL) and cooled to −78 °C. *n*-Butyllithium in hexanes (2.5 M, 2.61 mL, 6.53 mmol) was added dropwise, and the mixture was stirred for 1 h, after which chlorotrimethylsilane (0.90 mL, 7.09 mmol) was added. After 17 h the reaction was quenched with H_2O (10 mL), the THF was removed under reduced pressure, and the product was extracted into Et_2O (3 × 20 mL). The combined organic phase was dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure to give the product **13c** as a brown oil (1.385 g, 5.40 mmol, 99%). ESI MS: m/z found M^+ + Na 279.1182, calcd for $C_{16}H_{20}NaOSi$ 279.1176. IR: ν_{max} 1489, 1443, 1330, 1250, 1094, 1067, 990, 839, 754, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42−7.46 (m, 2H, Ar), 7.30−7.33 (m, 3H, Ar), 4.60 (q, J = 6.5 Hz, 1H, $CCH(CH_3)O$), 4.41 (d, J = 15.6 Hz, 1H, CCH_2O), 4.31 (d, J = 15.6 Hz, 1H, CCH_2O), 1.56 (d, J = 6.5 Hz, 3H, $CCH(CH_3)O$), 0.19 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.73, 128.39, 128.27, 122.54, 101.27, 91.31, 88.12, 85.54, 64.68, 56.62, 22.05, −0.18. ESMS+: m/z 279 $[M + Na]^+$.

4-Phenyl-3-butyn-2-yloxy(3-(*tert*-butyldimethylsilyl)prop-2-yne) (13d). This compound was synthesized by the same procedure as for **13c** using 4-phenyl-3-butyn-2-yloxy(prop-2-yne) (**12b**; 0.350 g, 1.90 mmol), *n*-butyllithium in hexanes (1.6 M, 1.40 mL, 6.53 mmol), and *tert*-butyldimethylsilylchloride (0.373 g, 2.48 mmol) and was purified by column chromatography on silica with a gradient elution from 100% hexane to 80/20 hexane/ethyl acetate to give the product **13d** as a yellow oil (0.421 g, 1.41 mmol, 74%). ESI MS: m/z found M^+ + Na 321.1637, calcd for $C_{19}H_{26}NaOSi$ 321.1645. IR: ν_{max} 2953, 2930, 2856, 1490, 1463, 1471, 1443, 1330, 1251, 1094, 1068, 990, 836, 824, 810, 775, 754, 689 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.42−7.46 (m, 2H, Ar), 7.28−7.34 (m, 3H, Ar), 4.64 (q, J = 6.8 Hz, 1H, $CCH(CH_3)O$), 4.41 (d, J = 15.8 Hz, 1H, CCH_2O), 4.33 (d, J = 15.8 Hz, 1H, CCH_2O), 1.55 (d, J = 6.8 Hz, 3H, $(CCH(CH_3)O)$, 0.95 (s, 9H, $Si(CH_3)_2C(CH_3)_3$) 0.12 (s, 6H, $Si(CH_3)_2C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.77, 128.43, 128.23, 122.54, 101.95, 89.68, 88.18, 87.25, 85.89, 64.36, 56.58, 26.05, 22.02, −4.68. ESMS+: m/z 321 $[M + Na]^+$.

3-Phenyl-2-propyn-1-yloxy(3-(trimethylsilyl)prop-2-yne)[23b] (13e). This compound was synthesized by the same procedure as for **13c** using 3-phenyl-2-propyn-1-yloxy(prop-2-yne) (1.00 g, 5.88 mmol), *n*-butyllithium in hexanes (1.6 M, 4.38 mL, 7.01 mmol), and chlorotrimethylsilane (0.96 mL, 7.56 mmol) was added. The product was isolated as an orange oil (1.249 g, 5.15 mmol, 88%). ESI MS: m/z found M^+ + Na 265.1018, calcd for $C_{15}H_{18}NaOSi$ 265.1019. IR: ν_{max} 2957, 2899, 1489, 1344, 1249, 1077, 998, 839, 755, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.42−7.49 (m, 2H, Ar), 7.28−7.35 (m, 3H, Ar), 4.47 (s, 2H, CH_2), 4.32 (s, 2H, CH_2), 0.19 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.8, 128.5, 128.3, 122.5, 100.7, 92.0, 86.7, 84.3, 57.4, 57.4, −0.2). ESMS+: m/z 265 $[M + Na]^+$.

Tricarbonyl(2,4-bis(trimethylsilyl)-7-*N*-*tert*-butoxycarbonylaminebicyclo[3.3.0]hepta-1,4-dien-3-one)iron (14). $Fe(CO)_5$ (1.56 mL, 11.9 mmol) and 1,7-bis(trimethylsilyl)-*N-tert*-butoxycarbonyldipropargylamine (**15**; 0.499 g, 1.48 mmol) were dissolved in dry toluene (10 mL) and heated at 130 °C in a sealed pressure tube for 24 h. The solution was cooled to room temperature before the pressure was released. Hot filtration and removal of the solvent under reduced pressure gave a brown solid (0.886 g). The product was purified by column chromatography on silica with a gradient elution from 98/2 hexane/ethyl acetate to 85/15 hexane/ethyl acetate to give the product **14** as a yellow solid (0.189 g, 0.374 mmol, 25%). Mp: 166−167 °C. ESI MS: m/z found M^+ + H 506.1122, calcd for $C_{21}H_{32}FeNO_6Si_2$ 506.1112. IR: ν_{max} 2070, 2016, 1994, 1695, 1620, 1415, 1363, 1243, 1165, 1109, 840, 766 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.32−4.52 (broad m, 4H, CH_2), 1.51 (s, 9H, $(CH_3)_3CCO_2N$), 0.26 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.80, 181.58, 154.56, 112.19, 111.76, 81.01, 69.55, 69.25, 47.57, 28.39, −1.04. ESMS+: m/z 506 $[M + H]^+$.

Tricarbonyl(tetraphenylcyclopentadienone)iron (8).[7a] $Fe_3(CO)_{12}$ (0.362 g, 0.653 mmol) and tetraphenylcyclopentadienone (0.250 g, 0.650 mmol) were dissolved in dry toluene (3 mL) and heated at 80 °C in a sealed pressure tube for 20 h, after which the solution was

cooled to room temperature and the solvent was removed under reduced pressure. The black solid was dissolved in ethyl acetate, the solution was filtered through Celite, and the solvent was removed under reduced pressure to give the product **8** as a yellow solid (0.311 g, 0.593 mmol, 91%). Mp: 174−175 °C dec. ESI MS: m/z found $M^+ + Na$ 547.0604, calcd for $C_{32}H_{20}FeNaO_4$ 547.0604. IR: ν_{max} 2061, 1987, 1639, 1498, 1444, 752, 695 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.55−7.61 (broad m, 4H, para *H*) 7.20−7.28 (broad m, 8H, meta *H*), 7.16 (broad d, J = 4.5, 8H, ortho *H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.48, 169.73, 131.73, 130.74, 130.24, 129.82, 128.64, 127.98, 127.97, 127.82, 103.97, 82.42. ESMS+: m/z 525 $[M + H]^+$.

Tricarbonyl(2,4-bis(phenyl)-7-oxybicyclo[3.3.0]hepta-1,4-dien-3-one)iron (10a). Compound **13a** (0.300 g, 1.22 mmol) and $Fe(CO)_5$ (0.48 mL, 3.65 mmol) were dissolved in dry toluene (3 mL) and heated at 130 °C for 24 h, after which the solution was cooled to room temperature and the solvent was removed under reduced pressure. The brown residue was filtered through Celite using a 9/1 hexane/ethyl acetate mixture to give an orange residue. The product was purified by column chromatography on silica with a gradient elution from 100% hexane to 80/20 hexane/ethyl acetate to give the product **10a** as a yellow-brown solid (0.196 g, 0.473 mmol, 39%). Mp: 218−220 °C dec. ESI MS: m/z found $M^+ + Na$ 437.0076, calcd for $C_{22}H_{14}FeNaO_5$ 437.0083. IR: ν_{max} 2064, 2004, 1634, 1055, 766, 693 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 7.0, 4H, Ar), 7.33−7.44 (m, 6H, phenyl), 5.21−5.27 (d, J = 12.1 Hz, 2H, CH_2), 5.08−5.13 (d, J = 12.1 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.63, 169.68, 131.46, 129.05, 128.57, 127.32, 100.55, 68.33, 65.82. ESMS+: m/z 415 $[M + H]^+$. A small, broad resonance from 6.8 to 7.8 ppm and a smaller broad resonance at 5.0 ppm in the ^1H NMR spectrum have not been assigned; these may be due to paramagnetic impurities.

Tricarbonyl(2,4-bis(phenyl)-6-methyl-7-oxybicyclo[3.3.0]-hepta-1,4-dien-3-one)iron (10b). These complexes (two diastereomers) were synthesized by the same procedure as for **10a**, using **13b** (0.300 g, 1.15 mmol) and $Fe(CO)_5$ (0.46 mL, 3.50 mmol), and were purified by column chromatography on silica with a gradient elution from 100% hexane to 60/40 hexane/ethyl acetate to give two diastereomers (1.2:1) of the product, which were separated. Minor diastereomer: brown powder (0.050 g, 0.117 mmol, 10%); mp 102−104 °C dec; ESI MS m/z found $M^+ + Na$ 451.0235, calcd for $C_{23}H_{16}FeNaO_5$ 451.0239; IR ν_{max} 2066, 1995, 1712, 1645, 1444, 1069, 752, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.06−8.11 (m, 2H, Ar), 7.86−7.93 (m, 2H, Ar), 7.32−7.45 (m, 6H, Ar), 5.64 (q, J = 6.4 Hz, 1H, ($CCH(CH_3)O$), 5.17 (s, 2H, CH_2), 1.54 (d, J = 6.4 Hz, 3H, ($CCH(CH_3)O$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.81, 171.75, 131.73, 131.46, 128.98, 128.95, 128.51, 128.31, 127.34, 126.99, 75.94, 66.31, 19.21; ESMS+ m/z 451 $[M + Na]^+$. A broad resonance from 6.5 to 7.6 ppm in the ^1H NMR spectrum has not been assigned; this may be due to paramagnetic impurities. Major diastereomer: brown powder (0.065 g, 1.52 mmol, 13%); mp 130−132 °C dec; ESI MS m/z found $M^+ + Na$ 451.0240, calcd for $C_{23}H_{16}FeNaO_5$ 451.0239; IR ν_{max} 2064, 2003, 1718, 1638, 1449, 1054, 768, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90−7.96 (m, 2H, Ar), 7.53−7.59 (m, 2H, Ar), 7.32−7.45 (m, 6H, Ar), 5.40 (q, J = 6.0 Hz, 1H, ($CCH(CH_3)O$), 5.25 (d, J = 13.2 Hz, 1H, CH_2), 5.03 (d, J = 13.2 Hz, 1H, CH_2) 1.67 (d, J = 6.0 Hz, 3H, ($CCH(CH_3)O$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.91, 131.34, 129.71, 129.04, 128.63, 128.56, 128.45, 127.26, 104.71, 104.56, 79.15, 75.04, 67.33, 30.90, 21.83; ESMS+ m/z 451 $[M + Na]^+$. A broad resonance from 6.6 to 7.8 ppm in the ^1H NMR spectrum has not been assigned; this may be due to paramagnetic impurities.

Tricarbonyl(2-(trimethylsilyl)-4-phenyl-6-methyl-7-oxybicyclo-[3.3.0]hepta-1,4-dien-3-one)iron (10c). These complexes (two diastereomers) were synthesized by the same procedure as for **10a**, using **13c** (0.300 g, 1.17 mmol) and $Fe(CO)_5$ (0.46 mL, 3.50 mmol), and were purified by column chromatography on silica with a gradient elution from 100% hexane to 40/60 hexane/ethyl acetate to give two diastereomers (2.7:1) of product, which were separated as brown oils. Minor diastereomer (0.060 g, 0.141 mmol, 12%): ESI MS m/z found $M^+ + H$ 425.0497, calcd for $C_{20}H_{21}FeO_5Si$ 425.0502; IR ν_{max} 2065, 2010, 1992, 1633, 1249, 1056, 842, 768, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99−8.03 (m, 2H, Ar), 7.29−7.40 (m, 3H, Ar), 5.57 (q, J = 6.4 Hz, 1H, $CCH(CH_3)O$), 4.81 (d, J = 12.8 Hz, 1H, CH_2), 4.71 (d, J = 12.8 Hz, 1H, CH_2), 1.52 (d, J = 6.4 Hz, 3H, CH_3), 0.33 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.86, 177.16, 131.85, 128.89, 128.23, 126.88, 108.46, 107.89, 77.25, 75.87, 66.08, 65.70, 18.98, −0.87; ESMS+ m/z 425 $[M + H]^+$. Major diastereomer (0.166 g, 3.91 mmol, 33%): ESI MS m/z found $M^+ + H$ 425.0501, calcd for $C_{20}H_{21}FeO_5Si$ 425.0502; IR ν_{max} 2064, 1998, 1635, 1250, 842 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48−7.52 (m, 2H, Ar), 7.30−7.40 (m, 3H, Ar), 5.36 (q, J = 6.4 Hz, 1H, $CCH(CH_3)O$), 4.79 (d, J = 13.2 Hz, 1H, CH_2), 4.71 (d, J = 13.2 Hz, 1H, CH_2), 1.65 (d, J = 6.4 Hz, 3H, CH_3), 0.31 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.88, 174.92, 129.73, 129.40, 128.40, 128.24, 113.20, 108.68, 81.58, 74.90, 66.72, 64.77, 21.67, −01.00; ESMS+ m/z 425 $[M + H]^+$.

Tricarbonyl(2-(*tert*-butyldimethylsilyl)-4-phenyl-6-methyl-7-oxybicyclo[3.3.0]hepta-1,4-dien-3-one)iron (10d). These complexes (two diastereomers) were synthesized by the same procedure as for **10a**, using **13d** (0.300 g, 1.01 mmol) and $Fe(CO)_5$ (0.40 mL, 3.04 mmol), and were purified by column chromatography on silica with a gradient elution from 100% hexane to 60/40 hexane/ethyl acetate to give two diastereomers (3.0:1) of product, which were separated. Minor diastereomer: yellow solid (0.066 g, 0.142 mmol, 14%); mp 124−126 °C; ESI MS m/z found $M^+ + H$, 467.0974, calcd for $C_{23}H_{26}FeO_5Si$ 467.0972; IR ν_{max} 2064, 1991, 1635, 1250, 1056, 826, 770, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99−8.05 (m, 2H, Ar), 7.29−7.39 (m, 3H, Ar), 5.56 (q, J = 6.8 Hz, 1H, $CCH(CH_3)O$), 4.81 (d, J = 13.2 Hz, 1H, CH_2), 4.71 (d, J = 13.2 Hz, 1H, CH_2), 1.53 (d, J = 6.8 Hz, 3H, CH_3), 1.01 (s, 9H, $SiC(CH_3)_3$) 0.47 (s, 3H, $Si(CH_3)_2C(CH_3)_3$), 0.08 (s, 3H, $Si(CH_3)_2C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.79, 176.89, 131.83, 128.91, 128.27, 126.96, 109.31, 108.14, 76.51, 75.84, 66.54, 65.86, 27.19, 18.96, 18.64, −5.01, −5.32; ESMS+ m/z 467 $[M + H]^+$. Major diastereomer: brown oil (0.181 g, 0.388 mmol, 39%); ESI MS m/z found $M^+ + H$ 467.0974, calcd for $C_{23}H_{26}FeO_5Si$ 467.0972; IR ν_{max} 2063, 1993, 1634, 1249, 1053, 825, 763, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47−7.53 (m, 2H, Ar), 7.29−7.41 (m, 3H, Ar), 5.38 (q, J = 6.0 Hz, 1H, $CCH(CH_3)O$), 4.79 (d, J = 13.2 Hz, 1H, CH_2), 4.73 (d, J = 13.2 Hz, 1H, CH_2), 1.65 (d, J = 6.0 Hz, 3H, CH_3), 0.97 (s, 9H, $SiC(CH_3)_3$) 0.51 (s, 3H, $Si(CH_3)_2C(CH_3)_3$), 0.06 (s, 3H, $Si(CH_3)_2C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.91, 174.68, 129.68, 129.55, 128.53, 128.38, 114.96, 108.03, 81.17, 74.98, 67.16, 65.36, 27.08, 21.82, 18.76, −5.16; ESMS+ m/z 467 $[M + H]^+$.

Tricarbonyl(2-(phenyl)-4-trimethylsilyl-7-oxybicyclo[3.3.0]-hepta-1,4-dien-3-one)iron (10e). This compound was synthesized by the same procedure as for **10a**, using **13e** (0.300 g, 1.24 mmol) and $Fe(CO)_5$ (0.49 mL, 3.73 mmol), and was purified by column chromatography on silica with a gradient elution from 100% hexane to 60/40 hexane/ethyl acetate to give the product as a yellow solid (0.253 g, 0.617 mmol, 50%). Mp: 129−133 °C;. ESI MS: m/z found $M^+ + H$ 411.0365, calcd for $C_{19}H_{19}FeO_5Si$ 411.0346. IR: ν_{max} 2058, 1993, 1627, 1246, 843, 761, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80−7.83 (m, 2H, Ar), 7.31−7.38 (m, 3H, Ar), 5.16−5.20 (d, J = 12.6 Hz, 1H, *CH*), 5.02−5.07 (d, J = 12.6 Hz, 1H, *CH*), 4.78−4.82 (d, J = 12.6 Hz, 1H, *CH*), 4.73−4.77 (d, J = 12.6 Hz, 1H, *CH*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.8, 176.0, 131.5, 129.0, 128.4, 127.2, 108.9, 104.4, 79.0, 68.3, 67.7, 65.8, −1.0. ESMS+: m/z 411 $[M + H]^+$.

Oxidation of 1-Phenylethanol using Iron Catalysts: Table 1. Complex **8** (10.0 mg, 19.1 μmol) and 1-phenylethanol (23.0 mg, 0.188 mmol) were dissolved in acetone (1 mL) and heated at 60 °C in a sealed pressure tube for 4 days, after which the solution was cooled to room

temperature and the solvent was removed under reduced pressure. The conversions were calculated from the integrations of the methyl peaks in the ^{1}H NMR spectra. The above procedure was repeated for the other complexes, and the conditions are shown in Table 1. Reactions with a 5 mol % catalyst loading were performed by doubling the quantity of 1-phenylethanol (46.0 mg, 0.377 mmol) without changing any other conditions.

Oxidation of 1-Phenylethanol using Iron Catalysts: Table 2. Complex **8** (10.0 mg, 19.1 μmol), trimethylamine *N*-oxide (2.10 mg, 18.9 μmol), and 1-phenylethanol (23.0 mg, 0.188 mmol) were dissolved in acetone (1 mL) and heated at 60 °C for 24 h. The reaction was monitored over time by GC (BP20 PEG column, T = 130 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas): R_T for acetophenone 4.7 min and for 1-phenylethanol 8.1 min. The above procedure was repeated for other complexes and substrates.

GC conditions: 1-(4-methoxyphenyl)ethanol (BP20 PEG column, T = 150 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas), R_T for 4′-methoxyacetophenone 13.4 min and for 1-(4-methoxyphenyl)ethanol 17.8 min; (anisyl)methanol (BP20 PEG column, T = 150 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas,. R_T for 4′-methoxybenzaldehyde 9.3 min and for anisylmethanol 22.5 min; 1-(4-chlorophenyl)ethanol (BP20 PEG column, T = 150 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas), R_T for 4′-chloroacetophenone 6.0 min and for 1-(4-chlorophenyl)ethanol 13.7 min; Cyclohexylmethyl alcohol (BP20 PEG column, T = 110 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas), R_T for cyclohexyl methyl ketone 3.2 min and for cyclohexylmethyl alcohol: 5.2 min.

Oxidation of 1-Phenylethanol using Iron Catalysts and Paraformaldehyde: Table 3. Complex **8** (10.0 mg, 19.1 μmol), trimethylamine *N*-oxide (2.1 mg, 18.9 μmol), 1-phenylethanol (23 mg, 0.188 mmol), and paraformaldehyde (29.0 mg, 0.966 mmol) were dissolved in toluene (1 mL) and heated at 60 °C for 24 h. After 4 h more paraformaldehyde (29.0 mg, 0.966 mmol) was added. The reaction was monitored over time by GC (BP20 PEG column, T = 130 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas): R_T for acetophenone 4.7 min, for 1-phenylethyl formate 5.0 min, and for 1-phenylethanol 8.1 min. Formates were independently synthesized, and standards were prepared in order to compare GC response factors.

GC conditions: 1-phenylethanol (Chrompac cyclodextrin-β-236 M 50 M column, T = 130 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas), R_T for acetophenone 13.4 min, for 1-phenylethyl formate 15.1 and 15.5 min, and for 1-phenylethanol 17.4 and 18.0 min; 1-(4-methoxyphenyl)ethanol (Chrompac cyclodextrin-β-236 M 50 M column, T = 130 °C, inj T = 220 °C, det T = 220 °C, 15 psi H_2 carrier gas), R_T for 4′-methoxyacetophenone 24.1 min, for 1-(4-methoxyphenyl)ethyl formate 23.7 and 24.8 min, and for 1-(4-methoxyphenyl)ethanol 25.5 and 26.4 min; (4-anisyl)methanol (Chrompac cyclodextrin-β-236 M 50 M column, T = 150 °C, inj T = 220 °C, det T = 220 °C, 15 psi H_2 carrier gas), R_T for 4′-methoxybenzaldehyde 8.6 min, for (4-methoxy)benzyl formate 10.4 min, and for (4-anisyl)methanol 11.7 min; 1-(4-chlorophenyl)ethanol (Chrompac cyclodextrin-β-236 M 50 M column, T = 150 °C, inj T = 220 °C, det T = 220 °C, 15 psi H_2 carrier gas), R_T for 4′-chloroacetophenone 7.3 min, for 1-(4-chlorophenyl)ethyl formate 8.8 and 9.1 min, and for 1-(4-chlorophenyl)ethanol 10.8 and 11.1 min.

1-Phenylethyl Formate.[24a−c] 1-Phenylethanol (0.150 g, 1.23 mmol) was dissolved in formic acid (5 mL) with 3 Å molecular sieves, and the mixture was stirred for 18 h, after which H_2O (5 mL) was added. The product was extracted into Et_2O (2 × 10 mL), the extracts were washed with H_2O (3 × 20 mL) and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica (90/10 hexane/ethyl acetate) to give the product as a colorless oil (0.112 g, 0.746 mmol, 61%). ESI MS: m/z found $M^+ - CO_2H$, 105.0705, calcd for C_8H_9 105.0699). IR: ν_{max} 2982, 2931, 1717, 1496, 1452, 1375, 1165, 1059, 1029, 992, 759, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (s, 1H, OC(O)H), 7.28−7.41 (m, 5H, Ar), 6.03 (q, J = 6.6 Hz, 1H, PhCH), 1.60 (d, J = 6.6 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.29, 140.83, 128.52, 128.09, 126.09, 72.14, 22.06. ESMS+: m/z 105 $[M - CO_2H]^+$.

1-(4-Methoxyphenyl)ethyl Formate.[24c] This compound was synthesized by the same procedure as for 1-phenylethyl formate using 1-(4-methoxyphenyl)ethanol (0.150 g, 0.986 mmol) and formic acid (5 mL) and was purified by column chromatography on silica (90/10 hexane/ethyl acetate) to give the product as a colorless oil (0.089 g, 0.494 mmol, 50%). ESI MS: m/z found M^+ + Na 203.0682, calcd for $C_{10}H_{12}NaO_3$ 203.0679. IR: ν_{max} 2933, 2837, 1718, 1613, 1514, 1459, 1297, 1247, 1169, 1033, 830 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (s, 1H, OC(O)H), 7.28−7.34 (m, 2H, Ar), 6.86−6.92 (m, 2H, Ar), 5.98 (q, J = 6.6 Hz, 1H, PhCH), 3.81 (s, 3H, OCH_3), 1.58 (d, J = 6.6 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.43, 159.45, 132.91, 127.67, 113.88, 71.93, 55.26, 21.83. ESMS+: m/z 135 $[M - CO_2H]^+$.

(4-Anisyl)methyl Formate.[24] This compound was synthesized by the same procedure as for 1-phenylethyl formate using (4-anisyl)methanol (0.070 g, 0.507 mmol) and formic acid (5 mL) and was purified by column chromatography on silica (90/10 hexane/ethyl acetate) to give the product as a colorless oil (0.037 g, 0.223 mmol, 44%). ESI MS: m/z found M^+ + Na 189.0526, calcd for $C_9H_{10}NaO_3$ 189.0522. IR: ν_{max} 2936, 2837, 1716, 1612, 1514, 1461, 1303, 1246, 1150, 1031, 820 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H, OC(O)H), 7.29−7.33 (m, 2H, Ar), 6.88−6.92 (m, 2H, Ar), 5.14 (s, 2H, PhCH_2), 3.81 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.87, 159.80, 130.24, 127.29, 113.99, 65.51, 55.27. ESMS+: m/z 121 $[M - CO_2H]^+$.

1-(4-Chlorophenyl)ethyl Formate.[24d] This compound was synthesized by the same procedure as for 1-phenylethyl formate using 1-(4-chlorophenyl)ethanol (0.150 g, 0.958 mmol) and formic acid (5 mL) and was purified by column chromatography on silica (90/10 hexane/ethyl acetate) to give the product as a colorless oil (0.102 g, 0.553 mmol, 58%). ESI MS: m/z found $M^+ - CO_2H$ 139.0310, calcd for C_8H_8Cl 139.0309. IR: ν_{max} 2984, 2930, 1719, 1494, 1452, 1409, 1375, 1342, 1162, 1091, 1058, 1014, 996, 823 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H, OC(O)H), 7.28−7.35 (m, 4H, Ar), 5.97 (q, J 6.5 Hz, 1H, PhCH), 1.56 (d, J 6.5 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.14, 139.37, 133.85, 128.71, 127.53, 71.38, 22.01. ESMS+: m/z 139 $[M - CO_2H]^+$.

Procedures for Attempted Hydroxycyclopentadienyl Hydride Complex Formation. *CO Hydrolysis and Hydride Formation Using NaOH.* Aqueous 1 M NaOH solution (0.96 mL) was added to a solution of **8** (40.0 mg, 95.6 μmol) in dry THF (4 mL). After 2.5 h a solution of 85% H_3PO_4 (0.03 mL) in H_2O (1 mL) was added and the product was extracted into Et_2O (3 × 5 mL), the extracts were dried over Na_2SO_4 and filtered, and the solvent was removed in vacuo. No hydride signals were observed in the ^{1}H NMR spectrum. The above procedure was repeated for complex **6**, and a signal at −12.07 ppm attributable to an iron hydride was observed in the ^{1}H NMR spectrum (see the Supporting Information).

Loss of CO and Hydride Formation Using BH_3. $BH_3 \cdot Me_2S$ (2 M in THF, 0.02 mL, 40.0 μmol) was added to a solution of **4** (0.010 g, 17.6 μmol) in dry THF (5 mL) cooled to −78 °C. After 1 h H_2O (0.1 mL) was added and the solution was warmed to room temperature, after which the solvent was removed in vacuo. Resonances at −9.86 and −18.37 ppm in the ^{1}H NMR spectrum indicate the presence of small quantities of the monomeric and dimeric hydride complexes, respectively. The same procedure was attempted with **8** and resulted in a broad peak at δ 13.81 in the ^{1}H NMR spectrum, which could indicate the presence of an iron formyl complex.

■ ASSOCIATED CONTENT

Supporting Information. Text, figures, and a CIF file giving ^{1}H and ^{13}C NMR spectra of novel compounds and X-ray crystallographic data for **10d** (minor isomer). This material is available free of charge via the Internet at http://pubs.acs.org.

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