(*Cyclopentadienone)iron-Shvo complexes; synthesis and applications to hydrogen transfer reactions.*

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ABSTRACT A series of (cyclopendienone)irontricarbonyl complexes were prepared using an intramolecular cyclisation 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 co-products 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 oxidised and reduced versions of each other; complex **2** removes two hydrogen atoms from an alcohol via a cyclic transition state (Figure 1) whilst complex **3** transfers two hydrogen atoms to a ketone or alcohol 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 isopropanol,[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.

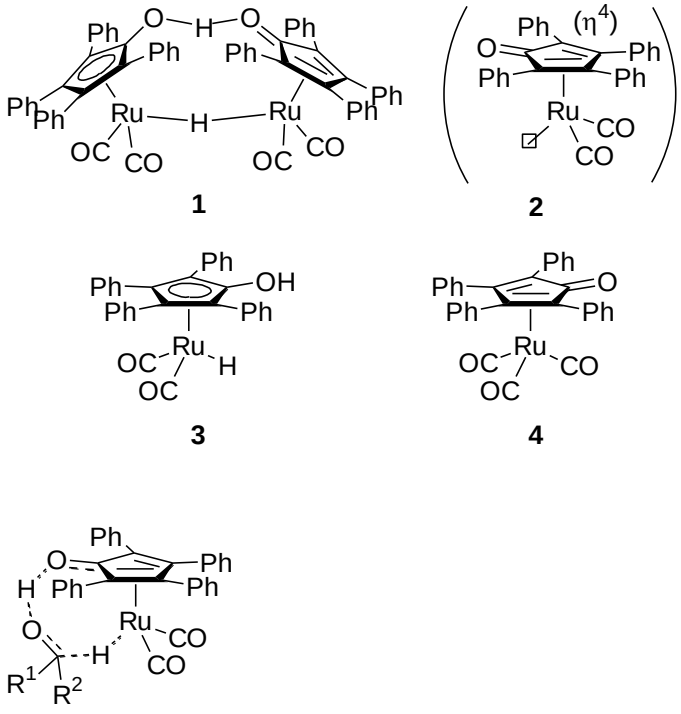
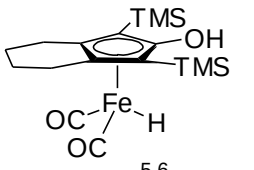


Figure 1. Mechanism of hydrogen transfer to C=O bonds: concerted 'outer sphere' process.

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 problematic due 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, have also recently been reported recently.[11]



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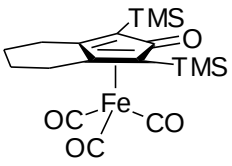

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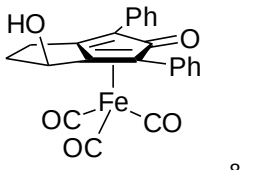

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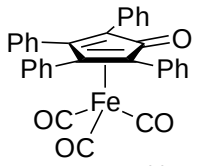

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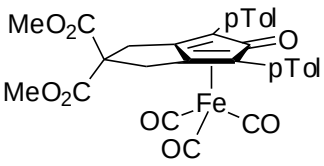

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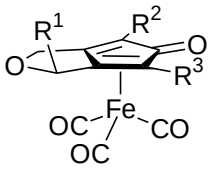

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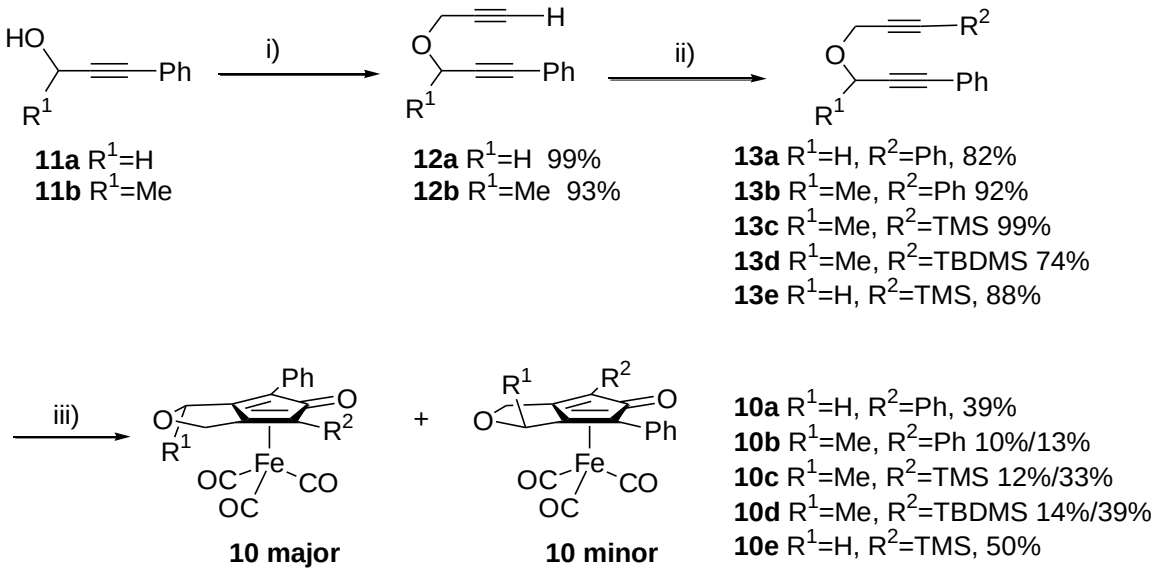
In previously reported work in this area, Casey and Guan have reported on the synthesis and applications of the related iron-hydride complex **5** to ketone hydrogenation and transfer hydrogenation.[6a-c] Hydride **5** was formed from the tricarbonyliron precursor **6**, using a process reported by Knölker.[6d] (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 cyclisation was used in the synthesis of **6**[8] by Pearson et al. who also noted that it was an effective method for the formation of derivatives **7** containing a chiral centre (diastereomeric ratio 1.8:1).[8] Similar iron-hydride complexes 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, whilst 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 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** and **11b**, which were first alkylated using propargyl bromide to the diynes **12a** and **12b** respectively. In the next step, either a trialkylsilyl or a phenyl group was introduced. The resulting diynes that were prepared were then cyclised using $Fe(CO)_5$ to the complexes shown. In the case of **10b-10d** 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** and **10c** have 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 characterised in diyne cyclisations with iron carbonyl reagents.[7] The separated diastereoisomers, where appropriate, were tested separately in the subsequent hydrogen transfer reactions.

Scheme 1. Synthesis of (cyclopentadienone)iron complexes.[a]



11a R^1=H
11b R^1=Me

12a R^1=H 99%
12b R^1=Me 93%

13a R^1=H, R^2=Ph, 82%
13b R^1=Me, R^2=Ph 92%
13c R^1=Me, R^2=TMS 99%
13d R^1=Me, R^2=TBDMS 74%
13e R^1=H, R^2=TMS, 88%

10 major

10 minor

10a R^1=H, R^2=Ph, 39%
10b R^1=Me, R^2=Ph 10%/13%
10c R^1=Me, R^2=TMS 12%/33%
10d R^1=Me, R^2=TBDMS 14%/39%
10e R^1=H, R^2=TMS, 50%

.

a Reagents and conditions: i) $BrCH_2CCH$, NaH, THF, 0°C. iii) For **13c, 13d, 13e**; *n*BuLi, THF, -78°C then R_3SiCl, -78°C-rt. For **13a, 13b**; PhI, $PdCl_2(PPh_3)_2$, CuI, NEt_3, 72h. iv) $Fe(CO)_5$, toluene, 130°C, 24h.

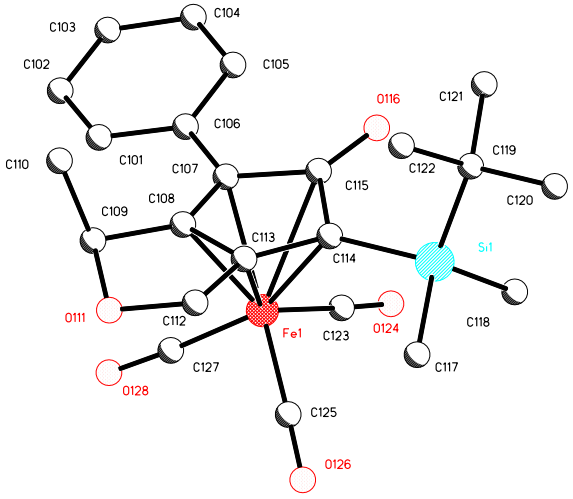
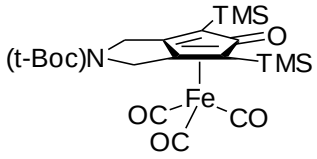


Figure 2. X-ray crystallographic structure of minor isomer of complex **10d**.[12] Picture showing one of two crystallographically independent but chemically identical enantiomeric molecules in the X-ray crystallographic structure.

In addition, the nitrogen-bridged derivative **14** was prepared by a similar intramolecular cyclisation of **15** (25% yield). An attempt was made to form complexes in which the R^2 = H, by cyclisation of **12a** and **12b**, however these were formed in low yields and were contaminated by side products, therefore these could not be tested in hydrogen transfer reactions.



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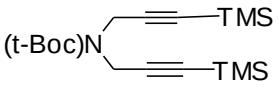

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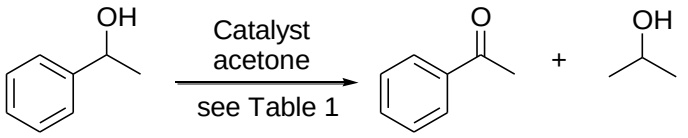
For comparative purposes, samples of the tetraphenyl complex **8** and the n-butyl-bridged complex **6** were also prepared, following literature methods. Complex **6** was prepared by cyclisation of the diyne precursor with iron pentacarbonyl (67%),[6] whilst **8** was made by direct complexation of 2,3,4,5-tetraphenylcyclopentadienone with triirondodecacarbonyl 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, ie. 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, 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 hydrolyse one of the CO ligands to form the active species, in agreement with results published by Williams.[10c] Whilst 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.

Table 1. Hydrogen transfer from 1-phenylethanol to acetone, initial tests.[a]



Entry	Complex	Catalyst (mol%)	[ketone] (mol dm^{-3})[b]	Added H_2O[c]	T (°C)	Time (days)	Conversion 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..

In view of the low conversions, efforts were made to synthesise 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 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.

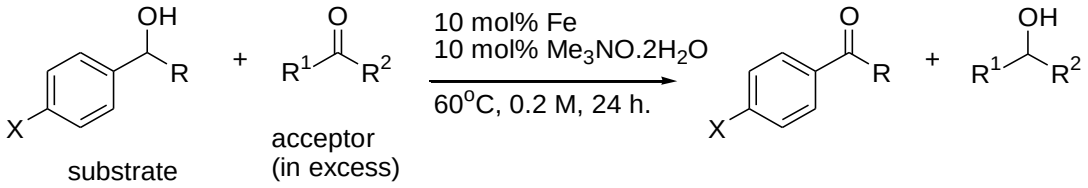
A similar approach by analogy with a communication by Ogoshi[13] involved using borane to donate a hydride to one of the CO ligands or directly to the metal centre via a ring-slip mechanism. This method enjoyed limited success using the *ruthenium* analogue of **8**, i.e. **4**; weak hydride signals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

oxidation process and disclosed extensive applications and mechanistic details.[10b] It was found that a vented vessel was required for best results ie 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 one molar equivalent of TMANO per mole of complex, improved *in situ* activation of iron cyclopentadienone complexes towards 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.

Table 2. Oxidation of 1-phenylethanol and derivatives catalysed by iron complexes activated in situ by TMANO.[a]



Entry	R	X	R^1	R^2	Catalyst	Conversion/%
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 (6h)
12	H	OMe	Me	Me	**8**	88 (5h) [c]
13	Me	Cl	Me	Me	**8**	48
14	$cC_6H_{11}CH(OH)Me$		Me	Me	**8**	86
15	Me	H	Me	H	**8**	43 [c]
16	Me	H	Et	H	**8**	24 [c]
17	Me	H	nPr	H	**8**	34 [c]
18	Me	OMe	nPr	H	**8**	63 [c]
19	H	OMe	nPr	H	**8**	15 [c]
20	Me	Cl	nPr	H	**8**	27 [c]
21	$cC_6H_{11}COMe$		nPr	H	**8**	22 [c]

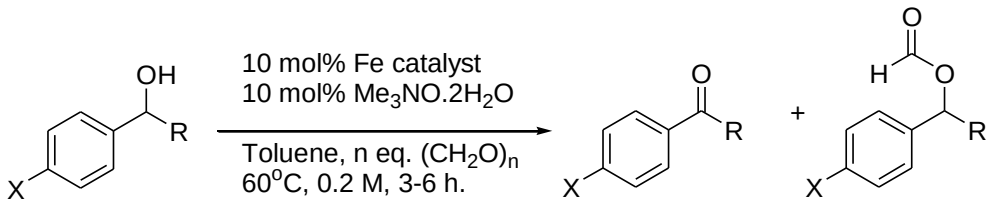
a. When acetone was the oxidant, it was used as the solvent. When an aldehyde was the oxidant, 5 equivalents were used and toluene was employed as solvent. b. In all cases, [ketone] = 0.2M. c. Trace or no formation of ester.

Some relatively volatile aldehydes were tested as acceptors for the reaction – in this case using a fivefold excess of aldehyde in toluene solution. Whilst 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 non-chiral **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 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 more quickly oxidized in higher conversions. We are not aware of a similar transformation using an iron based catalyst.

Table 3. Reaction of 1-phenylethanol in the presence of paraformaldehyde with iron complexes.[a]



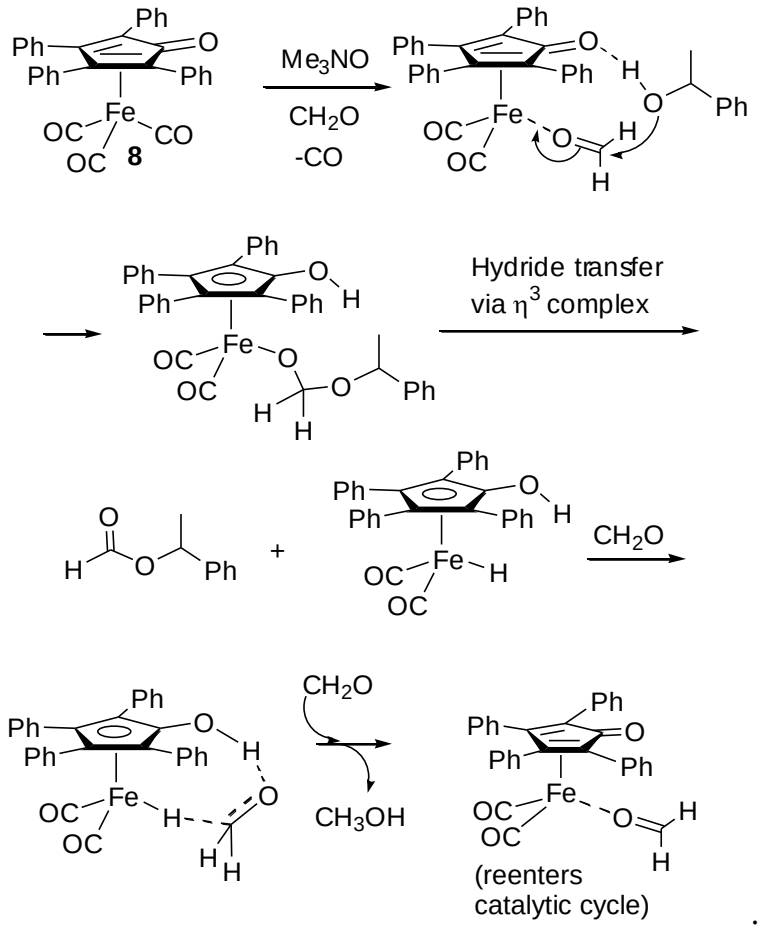
Entry	Complex[b]	X	R	n	Total Conversion (%)[c]	Selectivity	
						Ketone	Formate
1	**6**	H	Me	5	67 (6 h)	26	74
2	**8**	H	Me	5	88 (6 h)	56	44
3	**10a**	H	Me	5	30 (6 h)	26	74
4	**10b major**	H	Me	5	24 (6 h)	29	71
5	**10b minor**	H	Me	5	7 (6 h)	39	61
6	**10c major**	H	Me	5	98 (6 h)	52	48
7	**10c minor**	H	Me	5	85 (6 h)	22	78
8	**10d major**	H	Me	5	34 (6 h)	41	59
9	**10d minor**	H	Me	5	71 (6 h)	22	78
10	**10e**	H	Me	5	96 (5 h)	32	68
11	**14**	H	Me	5	78 (6 h)	42	58

12	**10e**	H	Me	10	94 (5 h)	19	81
13	**10e**	H	Me	15	99 (4 h)	15	85
14	**10e**	H	Me	25	80 (6 h)	14	86
15	**8**	OMe	Me	5	93 (6 h)	70	30
16	**8**	OMe	H	5	97 (3 h)	55	45
17	**8**	Cl	Me	5	94 (3 h)	65	35
18	**10e**	OMe	Me	5	96 (6 h)	50	50
19	**10e**	OMe	H	5	99 (3 h)	19	81
20	**10e**	Cl	Me	5	91 (6 h)	24	76

a. In all cases, [ketone] = 0.2 M, in cases where the reaction time is 24 h, a further 5 eq. 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 formate may be formed by trapping of the initial oxidation product (ketone) with a molecule of formaldehyde and subsequent hydride transfer (Scheme 2). The hydride transfer step would be required to take place via a η^5-η^3 slippage of the cyclopenedienyl ring, as has been proposed for related systems.[4] Alternatively, a hemiacetal may be lost and subsequently oxidized through a Tishchenko-type mechanism, catalysed by the complex.[18a] Subsequent to the completion of this series of experiments, a report on the formylation of amines using paraformaldehyde using iridium complexes was published,[18b] the mechanism of which may have features in common with that shown in Scheme 2.

Scheme 2. Proposed mechanism for formation of formate.



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 tetraphenyl(cyclopentadienone)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 relative low toxicity of iron compared to 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, visualized using UV 254 nm and phosphomolybdic acid (PMA), ninhydrin, potassium permanganate or 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 chloroform. Coupling constants (*J)* are measured in Hertz. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR Golden Gate. 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. Dry solvents were purchased and used as received. The following compounds are known and have been fully characterised; N-tert-butoxycarbonyl dipropargylamine,[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**,[23a] 4-phenyl-3-butyn-2-yloxy(3-phenylprop-2-yne) **13b**,[21] tricarbonyl(2,4-bis(trimethylsilyl)bicyclo[4.3.0]nona-1,4-dien-3-one)iron **6**.[8]

1,7-Bis(trimethylsilyl)-N-tert-butoxycarbonyl dipropargylamine **15**. N-*tert*-Butoxycarbonyl dipropargylamine[19] (1.50 g, 7.78 mmol) was dissolved in dry THF (50 mL) and cooled to -78 °C. 1.6 M n-Butyllithium in hexanes (10.0 mL, 16.0 mmol) was added dropwise and the mixture was allowed to stir for 2 h after which time chlorotrimethylsilane (2.00 mL, 15.6 mmol) was added and the solution was allowed to warm 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 x 50 mL), dried over $MgSO_4$, 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 %). (Found (ESI): M^+ + Na, 360.1802. $C_{17}H_{31}NNaO_2Si_2$ requires 360.1791); 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, C*H*$_2$), 1.47 (s, 9H, (C*H*$_3$)$_3$CCO$_2$N), 0.16 (s, 18H, Si(C*H*$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.49, 154.40, 100.86, 80.77, 36.00, 28.29, -0.11; *m*/*z* (ESMS+) 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 allowed to stir 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 x 20 mL). The combined organic phase was dried over Na_2SO_4, 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 %). (Found (ESI): M^+ + Na, 279.1182. $C_{16}H_{20}NaOSi$ requires 279.1176); 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, CC*H*(CH$_3$)O), 4.41 (d, *J* = 15.6 Hz, 1H, CC*H*$_2$O), 4.31 (d, *J* =15.6 Hz, 1H, CC*H*$_2$O), 1.56 (d, *J* = 6.5 Hz, 3H, CCH(C*H*$_3$)O), 0.19 (s, 9H, Si(C*H*$_3$)$_3$); ^{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; *m*/*z* (ESMS+) 279 $[M + Na]^+$.

4-Phenyl-3-butyn-2-yloxy(3-(tert-butyldimethylsilyl)prop-2-yne) **13d**. This compound was synthesised 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*-butyldimethylsilane (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 %). (Found (ESI): M^+ + Na, 321.1637. $C_{19}H_{26}NaOSi$ requires 321.1645); 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, CC*H*(CH_3)O), 4.41 (d, *J* = 15.8 Hz, 1H, CC*H*$_2$O), 4.33 (d, *J* = 15.8 Hz, 1H, CC*H*$_2$O), 1.55 (d, *J* = 6.8 Hz, 3H, (CCH(C*H*$_3$)O), 0.95 (s, 9H, Si(CH_3)$_2$C(C*H*$_3$)$_3$) 0.12 (s, 6H, Si(C*H*$_3$)$_2$C(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; *m*/*z* (ESMS+) 321 $[M + Na]^+$.

3-Phenyl-2-propyn-1-yloxy(3-(trimethylsilyl)prop-2-yne),[23b] **13e**. This compound was synthesised 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 %). (Found (ESI): M^+ + Na, 265.1018. $C_{15}H_{18}NaOSi$ requires 265.1019); ν_{max} 2957, 2899, 1489, 1344, 1249, 1077, 998, 839, 755, 690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.49 (m, 2H, Ar), 7.28-7.35 (m, 3H, Ar), 4.47 (s, 2H, C*H*$_2$), 4.32 (s, 2H, C*H*$_2$), 0.19 (s, 9H, Si(C*H*$_3$)$_3$); ^{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); *m*/*z* (ESMS+) 265 $[M + Na]^+$.

Tricarbonyl(2,4-bis(trimethylsilyl)-7-N-tert-butoxycarbonylamine-bicyclo[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*-butoxycarbonyl dipropargylamine **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 allowed to cool to room temperature before releasing the pressure. 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; (Found (ESI): M^+ + H, 506.1122. $C_{21}H_{32}FeNO_6Si_2$ requires 506.1112); ν_{max} 2070, 2016, 1994, 1695, 1620, 1415, 1363, 1243, 1165, 1109, 840, 766 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32-4.52 (broad m, 4H, C*H*$_2$), 1.51 (s, 9H, (C*H*$_3$)$_3$CCO$_2$N), 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; *m*/*z* (ESMS+) 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 allowed to cool to room temperature and the solvent was removed under reduced pressure. The black solid was dissolved in ethyl acetate, 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 (decomp.); (Found (ESI): M^+ + Na, 547.0604. $C_{32}H_{20}FeNaO_4$ requires 547.0604); 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; *m*/*z* (ESMS+) 525 $[M + H]^+$.

Tricarbonyl(2,4-bis(phenyl)-7-oxy-bicyclo[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 allowed to cool to room temperature and the solvent was removed under reduced pressure. The brown residue was filtered through celite using a 9:1 mixture of hexane:ethyl acetate 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 (decomp.); (Found (ESI): M^+ + Na, 437.0076. $C_{22}H_{14}FeNaO_5$ requires 437.0083); 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; *m*/*z* (ESMS+) 415 $[M + H]^+$. A small, broad resonance

exists from 6.8-7.8 ppm and a smaller broad resonance at 5.0 ppm in the ^{1}H NMR spectrum that have not been assigned; these may be due to paramagnetic impurities.

Tricarbonyl(2,4-bis(phenyl)-6-methyl-7-oxy-bicyclo[3.3.0]hepta-1,4-dien-3-one)iron **10b**. These complexes (two diastereomers) were synthesised 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 product which were separated. Minor diastereomer; brown powder (0.050 g, 0.117 mmol, 10 %). Mp 102-104 °C (decomp.); (Found (ESI): M^+ + Na, 451.0235. $C_{23}H_{16}FeNaO_5$ requires 451.0239); ν_{max} 2066, 1995, 1712, 1645, 1444, 1069, 752, 697 cm^{-1}; ^{1}H 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, (CC*H*(CH_3)O), 5.17 (s, 2H, C*H*$_2$), 1.54 (d, *J* = 6.4 Hz, 3H, (CCH(C*H*$_3$)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; *m*/*z* (ESMS+) 451 $[M + Na]^+$. A broad resonance exists from 6.5-7.6 ppm in the ^{1}H NMR spectrum that 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 (decomp.); (Found (ESI): M^+ + Na, 451.0240. $C_{23}H_{16}FeNaO_5$ requires 451.0239); ν_{max} 2064, 2003, 1718, 1638, 1449, 1054, 768, 694 cm^{-1}; ^{1}H 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, (CC*H*(CH_3)O), 5.25 (d, *J* = 13.2 Hz, 1H, C*H*$_2$), 5.03 (d, *J* = 13.2 Hz, 1H, CH_2) 1.67 (d, *J* = 6.0 Hz, 3H, (CCH(C*H*$_3$)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; *m*/*z* (ESMS+) 451 $[M + Na]^+$. A broad resonance exists from 6.6-7.8 ppm in the ^{1}H NMR spectrum that has not been assigned; this may be due to paramagnetic impurities.

Tricarbonyl(2-(trimethylsilyl)-4-phenyl-6-methyl-7-oxy-bicyclo[3.3.0]hepta-1,4-dien-3-one)iron **10c**. These complexes (two diastereomers) were synthesised 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 %) (Found (ESI): M^+ + H, 425.0497. $C_{20}H_{21}FeO_5Si$ requires 425.0502); 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, CC*H*(CH_3)O), 4.81 (d, *J* = 12.8 Hz, 1H, C*H*$_2$), 4.71 (d, *J* = 12.8 Hz, 1H, C*H*$_2$), 1.52 (d, *J* = 6.4 Hz, 3H, C*H*$_3$), 0.33 (s, 9H, Si(C*H*$_3$)$_3$); ^{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; *m*/*z* (ESMS+) 425 $[M + H]^+$. Major diastereomer (0.166 g, 3.91 mmol, 33 %) (Found (ESI): M^+ + H, 425.0501. $C_{20}H_{21}FeO_5Si$ requires 425.0502); 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, CC*H*(CH_3)O), 4.79 (d, *J* = 13.2 Hz, 1H, C*H*$_2$), 4.71 (d, *J* = 13.2 Hz, 1H, C*H*$_2$), 1.65 (d, *J* = 6.4 Hz, 3H, C*H*$_3$), 0.31 (s, 9H, Si(C*H*$_3$)$_3$); ^{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; *m*/*z* (ESMS+) 425 $[M + H]^+$.

Tricarbonyl(2-(tert-butyldimethylsilyl)-4-phenyl-6-methyl-7-oxy-bicyclo[3.3.0]hepta-1,4-dien-3-one)iron **10d**. These complexes (two diastereomers) were synthesised 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; (Found (ESI): M^+ + H, 467.0974. $C_{23}H_{26}FeO_5Si$ requires 467.0972); 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, CC*H*(CH_3)O), 4.81 (d, *J* = 13.2 Hz, 1H, C*H*$_2$), 4.71 (d, *J* = 13.2 Hz, 1H, C*H*$_2$), 1.53 (d, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.01 (s, 9H, SiC(C*H*$_3$)$_3$) 0.47 (s, 3H, Si(*CH*$_3$)$_2$C(CH_3)$_3$), 0.08 (s, 3H, Si(C*H*$_3$)$_2$C(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; *m*/*z* (ESMS+) 467 $[M + H]^+$. Major diastereomer, brown oil (0.181 g, 0.388 mmol, 39 %) (Found (ESI): $M^+ + H$, 467.0974. $C_{23}H_{26}FeO_5Si$ requires 467.0972); 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, CC*H*(CH_3)O), 4.79 (d, *J* = 13.2 Hz, 1H, C*H*$_2$), 4.73 (d, *J* = 13.2 Hz, 1H, C*H*$_2$), 1.65 (d, *J* = 6.0 Hz, 3H, C*H*$_3$), 0.97 (s, 9H, SiC(C*H*$_3$)$_3$) 0.51 (s, 3H, Si(C*H*$_3$)$_2$C(CH_3)$_3$), 0.06 (s, 3H, Si(C*H*$_3$)$_2$C(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; *m*/*z* (ESMS+) 467 $[M + H]^+$.

Tricarbonyl(2-(phenyl)-4-trimethylsilyl-7-oxy-bicyclo[3.3.0]hepta-1,4-dien-3-one)iron, **10e**. This compound was synthesised 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; (Found (ESI): $M^+ + H$, 411.0365. $C_{19}H_{19}FeO_5Si$ requires 411.0346); 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, C*H*), 5.02-5.07 (d, *J* = 12.6 Hz, 1H, C*H*), 4.78-4.82 (d, *J* = 12.6 Hz, 1H, C*H*), 4.73-4.77 (d, *J* = 12.6 Hz, 1H, C*H*); ^{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; *m*/*z* (ESMS+) 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 allowed to cool to room temperature and the solvent was removed under reduced pressure. The conversions were calculated from the integrations of the methyl peaks in the ^1H NMR spectra. The above procedure was repeated for the other complexes and conditions 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: Acetophenone: 4.7 minutes. 1-Phenylethanol: 8.1 minutes. 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: 4'-Methoxyacetophenone: 13.4 minutes. 1-(4-Methoxyphenyl)ethanol: 17.8 minutes. (*Anisyl)methanol*: (BP20 PEG column, T = 150 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas). R_T: 4'-Methoxybenzaldehyde: 9.3 minutes. Anisylmethanol: 22.5 minutes. *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: 4'-Chloroacetophenone: 6.0 minutes. 1-(4-Chlorophenyl)ethanol: 13.7 minutes. *Cyclohexylmethylalcohol*; (BP20 PEG column, T = 110 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas). R_T: Cyclohexylmethylketone: 3.2 minutes. Cyclohexylmethylalcohol: 5.2 minutes.

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: Acetophenone: 4.7 minutes, 1-Phenylethyl formate: 5.0 minutes. 1-Phenylethanol: 8.1 minutes. Formates were independently synthesised and standards were prepared in order to compare GC response factors.

GC conditions: *1-Phenylethanol* (Chrompac cyclodextrin-β-236M 50M column, T = 130 °C, inj T = 220 °C, det T = 220 °C, 15 psi He carrier gas). R_T: Acetophenone: 13.4 minutes. 1-Phenylethyl formate: 15.1, 15.5 minutes. 1-Phenylethanol: 17.4, 18.0 minutes, *1-(4-Methoxyphenyl)ethanol* (Chrompac cyclodextrin-β-236M 50M column, T = 130 °C, inj T = 220 °C, det T = 220 °C, 15 psi H_2 carrier gas). R_T: 4'-Methoxyacetophenone: 24.1 minutes. 1-(4-Methoxyphenyl)ethyl formate: 23.7, 24.8 minutes. 1-(4-Methoxyphenyl)ethanol: 25.5, 26.4 minutes. (4-*Anisyl)methanol* (Chrompac cyclodextrin-β-236M 50M column, T = 150 °C, inj T = 220 °C, det T = 220 °C, 15 psi H_2 carrier gas). R_T: 4'-Methoxybenzaldehyde: 8.6 minutes. (4-Methoxy)benzyl formate: 10.4 minutes. (4-Anisyl)methanol: 11.7 minutes. *1-(4-Chlorophenyl)ethanol* (Chrompac cyclodextrin-β-236M 50M column, T = 150 °C, inj T = 220 °C, det T = 220 °C, 15 psi H_2 carrier gas). R_T: 4'-Chloroacetophenone: 7.3 minutes. 1-(4-Chlorophenyl)ethyl formate: 8.8, 9.1 minutes. 1-(4-Chlorophenyl)ethanol: 10.8, 11.1 minutes.

1-Phenylethylformate.[24a-c] 1-Phenylethanol (0.150 g, 1.23 mmol) was dissolved in formic acid (5 mL) with 3 Å molecular sieves and left to stir for 18 h after which H_2O (5 mL) was added. The product was extracted into Et_2O (2 x 10 mL), washed with H_2O (3 x 20 mL), 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 colourless oil (0.112 g, 0.746 mmol, 61 %). (Found (ESI): M^+ - CO_2H, 105.0705. C_8H_9 requires 105.0699); ν_{max} 2982, 2931, 1717, 1496, 1452, 1375, 1165, 1059, 1029, 992, 759, 697 cm^{-1}; ^1H 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, PhC*H*), 1.60 (d, *J* = 6.6 Hz, 3H, CH_3); ^{13}C NMR δ (75 MHz, $CDCl_3$) 160.29, 140.83, 128.52, 128.09, 126.09, 72.14, 22.06; *m*/*z* (ESMS+) 105 $[M - CO_2H]^+$.

1-(4-Methoxyphenyl)ethylformate.[24c] This compound was synthesised by the same procedure as for 1-phenylethylformate 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 colourless oil (0.089 g, 0.494 mmol, 50 %). (Found (ESI): M^+ + Na, 203.0682. $C_{10}H_{12}NaO_3$ requires

203.0679); ν_{max} 2933, 2837, 1718, 1613, 1514, 1459, 1297, 1247, 1169, 1033, 830 cm^{-1}; ^1H 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, PhC*H*), 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; *m*/*z* (ESMS+) 135 $[M - CO_2H]^+$.

(4-Anisyl)methylformate.[24] This compound was synthesised by the same procedure as for 1-phenylethylformate 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 colourless oil (0.037 g, 0.223 mmol, 44 %). (Found (ESI): M^+ + Na, 189.0526. $C_9H_{10}NaO_3$ requires 189.0522); ν_{max} 2936, 2837, 1716, 1612, 1514, 1461, 1303, 1246, 1150, 1031, 820 cm^{-1}; ^1H 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; *m*/*z* (ESMS+) 121 $[M - CO_2H]^+$.

1-(4-Chlorophenyl)ethylformate.[24d] This compound was synthesised by the same procedure as for 1-phenylethylformate 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 colourless oil (0.102 g, 0.553 mmol, 58 %). (Found (ESI): M^+ - CO_2H, 139.0310. C_8H_8Cl requires 139.0309); ν_{max} 2984, 2930, 1719, 1494, 1452, 1409, 1375, 1342, 1162, 1091, 1058, 1014, 996, 823 cm^{-1}; ^1H 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, PhC*H*), 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; *m*/*z* (ESMS+) 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 x 5 mL), dried over

Na_2SO_4, filtered and the solvent removed in vacuo. No hydride signals were observed in the ^1H 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 ^1H NMR spectrum (See Supporting Information).

Loss of CO and Hydride Formation Using BH_3. $BH_3.Me_2S$ (2M 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 allowed to warm to room temperature after which the solvent was removed in vacuo. Resonances at -9.86 and -18.37 ppm in the ^1H 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 ^1H NMR spectrum which could indicate the presence of an iron formyl complex.

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Supporting Information Available. ^1H and ^{13}C NMR spectra of novel compounds, X-ray crystallographic data for **10d (**minor isomer). This material is free of charge *via* the Internet on the World Wide Web at http://pubs.acs.org.

References.

1) (a) Blum, Y.; Shvo, Y. *J. Organomet. Chem.* **1985**, *282*, C7-C10. (b) Blum, Y.; Czarkle, D.; Rahamim, Y.; Shvo, Y. *Organometallics*, **1985**, *4*, 1459-1461. (c) Shvo, Y.; Czarkie, D.; Rahamim, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7400-7402. (d) Menashe, N.; Salant, E.; Shvo, Y. *J. Organomet. Chem.* **1996**, *514*, 97-102. (e) Sears, C. T.; Stone, F. G. A. *J. Organomet. Chem.* **1968**, *11*, 644; (f) Bruce, M. I.; Knight, J. R. *J. Organomet. Chem.* **1968**, *12*, 411-413. (g) Blum, Y.; Shvo, Y.; Chodosh, D. F. *Inorg. Chim. Acta.* **1985**, *97*, L25-L26. (h) Conley, B. L.; Pennington-Boggio, M. K.; Boz, E.; Williams, T. J. *Chem. Rev.* **2010**, *110*, 2294-2312. (i) Karvembu, R.; Prabhakaran, R.; Natarajan, K.; *Coord. Chem. Rev.* **2005**, *249*, 911-918.

2) (a) Larsson, A. L. E. Persson, B. A.; Bäckvall, J.-E. *Angew. Chem. Int. Edn.* **1997**, *36*, 1211-1212. (b) Persson, B. A.; Larsson, A. I. E.; Le Ray, M.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1999**, *121*, 1645-1650. (c) Pamies, O.; Bäckvall, J.-E. *J. Org. Chem.* **2001**, *66*, 4022-4025. (c) Persson, B. A.; Huerta, F. F.; Bäckvall, J.-E. *J. Org. Chem.* **1999**, *64*, 5237-5240.

3) (a) Samec, J. S. M.; Bäckvall, J.-E. *Chem. Eur. J.* **2002**, *8*, 2955-2961. (b) Pamies, O.; Ell, A. H.; Samac, J. S. M.; Hermanns, N.; Bäckvall, J.-E. *Tetrahedron Lett.* **2002**, *43*, 4699-4702. (c) Paetzold, J.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2005**, *127*, 17620-17621. (d) Thalén, L. K.; Zhao, D.; Sortais, J.-B.; Paetzold, J.; Hoben, C.; Bäckvall, J.-E. *Angew. Chem. Int. Edn.* **2009**, *15*, 3403-3410.

4) (a) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090-1100. (b) Johnson, J. B.;Bäckvall, J.-E. *J. Org. Chem.* **2003**, *68*, 7681-7684. (c) Comas-Vives, A.; Ujaque, G.; Lledós, A. *Organometallics* **2007**, *26*, 4135-4144. (d) Casey, C. P.; Beetner, S. E.; Johnson, J. B. *J. Am. Chem. Soc.* **2008**, *130*, 2285-2295. (e) Éll, H.; Johnson, J. B.; Bäckvall, J.-E. *Chem. Commun.* **2003**, 1652-1653. (f) Samec, J. S. M.; Éll, A. H.; Bäckvall, J.-E. *Chem. Commun.* **2004**, 2748-2749. (g) Casey, C. P.; Johnson, J. B. *J. Am. Chem. Soc.* **2005**, *127*, 1883-1894. (h) Samec, J. S. M.; Éli, A.; Åberg, J. B.; Privalov, T.; Eriksson, L.; Bäckvall, J.-M. *J. Am. Chem. Soc.* **2006**, *128*, 14293-14305. (i) Primalov, T.; Samec, J. S. M.; Bäckvall, J.-E *Organometallics* **2007**, *26,* 2840-2848. (j) Casey, C. P.; Clark, T. B.; Guzei, I. A. *J. Am. Chem. Soc.* **2007**, *129*, 11821-11827. (k) Casey, C. P.;

Bikzhanova, G. A.; Cui, Q.; Guzei, I. A. *J. Am. Chem. Soc.* **2005**, *127*, 14062-14071. (i) Casey, C. P.; Johnson, C. P. *Can. J. Chem.* **2005**, *83*, 1339-1349. (k) Samec, J. S. M.; Bäckvall, J.-E.; Andersson, P. G.; Brandt, P. *Chem. Soc. Rev.* **2006**, *35*, 237-248. (l) Clapham S. E.; Hadzovic A.; Morris R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201-2237.

5) (a) Johnson, T. C.; Morris, D. J.; Wills, M. *Chem. Soc. Rev*., **2010**, *39*, 81 – 88. (b) Navarro, R. M.; M.A. Peña, M. A.; Fierro, J. L. G. *Chem. Rev.*, **2007**, *107*, 3952-3991. (c) S. Enthaler, S. *ChemSusChem* **2008**, *1*, 801-804. (d) Turner, J. A. *Science*, **2004**, *305*, 972-974 (e) Hydrogen as a Future Energy Carrier, Ed. Zuttel, A.; Borgschulte, A.; Schlapbach, L. Wiley VCH, **2008**.

6) (a) Casey, C. P. Guan, H. *J. Am. Chem. Soc.* **2007**, *129*, 5816-5817. (b) Casey, C. P.; Guan, H. *J. Am. Chem. Soc.* **2009**, *131*, 2499-2507. (c) Bullock, R. M. *Angew. Chem. Int. Edn.* **2007**, *46*, 7360-7363. (d) Knölker, H.-J.; Baum, E.; Goesmann, H.; Klauss, R. *Angew. Chem. Int. Edn.* **1999**, *38*, 2064-2066. (e) Zhang, H. H.; Chen, D. Z.; Zhang, Y. H.; Zhang, G. Q.; Liu, J. B. *Dalton Transactions* **2010**, *39*, 1972-1978. (f) Knölker, H.-J.; Heber, J. *Synlett* **1993**, 924-926. (g) Knölker, H.-J.; Heber, J.; Mahler, C. H. *Synlett* **1992**, 1002-1004.

7) (a) Schrauzer, G. N. *J. Am. Chem. Soc.* **1959**, *81*, 5307-5310. Schrauzer used $Fe(CO)_5$ as well but photochemical conditions were necessary, the reaction would not proceed thermally. (b) Weiss, E.; Merenyi, R. G.; Hubel, W. *Chemistry and Industry* **1960**, 407-408.

8) Pearson, A. J.; Shively Jr., R. J.; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096-4104.

9) Shackleton, T. A.; Mackie, S. C.; Fergusson, S. B.; Johnson, L. J.; Baird, M. C. *Organometallics* **1990**, *9*, 2248-2253.

10) (a) Coleman, M. G.; Brown, A. N.; Bolton, B. A.; Guan, H. *Adv. Synth. Catal.* **2010**, *352*, 967-970. (b) Moyer, S. A.; Funk, T. W. *Tetrahedron Lett.* **2010**, *51*, 5430-5433. (c) M. K. Thorson, K. L. Klinkel, J. Wang and T. J. Williams, *Eur. J. Inorg. Chem.* **2009**, 295-302.

11) (a) Sui-Seng, C.; Haque, F. N.; Hadzovic, A.; Pütz, A.-M.; Reuss, V.; Meyer, N.; Lough, A. J.; Zimmer-De Iuliis, M.; Morris, R. H. *Inorg. Chem.* **2009**, *48*, 735-743. (b) Sui-Seng, C.; Freutel, F.; Lough, A. J.; Morris, R. H. *Angew. Chem. Int. Ed.* **2008**, *47*, 940-943. (c) Meyer, N.; Lough, A. J.; Morris, R. H. *Chem.-Eur. J.* **2009**, *15*, 5605-5610. (d) Morris, *Chem. Soc. Rev.* **2009**, *38*, 2282-2291. (e) Mikhailine, A.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 1394-1395. (f) Enthaler, S.; Erre, G.; Tse, M. K.; Junge, M. K.; Beller, M. *Tetrahedron Lett.* **2006**, *47*, 8095-8099. (g) Enthaler, S.; Spilker, B.; Erre, G.; Junge, K.; Tse, M. K.; Beller, M. *Tetrahedron* **2008**, *64*, 3867-3876. (h) Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 3317-3321. (i) Zhou, S.; Fleischer, S.; Junge, K.; Das, S.; Addis, D.; Beller, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 8121-8125. (j) Hosokawa, S.; Ito, J.-I.; Nishiyama, H. *Organometallics*, **2010**, *29*, 5773-5775.

12) Crystal Data; $C_{23}H_{26}FeO_5Si$, M = 466.38, Monoclinic, space group P2(1)/n a = 23.8945(7), b = 7.1593(2), c = 27.4516(8) Å, $\alpha = 90°$, $\beta = 106.380(3)°$, $\gamma = 90°$, U = 4505.5(2) Å ^{3} (by least squares refinement on 7326 reflection positions), T =100(2) K, $\lambda = 0.71073$ Å, Z = 8, D(cal) = 1.375 Mg/m^3, F(000) = 1952. $m\upsilon$(MoK-α) = 0.753 mm^{-1}. CCDC 799783.

13) Ogoshi, S.; Kato, K.; Ohashi, M.; Kurosawa, H. *Dalton Trans.* **2008**, 2232-2234.

14) (a) Casey, C. P.; Meszaros, M. W.; Neumann, S. M.; Gennick Cesa, I.; Haller, K. J. *Organometallics* **1985**, *4*, 143-149. (b) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544-2545. (c) Brown, D. A.; Glass, W. K.; Turki Ubeid, M. *Inorg. Chim. Acta* **1984**, *89*, L47-L48.

15) (a) Luh, T.-Y. *Coord. Chem. Rev.* **1984**, *60*, 255-276. (b) Dasgupta, B.; Donaldson, W. A. *Tetrahedron Lett.* **1998**, *39*, 343-346. (b) Pearson, A. J.; Kwak, Y. *Tetrahedron Lett.* **2005**, *46*, 5417-5419.

16) Bailey, N. A.; Jassal, V. S.; Vefghi, R.; C. White, C. *J. Chem. Soc. Dalton Trans.* **1987**, 2815-2822.

17) (a) Pearson, A. J.; Shively Jr, R. J. *Organometallics* **1994**, *13*, 578-584. (b) Eekhof, J. H.; Hogeveen, H.; Kellogg, R. M. *Chem. Commun.* **1977**, 705. (c) Knölker, H.-J.; Baum, E.; Heber, J. *Tetrahedron Lett.* **1992**, *36*, 7647-7650.

18) (a) We thank a referee for this suggestion. (b) Saidi, O.; Bamford, M. J.; Blacker, A. J.; Lynch, J.; Marsden, S. P.; Plucinski, P.; Watson, R. J.; Williams, J. M. J. *Tetrahedron Lett.* **2010**, *51*, 5804-5806.

19) Boger, D. L.; Lee, J. K.; Goldberg, J.; Jin, Q. *J. Org. Chem.* **2000**, *65*, 1467-1474.

20) McDonnell Bushnell, L. P.; Evitt, E. R.; Bergman, R. G. *J. Organomet. Chem.* **1978**, *157*, 445-456.

21) Taylor, C. J.; Motevalli, M.; Richards, C. J. *Organometallics* **2006**, *25*, 2899-2902.

22) Boñaga, L. V. R.; Zhang, H.-C.; Maryanoff, B. E. *Chem. Commun.* **2004**, 2394-2395.

23) Lian, J.-J.; Chen, P.-C.; Lin, Y.-P.; Ting, H.-C.; Liu, R.-S. *J. Am. Chem. Soc.* **2006**, *128*, 11372-11373. (b) K. Tamao, K. Kobayashi and Y. Ito, *J. Org. Chem*, **1989**, *54*, 3517-3519.

24) (a) K. Niknam and D. Saberi, *Appl. Catal. A-Gen*, **2009**, *366*, 220-225. (b) K. Niknam, M.A. Zolfigol, M. Khonbazi and D. Saberi, *Chinese J. Chem*, **2009**, *27*, 1548-1552. (c) M. Jereb, D. Vražič and M. Zupan, *Tet, Lett*, **2009**, *50*, 2347-2352. (d) T. Yuzuri et al., *J. Chem. Soc., Perkin Trans*, **2000**, *2*, 1243-1249.

25) Fletcher, D. A.; McMeeking R. F.; Parkin, D. J. Chem. Inf. Comput. Sci. 1996, 36, 746-749.

SYNOPSIS TOC: