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Oxymethylation of Iron Complexes [(cp)Fe(CO)$_2$(R)] with HMMe$_3$ (M = Sn, Si; cp = C$_5$H$_5$) leading to R–CH$_2$OH *via* a Formylation–Hydrometallation Sequence

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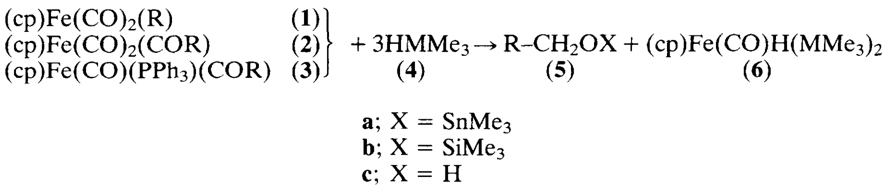
Thermal reaction of (cp)Fe(CO)$_2$(R), (cp)Fe(CO)$_2$(COR), and (cp)Fe(CO)(PPh$_3$)(COR) (cp = C$_5$H$_5$) with 3 equivalents of trimethyl-stannane or -silane, affords R–CH$_2$OH (or R–CH$_2$OSiMe$_3$) and (cp)Fe(CO)H(MMe$_3$)$_2$ in good yields; the reaction sequence follows initial reduction of transient co-ordinatively unsaturated acyl species to give the aldehyde and successive hydrometallation by the action of Me$_3$M–Fe intermediates.

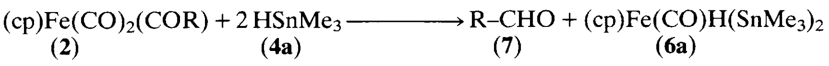
Reductive cleavage of carbon–transition metal bonds has been extensively studied, because similar reactions are assumed in the product-releasing step of various catalytic reactions such as hydrogenation of alkenes and carbon monoxide, and hydroformylation.[1] It is well known that the H–M bonds of metal hydrides of group 14 elements exhibit similar reactivities (*e.g.* oxidative addition and reduction) to the H–H bond of dihydrogen,[1] and their use instead of dihydrogen is advantageous in reduction of oxygen-containing functional groups because of the oxygenophilicity of M.[2] As an example, we



$$\left.\begin{array}{ll}\mathrm{(cp)Fe(CO)_2(R)} & \mathbf{(1)}\\ \mathrm{(cp)Fe(CO)_2(COR)} & \mathbf{(2)}\\ \mathrm{(cp)Fe(CO)(PPh_3)(COR)} & \mathbf{(3)}\end{array}\right\} + \underset{\mathbf{(4)}}{\mathrm{3HMMe_3}} \rightarrow \underset{\mathbf{(5)}}{\mathrm{R\text{–}CH_2OX}} + \underset{\mathbf{(6)}}{\mathrm{(cp)Fe(CO)H(MMe_3)_2}}$$

a; X = SnMe$_3$
b; X = SiMe$_3$
c; X = H

Scheme 1. *Conditions:* benzene, heat. R = CH$_2$CH$_2$Ph.



$$\underset{\mathbf{(2)}}{\mathrm{(cp)Fe(CO)_2(COR)}} + \underset{\mathbf{(4a)}}{\mathrm{2\,HSnMe_3}} \longrightarrow \underset{\mathbf{(7)}}{\mathrm{R\text{–}CHO}} + \underset{\mathbf{(6a)}}{\mathrm{(cp)Fe(CO)H(SnMe_3)_2}}$$

Scheme 2. *Conditions:* *hν*, benzene.

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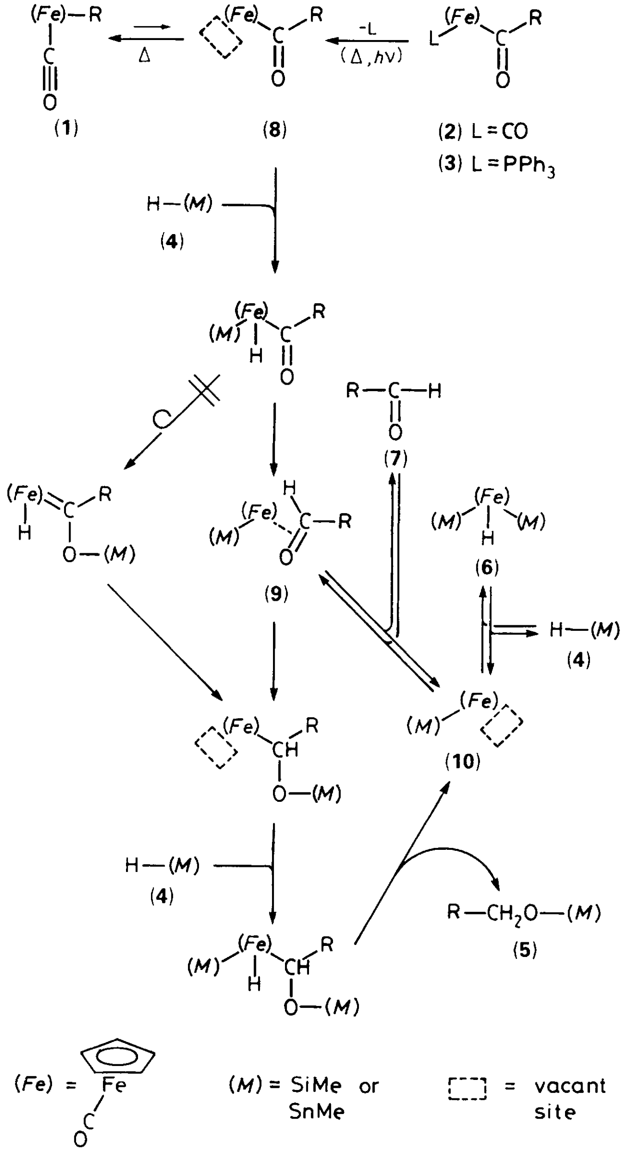
$$\underset{(1)}{(cp)Fe(CO)_2(R)} + \underset{(4)}{2HMMe_3} \longrightarrow \underset{(7)}{R\text{-}CHO} + \underset{(6)}{(cp)Fe(CO)H(MMe_3)_2} \qquad \text{Step I}$$

$$\underset{(7)}{R\text{-}CHO} + \underset{(4)}{HMMe_3} \xrightarrow{[Fe]} \underset{(5)}{R\text{-}CH_2OMMe_3} \qquad \text{Step II}$$

Scheme 3



Scheme 4

previously reported the catalytic hydrosilylation of acyl-metal complexes.[3] In this paper we disclose the results of the uncatalysed reaction of organoiron complexes with $HMMe_3$ (M = Si, Sn).

Reactions of alkyl- and acyl-iron complexes, $(cp)Fe(CO)_2(R)$ (**1**), $(cp)Fe(CO)_2(COR)$ (**2**), and $(cp)Fe(CO)(PPh_3)(COR)$ (**3**) (R = $PhCH_2CH_2$; cp = C_5H_5), with $HMMe_3$ [(**4a**) M = Sn; (**4b**) M = Si] in heated benzene afforded the oxymethylated product $R\text{-}CH_2OH$ (**5c**) or $R\text{-}CH_2OSiMe_3$ (**5b**) in good yields accompanied by the formation of $(cp)Fe(CO)(H)(MMe_3)_2$ (**6**)† (Scheme 1; Table 1, entries 1—6). On the other hand, photolysis of $(cp)Fe(CO)_2(COR)$ (**2**) in the presence of $HSnMe_3$ (**4a**) produced RCHO (**7**) instead of (**5**) (Scheme 2; Table 1, entry 9).

These results suggest that the present oxymethylation reaction of the alkyliron complex (**1**) consists of two consecutive reactions, *i.e.* formylation (Scheme 3, Step I) and hydrometallation (Scheme 3, Step II), and a plausible mechanism similar to that of the $Co_2(CO)_8$ catalysed oxymethylation[2] is shown in Scheme 4.

The complex $(cp)Fe(CO)_2(R)$ (**1**) is in equilibrium with a co-ordinatively unsaturated acyl intermediate (**8**). Oxidative addition of (**4**) and subsequent reductive elimination of the acyl and hydride ligands produces (**9**). Dissociation of RCHO (**7**) followed by oxidative addition to the residue (**10**) terminates Step I. Under thermal reaction conditions, successive reductive elimination from (**6**) forms (**10**), which incorporates RCHO to regenerate (**9**). Insertion of the >C=O bond into the Fe–M bond, oxidative addition of (**4**), and reductive elimination of the hydride and alkyl moieties, afford the oxymethylated products (**5**) and (**10**). The latter is converted to (**6**) by the reaction with (**4**). While we cannot detect any intermediates, the following observations support the mechanism. (i) Since both alkyl and acyl complexes give the same products, the common reactive intermediate is assumed to be a co-ordinatively unsaturated acyl species (**8**). (ii) During the thermal reaction of $(cp)Fe(CO)_2(R)$ (**1**) with $HSnMe_3$ (**4a**), a small amount of aldehyde (**7**) leaking from the reaction sequence, which was finally converted to (**5**), was detected by ^1H NMR and GLC analyses. In addition, RCHO (**7**) was obtained quantitatively by a 1:1 reaction of (**1**) and (**4a**) (Scheme 5). In contrast to the Sn system, no trace of RCHO was detected during the thermal reactions with $HSiMe_3$. Insertion of the >C=O into the Fe–Si bond may proceed more readily under the reaction conditions because of the larger oxygenophilicity of Si. (iii) The reverse reaction from (**7**) and (**6**) has been confirmed by a separate reaction. When (**10a**) was generated *in situ* by thermolysis (120 °C) of (**6a**) (10 mol%) in the presence of RCHO and $HSnMe_3$, catalytic hydrometallation was completed within 1 h to give (**5**). Even $(cp)_2Fe_2(CO)_4$ exhibited catalytic activity.[4] In a control experiment carried out in the absence of iron complexes, the rate of uncatalysed hydrostannylation was very low. (iv) A

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† *Analytical data* for (**6a**): orange–yellow waxy solid; ^1H NMR (C_6D_6) δ −13.39 (1H, s, FeH), 0.44 (18H, s, $SnMe_3$), 4.01 (5H, s, C_5H_5); ^{13}C NMR (C_6D_6) δ −3.28 ($SnMe_3$), 79.36 (C_5H_5), 213.31 (CO). (**6b**): pale yellow oil; ^1H NMR (C_6D_6) δ −13.97 (1H, s, FeH), 0.48 (18H, s, $SiMe_3$), 4.04 (5H, s, C_5H_5); ^{13}C NMR (C_6D_6) δ 9.48 ($SiMe_3$), 83.54 (C_5H_5), 213.91 (CO). Satisfactory elemental analyses were obtained for both (**6a**) and (**6b**).

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Table 1. Distribution of products obtained by the reaction of iron complexes with $HMMe_3$.[a]

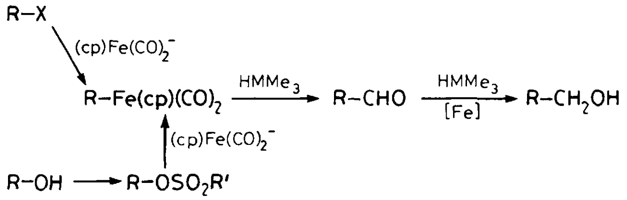
Entry	Complex	M	Reaction conditions	RCH_2OX (**5**)	RCHO (**7**)	RH	(cp)Fe(CO)H-$(MMe_3)_2$ (**6**)
1	(**1**)	Sn	60 °C, 13 h	94	0	—[b]	88
2	(**1**)	Si	90 °C, 9 h[c]	98	0	0	91
3	(**2**)	Sn	120 °C, 7 h	96	—[b]	0	73
4	(**2**)	Si	120 °C, 10 h[d,e]	53	0	—[b]	0
5	(**3**)	Sn	120 °C, 6 h	91	—[b]	—[b]	91
6	(**3**)	Si	120 °C, 10 h[d,f]	83	0	0	0
7	(**1**)	Sn	*h*ν, 7 h	—[b]	0	86	85
8	(**1**)	Si	*h*ν, 12 h[d,e]	0	0	70	47
9	(**2**)	Sn	*h*ν, 6 h	0	79	0	82
10	(**2**)	Si	*h*ν, 15 h[d,e]	22	5	28	24
11	(**3**)	Sn	*h*ν, 24 h	—[b]	0	37	0
12	(**3**)	Si	*h*ν, 18 h[d,e]	0	—[b]	42	0

[a] NMR spectroscopy (C_6D_6) on *ca.* 0.1 mmol scale. Yields of (**5**), (**7**), and RH were determined by GLC and that of $(cp)FeH(CO)(MMe_3)_2$ by ^1H NMR. Conversion: 100% except for entry 6. [b] <3%. [c] $[(cp)Fe(CO)]_4$ was also formed in 10% yield. [d] Small amounts of $PhCH_2CH{=}CHOSiMe_3$ were also formed. [e] $(cp)_2Fe_2(CO)_4$ was also formed. [f] Conversion: 54%.

$$\underset{(\mathbf{1})}{(cp)Fe(CO)_2(R)} + \underset{(\mathbf{4a})}{HSnMe_3} \longrightarrow$$

$$\underset{(\mathbf{7})\ 45\%}{(1/2)R\text{–}CHO} + \underset{50\%}{(1/2)(cp)Fe(CO)H(SnMe_3)_2} + (1/2)(\mathbf{1})$$

Scheme 5. *Conditions:* 60 °C, benzene.



Scheme 6

reaction pathway *via* an oxycarbene intermediate[5] is ruled out, because the formation of aldehyde cannot be accounted for by this intermediate. (v) Since the addition of azoisobutyronitrile (AIBN) retards the reaction, a radical mechanism is eliminated. (vi) If the co-ordinatively unsaturated acyl intermediate is not available, simple hydrogenolysis of the metal–carbon bond produces R–H, as reported by Wrighton *et al.*[6] (Table 1, entries 7, 8, 10—12).

On the basis of the reaction temperatures, the reactivities of $HSnMe_3$ (**4a**) and the alkyl complex (**1**) are estimated to be greater than those of $HSiMe_3$ (**4b**) and the acyl complexes (**2**) and (**3**), respectively, and should be related to the ease of formation of (**8**) and/or oxidative addition of (**4**). When a mixture of (**1**) and (**2**) was treated with (**4a**) at 60 °C, only (**1**) was consumed and (**2**) was left unaffected. In addition, the formation of R–H on photolysis of (**2**) with (**4b**) (Table 1, entry 10) results from the initial decarbonylation to give (**1**), which is actually detected by ^1H NMR, followed by hydrogenolysis. In this case photochemically generated (**8**) is not completely trapped by (**4b**) at room temperature, although (**4a**) efficiently traps (**8**) under the same reaction conditions (Scheme 2; Table 1, entry 9).

While we report here the results of phenethyl derivatives and $HMMe_3$, because of ease of handling or analyses, similar results were obtained using other alkyliron complexes or $HSnBu_3$. Alkyliron complexes of the type $(cp)Fe(CO)_2(R)$ are not only readily accessible by various methods such as metallation of alkyl halides (R–X) or sulphonic acid esters ($R\text{–}OSO_2R'$) with the ferrate $(cp)Fe(CO)_2^-$, but also are thermally robust.[7] Thus, the present study reveals that $(cp)Fe(CO)_2^-$ serves as a nucleophilic oxymethylating reagent as well as an alcohol-homologating reagent, as shown in Scheme 6.

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