

Oxymethylation of Iron Complexes [(cp)Fe(CO)₂(R)] with HMMe₃ (M = Sn, Si; cp = C₅H₅) leading to R-CH₂OH *via* a Formylation-Hydrometallation Sequence

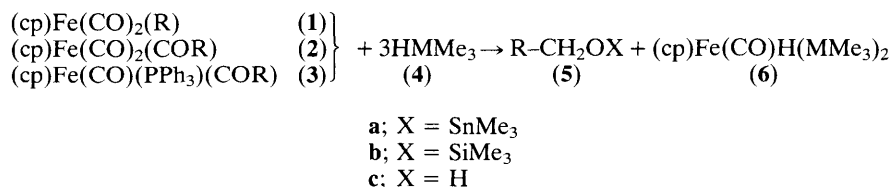
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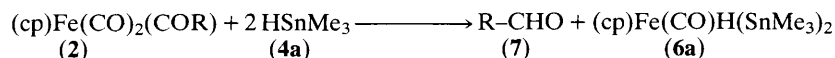
Thermal reaction of (cp)Fe(CO)₂(R), (cp)Fe(CO)₂(COR), and (cp)Fe(CO)(PPh₃)(COR) (cp = C₅H₅) with 3 equivalents of trimethyl-stannane or -silane, affords R-CH₂OH (or R-CH₂OSiMe₃) and (cp)Fe(CO)H(MMe₃)₂ in good yields; the reaction sequence follows initial reduction of transient co-ordinatively unsaturated acyl species to give the aldehyde and successive hydrometallation by the action of Me₃M-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

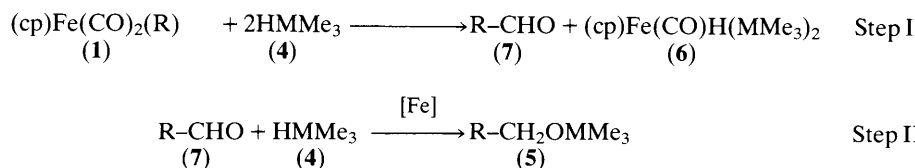
metal hydrides of group 14 elements exhibit similar reactivities (*e.g.* oxidative addition and reduction) to the H-H bond of dihydrogen,¹ and their use instead of dihydrogen is advantageous in reduction of oxygen-containing functional groups because of the oxygenophilicity of M.² As an example, we



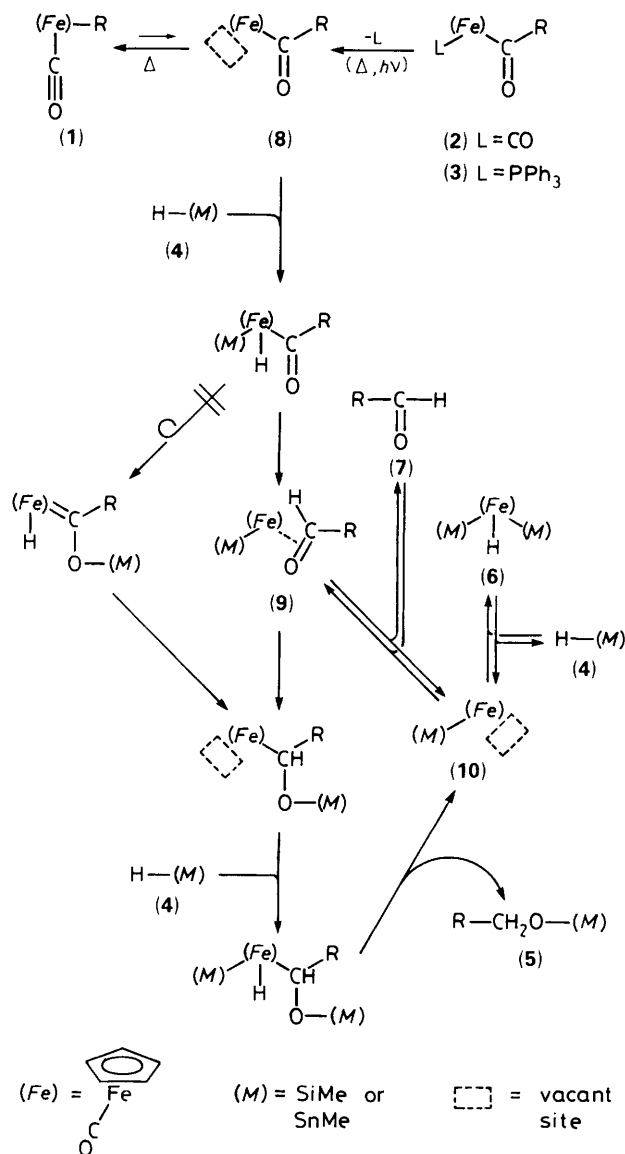
Scheme 1. Conditions: benzene, heat. R = CH₂CH₂Ph.



Scheme 2. Conditions: *hν*, benzene.



Scheme 3



Scheme 4

HMMe₃ [(4a) M = Sn; (4b) M = Si] in heated benzene afforded the oxymethylated product R-CH₂OH (5c) or R-CH₂OSiMe₃ (5b) in good yields accompanied by the formation of (cp)Fe(CO)(H)(MMe₃)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 HSnMe₃ (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 Co₂(CO)₈ catalysed oxymethylation² 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 HSnMe₃ (4a), a small amount of aldehyde (7) leaving 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 HSiMe₃. 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 HSnMe₃, catalytic hydrometallation was completed within 1 h to give (5). Even (cp)₂Fe₂(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

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 HMMe₃ (M = Si, Sn).

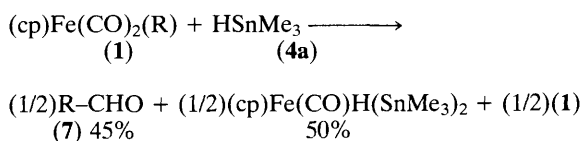
Reactions of alkyl- and acyl-iron complexes, (cp)Fe(CO)₂(R) (1), (cp)Fe(CO)₂(COR) (2), and (cp)Fe(CO)(PPh₃)(COR) (3) (R = PhCH₂CH₂; cp = C₅H₅), with

[†] Analytical data for (6a): orange-yellow waxy solid; ¹H NMR (C₆D₆) δ -13.39 (1H, s, FeH), 0.44 (18H, s, SnMe₃), 4.01 (5H, s, C₅H₅); ¹³C NMR (C₆D₆) δ -3.28 (SnMe₃), 79.36 (C₅H₅), 213.31 (CO). (6b): pale yellow oil; ¹H NMR (C₆D₆) δ -13.97 (1H, s, FeH), 0.48 (18H, s, SiMe₃), 4.04 (5H, s, C₅H₅); ¹³C NMR (C₆D₆) δ 9.48 (SiMe₃), 83.54 (C₅H₅), 213.91 (CO). Satisfactory elemental analyses were obtained for both (6a) and (6b).

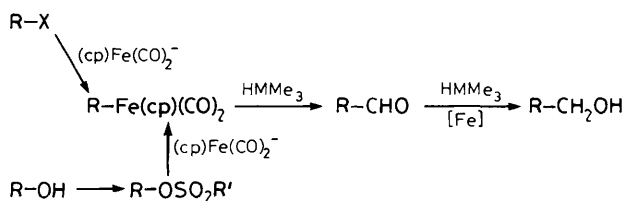
Table 1. Distribution of products obtained by the reaction of iron complexes with HMMe_3 .^a

Entry	Complex	M	Reaction conditions	RCH ₂ OX (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	<i>hν</i> , 7 h	— ^b	0	86	85
8	(1)	Si	<i>hν</i> , 12 h ^{d,e}	0	0	70	47
9	(2)	Sn	<i>hν</i> , 6 h	0	79	0	82
10	(2)	Si	<i>hν</i> , 15 h ^{d,e}	22	5	28	24
11	(3)	Sn	<i>hν</i> , 24 h	— ^b	0	37	0
12	(3)	Si	<i>hν</i> , 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)(MMe₃)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 PhCH₂CH=CHOSiMe₃ were also formed. ^e (cp)₂Fe₂(CO)₄ was also formed. ^f Conversion: 54%.



Scheme 5. Conditions: 60 °C, benzene.

**Scheme 6**

reaction pathway via an oxycarbene intermediate⁵ 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-OSO₂R') 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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