Synthesis and Hydrolysis of [Alkenyl(alkoxy)carbene]manganese Complexes: Evidence for a Transient Allylic Intermediate on the Way to α,β-Unsaturated Aldehydes

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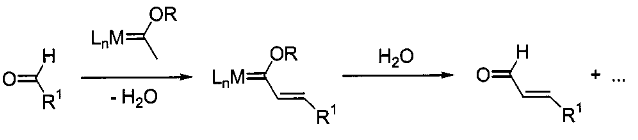
Keywords: Manganese / Carbenes / Hydrolyses / Aldehydes / Vinylogation

A variety of alkenylcarbene complexes [Cp′(CO)$_2$Mn=C(OEt)CH=CHR] (**3**) (Cp′ = η^5-MeC$_5$H$_4$) was obtained in a straightforward manner upon aldol condensation of [Cp′(CO)$_2$Mn=C(OEt)CH$_3$] (**1**) with aromatic and α,β-unsaturated aldehydes RC(H)O (**2**). The reaction is totally stereoselective, giving (*E*)- or (*all-E*)-alkenylcarbenes only. The protonation of **3** at low temperature followed by reaction with water affords the α,β-unsaturated aldehyde complexes [Cp′(CO)$_2$Mn(η^2-RCH=CHCHO] (**5**), from which the aldehydes RC(H)=C(H)C(H)O (**6**) were displaced by acetonitrile. The intermediate aldehyde complexes are shown to result from the hydrolysis of a transient cationic π-allyl species [Cp′(CO)$_2$Mn(η^3-RCHCHC(OEt)H]$^+$ ([**4**]$^+$) formed upon protonation of **3**.

Introduction

Alkenyl-alkoxy-substituted Fischer carbene complexes have been shown in some cases to release α,β-unsaturated aldehydes upon hydrolysis, with optimum efficiency at high pH values.[1,2] Though mechanistically clear under such conditions,[2b] the reaction has received little attention as a synthetic procedure. Yet, if we keep in mind that alkenyl-alkoxy-substituted Fischer carbenes can be obtained upon aldol condensation of alkyl(alkoxy)carbene complexes with aldehydes,[3,4] their hydrolysis can be regarded as part of a potential process for the homologation of aldehydes into α,β-unsaturated aldehydes (Scheme 1).

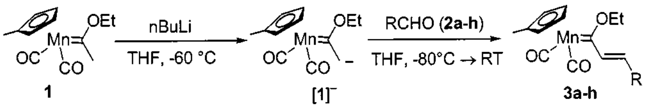


Scheme 1

The vinylogation of aldehydes is of special interest for the synthesis of molecular materials[5] and natural products.[6] Though several procedures derived from general olefination reactions have been devised,[7] the search for easy-to-handle, selective, and versatile reagents is still of current interest.[7e,8] As part of an ongoing effort to develop synthetically useful reactions employing cheap and readily available group-7 Fischer carbene complexes obtained from [Cp′Mn(CO)$_3$] (Cp′ = η^5-MeC$_5$H$_4$),[9] we were challenged to examine the scope of [Cp′(CO)$_2$Mn=C(OEt)CH$_3$] (**1**) for the above reaction. The present paper deals with the results of our investigation and provides insight into the mechanism of the hydrolysis of alkenyl-substituted Fischer carbene complexes under acidic conditions.[10]

Results and Discussion

The carbenemanganese anion [Cp′(CO)$_2$Mn=C(OEt)-CH$_2$]$^-$ ([**1**]$^-$), generated in situ by addition of *n*BuLi to a THF solution of [Cp′(CO)$_2$Mn=C(OEt)CH$_3$] (**1**) cooled at −60 °C,[11] was treated at low temperature with one molar equivalent of various aromatic and α,β-unsaturated aldehydes RCHO (**2a−h**, Table 1). An aldol/elimination reaction subsequently occurred upon return to room temperature, giving the corresponding alkenyl(alkoxy)carbenes [Cp′(CO)$_2$Mn=C(OEt)CH=CHR] (**3a−h**) in valuable yields (Scheme 2, Table 1, entries 1−8).



Scheme 2. Aldol condensation of **1** with aldehydes **2a−h**

This sequence was reproduced with a dialdehyde, namely 1,1′-bis(formyl)ferrocene. Depending on the stoichiometry, the reaction could be directed toward either [{η^5-(Cp′(CO)$_2$Mn=C(OEt)CH=CHC$_5$H$_4$)}Fe{η^5-C$_5$H$_4$CHO}] (**3i$_1$**), or [{η^5-(Cp′(CO)$_2$Mn=C(OEt)CH=CHC$_5$H$_4$}$_2$Fe] (**3i$_2$**) (Scheme 3, Table 1, entries 9−10).

Complexes **3a−i** were characterized by ^{1}H-, ^{13}C-, and (when necessary) HMQC ^{1}H-^{13}C NMR analysis.[12] Their formation is totally stereoselective, giving (*E*) (for **3a−b**, **f**, **i**) or (*all-E*) (for **3c−e**, **g−h**) isomers only, as indicated by $^3J_{HH}$ coupling constants of ca. 15 Hz for the protons adjacent to the carbon−carbon double bonds.

In a first attempt to release α,β-unsaturated aldehydes from the above alkenyl(alkoxy)carbenes upon hydrolysis in

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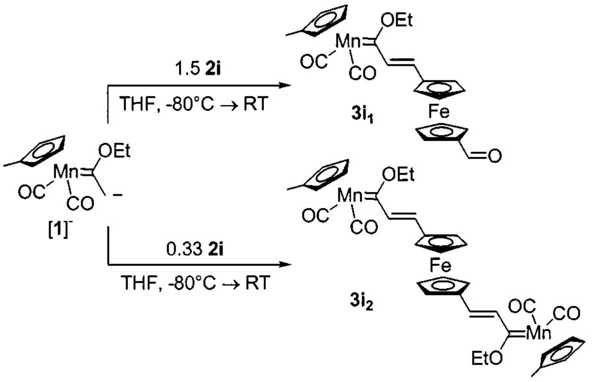
Table 1. Aldol condensation of **1** with aldehydes **2**, hydrolysis of **3**, and demetalation of the α,β-unsaturated aldehydes **6** (see Schemes 2−5)

Entry	Aldehyde RCHO (**2**)[a]	Product series	Yield (%)[f] **3**[g]	**5**[j]	**6**[k]
1	PhCHO	**a**	59	87	95
2	FcCHO	**b**	87	83	96
3	(*E*)-PhCH=CHCHO	**c**	65	88	92
4	(*E*)-MeCH=CHCHO	**d**	64	73	75
5	(*E*)-PhCH=C(Me)CHO	**e**	66	72	97
6	1,4-$Me_2NC_6H_4CHO$	**f**	85	72	97
7	(*E*)-FcCH=CHCHO[b]	**g**	77	72	97
8	(*E*,*E*)-PhCH=CHCH=CHCHO[c]	**h**	54	92	98
9	1,1′-diformylferrocene[d]	**i$_1$**	86[h]	89	93
10	1,1′-diformylferrocene[e]	**i$_2$**	71[i]	80	98

[a] 1 equiv. of **2** vs. [**1**]$^-$ was used, unless otherwise noted. − [b] Prepared from **2b** using **1** as a vinylogation reagent. − [c] Prepared from **2c** using **1** as a vinylogation reagent. − [d] 1.5 equiv. of **2i** vs. [**1**]$^-$ was used. − [e] 0.33 equiv. of **2i** vs. [**1**]$^-$ was used. − [f] Yields of isolated products. − [g] See Scheme 2. − [h] Based on [**1**]$^-$. − [i] Based on **2i**. − [j] See Scheme 4. − [k] See Scheme 5; except hitherto unkown **6i$_1$**, which has been fully characterized,[12] the aldehydes were identified by comparison of their NMR spectra with literature data, or data recorded directly from authentic samples.



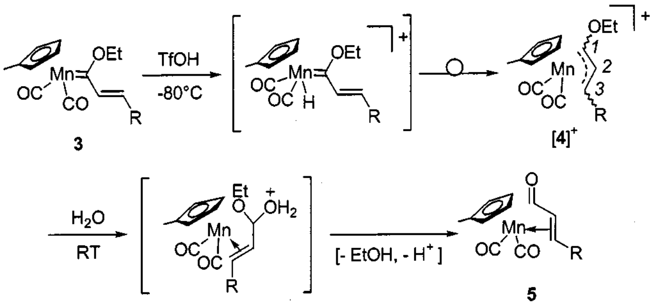
Scheme 3. Aldol condensation of **1** with 1,1′-diformylferrocene (**2i**)

basic conditions, **3c** was treated with urotropine in the presence of water according to a procedure Aumann et al. described for group-6 analogs.[1] No reaction was observed after 24 hours. This may be attributed to the insufficient electrophilic character of the carbene carbon atom that disfavors the required nucleophilic attack of hydroxide ions.[1,2b]

Keeping in mind that Fischer carbene complexes can be protolytically cleaved to form the corresponding aldehydes,[10] we next treated complexes **3** with one equivalent of TfOH at −80 °C in CH_2Cl_2 (but two equivalents in the case of **3f**[13] and in the case of the dialkenylcarbene **3i$_2$**). An instantaneous reaction occurred, leading to a fairly stable species, whose IR spectra displayed two bands at ca. 2015 and 1970 cm^{-1} characteristic of $[Cp'(CO)_2MnLX]^+$-type complexes.[14,15] These were indeed identified as the π-allyl species $[Cp'(CO)_2Mn(\eta^3\text{-RCHCHC(OEt)H})]^+$ ([**4**]$^+$) on the basis of ^{1}H-, ^{13}C-, and HMQC ^{1}H-^{13}C NMR spectroscopy for [**4a**−**c**]$^+$.[12] In particular, the signals of the protons H^1, H^2, and H^3 within the π-allyl moiety (see Scheme 4) in [**4c**]$^+$ were observed at δ = 6.12, 5.55, and 3.41, respectively, in the ^{1}H dimension, and they correlate with the signals observed at δ = 138.1, 77.3, and 62.2 in the ^{13}C dimension. The proton H^1 clearly originates from TfOH, since the NMR spectrum of [D-**4c**]$^+$, generated from **3c** upon treatment with TfOD, does not show any resonance in the area around δ = 6.12. Within the $^{13}C\{^1H\}$-NMR sensitivity and resolution limits, the formation of [**4a**−**c**]$^+$ is quantitative and stereoselective. However, due to the systematic formation of paramagnetic impurities, their stereochemistry could not be determined by ^{1}H NMR.

When an excess of water was added to CH_2Cl_2 solutions of [**4a**−**i**]$^+$, IR monitoring showed the gradual disappearance of the bands due to [**4a**−**i**]$^+$ whereas three new bands grew at ca. 1965, 1905, and 1670 cm^{-1} indicative of the formation of the α,β-unsaturated aldehyde complexes $[Cp'(CO)_2Mn(\eta^2\text{-RCH=CHCHO})]$ (**5a**−**i**) (Scheme 3, Table 1).[16] The NMR data of **5a**−**i** clearly indicate that the α,β-unsaturated aldehyde ligand is coordinated in an η^2 fashion through the carbon−carbon double bond adjacent to the aldehyde function, and that the (*E*) or (*all-E*) arrangement of the alkenyl moieties in **3a**−**i** is maintained through their conversion into **5a**−**i**.[12] Finally, when [D-**4c**]$^+$ was treated with water, the deuterium label on C^1 was totally retained in the aldehyde function of $[Cp'(CO)_2Mn(\eta^2\text{-PhCH=CHCH=CDO})]$ [D-**5c**].[17]

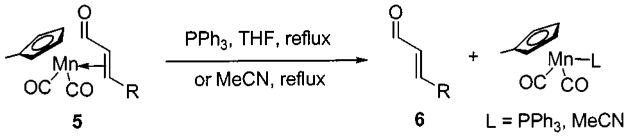
The overall transformation of the alkenyl(alkoxy)carbene complexes **3** into the α,β-unsaturated aldehyde complexes **5** is depicted in Scheme 4.



Scheme 4. Proposed mechanism for the formation of **5**

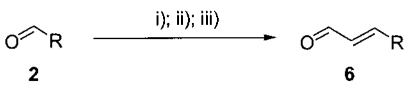
Though no intermediate hydride species could be observed, the context of chemistry and the results of previous studies on protonation reactions of electron-rich carbene complexes suggest that [**4**]$^+$ is likely to result from a protonation of **3** at the metal center followed by hydride migration to the carbene carbon atom,[18,19] and concomitant stabilization of the resulting 16e$^-$ species by coordination of the pendant alkenyl moiety.[20] Upon addition of water, hydrolysis of the highly electrophilic π-allyl ligand in [**4**]$^+$[15c] would then take place through initial nucleophilic addition of water (or hydroxide ions) at the carbon atom bearing the ethoxy group to give the final aldehyde complexes **5**.

Finally, the α,β-unsaturated aldehydes RCH=CHCHO (**6**, Table 1) could be released in nearly quantitative yields by displacement by triphenylphosphane in THF, or by acetonitrile in neat acetonitrile, under refluxing conditions (Scheme 5).



Scheme 5. Demetalation of the α,β-unsaturated aldehydes **6**

Considering the satisfactory yields of the individual steps, as well as the efficient demetalation of the newly formed α,β-unsaturated aldehydes from the final complex, we logically became interested in a possible application of the above sequence to the vinylogation of aldehydes. A one-vessel procedure was thus developed (Scheme 6) giving the α,β-unsaturated aldehydes **6** in synthetically useful yields.



Scheme 6. Reagents and reaction conditions: i) [**1**]$^-$, -78°C → 20°C, THF; ii) HCl (aq.), MeCN; iii) reflux

The best performances were recorded with formylferrocene (**2b**) and 4-(dimethylamino)benzaldehyde (**2f**) giving the corresponding vinylogated aldehydes **6b** and **6f** in 75%, and 68% yield, respectively. A practical limitation of the procedure is still the need of chromatographic workup to separate the newly formed aldehyde **6** from its precursor **2**.

In conclusion, whereas a recurrent problem with organometallic synthons is the difficulty to establish the mechanism of their participation in organic reactions, the carbenemanganese system disclosed here appears to be both synthetically useful and amenable to mechanistic studies due to the relative stability of the intermediates. In particular, we suggest that the mechanism established here for the hydrolysis of the (alkenylcarbene)manganese complexes under acidic conditions may serve as a model for parallel transformations occurring in related systems.[2b,10d]

Experimental Section

General Remarks: All synthetic manipulations were carried out using standard Schlenk techniques under dry N_2. THF used for the synthesis was distilled under N_2 from Na/benzophenone ketyl just before use. Other solvents were purified according to standard procedures, and stored under N_2. A liquid N_2/2-propanol slush bath was used to maintain samples at the desired low temperature. – Chromatographic separations were performed on alumina. – [Cp′(CO)$_2$Mn=C(OEt)CH$_3$] (**1**) was prepared by modifications of literature procedures for related complexes.[21] 1,1′-Diformylferrocene (**2i**) was synthesized according to a published procedure.[22] – Solution-IR spectra were recorded with Perkin–Elmer 225 or Perkin–Elmer 983 spectrophotometers with 0.1-mm cells equipped with CaF$_2$ windows. – ^{1}H- and ^{13}C-NMR spectra were obtained with Bruker AC200, WM250, DPX300, or AMX400 spectrometers and were referenced to the residual signals of the solvents. – Mass spectra were recorded with a Nermag R10–10 mass spectrometer. – Microanalyses were performed with a Perkin–Elmer 2400 CHN analyzer.

1. Typical Procedure for the Synthesis of the Alkenyl(alkoxy)carbene Complexes [Cp′(CO)$_2$Mn=C(OEt)CH=CHR] (3) as Illustrated for 3c [R = (*E*)-PhCH=CH]: The carbene anion [**1**]$^-$ was generated in situ by addition of *n*BuLi (0.630 mL of a 1.6 M solution in hexanes, 1.1 mmol) to a solution of [Cp′(CO)$_2$Mn=C(OEt)CH$_3$] (**1**, 0.260 g, 1.0 mmol) in THF (15 mL) at -60°C. After stirring for 20 min, the solution was cooled to -80°C and (*E*)-cinnamaldehyde (**2c**, 0.125 mL, 1.0 mmol) was added. The cooling bath was removed to allow the reaction medium to reach room temperature gradually. After stirring for an additional 1 h, the solvents were removed under vacuum. The brown oily residue was extracted with pentane (ca. 20 mL), and applied on top of an alumina column. Elution with pentane afforded a yellow band which was discarded. Elution with a diethyl ether/pentane (1:10) mixture gave a brown band containing [Cp′(CO)$_2$Mn=C(OEt)CH=CHCH=CHPh] (**3c**), which was isolated as a brown solid after removal of the solvents under vacuum (0.245 mg, 0.65 mmol, 65% yield). – $C_{21}H_{21}MnO_3$ (376.33): calcd. C 67.02, H 5.58; found C 67.13, H 5.65. – Mp 94–96°C. – IR (ν_{CO}, THF): $\tilde{\nu}$ = 1940, 1876 cm^{-1}. – NMR ^{1}H (C_6D_6, 250 MHz, 298 K): δ = 7.27–7.09 (Ph), 7.00 (m, 1 H, H^2, J_{H2H3} = 15 Hz), 6.73 (m, 1 H, H^3, J_{H3H4} = 11 Hz), 6.63 (m, 2 H, H^4 and H^5, J_{H3H4} = 11 Hz, J_{H5H4} = 15 Hz), 4.82 (q, 2 H, OC*H*$_2$CH$_3$, J_{HH} = 7 Hz), 4.55–4.35 (m, 4 H, Me*Cp*), 1.71 (s, 3 H, *Me*Cp), 1.29 (t, 3 H, OCH$_2$C*H*$_3$). – NMR ^{13}C{^{1}H} (C_6D_6, 63 MHz, 298 K): δ = 316.1 (C^1), 233.9 (MnCO), 143.4 (C^2), 139.4 (C^5), 137.2–126.8 (Ph), 128.6 (C^3), 123.4 (C^4), 104.1, 87.7, 86.5 (Me*Cp*), 71.6 (O*C*H$_2$CH$_3$), 14.8 (OCH$_2$*C*H$_3$), 13.4 (*Me*Cp). – MS (EI); *m/z*: 376 [M$^+$].

2. In Situ Formation of the π-Allyl Complexes Cp′(CO)$_2$Mn(η^3-RCHC)C(OEt)H]$^+$ ([4][TfO]) as Illustrated for [4c][TfO] [R = (*E*)-PhCH=CH]: TfOH (0.018 mL, 0.2 mmol) was added to a solution of [Cp′(CO)$_2$Mn=C(OEt)CH=CHCH=CHPh] (**3c**, 0.080 mg, 0.2 mmol) in CD$_2$Cl$_2$ (1 mL) at -80°C. The brown solution instantaneously turned red. The reaction mixture was allowed to reach room temperature, and the solution was filtered through a plug of celite directly into an NMR tube for analysis. Complex [D-**4c**][TfO] was generated in a similar manner from **3c** and TfOD. – IR (ν_{CO}, CH$_2$Cl$_2$): $\tilde{\nu}$ = 2010, 1970 cm^{-1}. – ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 223 K): δ = 7.7–7.3 (m, 5 H, Ph), 7.2–6.7 (m, 2 H, H^4 and H^5), 6.12 [s (br.), 1 H, H^1], 5.55 [s (br.), 1 H, H^2], 5.3–4.9 (m, 4 H, Me*Cp*), 4.30 [s (br.), 2 H, OC*H*$_2$CH$_3$], 3.41 [s (br.), 1 H, H^3], 1.73 (s, 3 H, *Me*Cp), 1.29 [s (br.), 3 H, OCH$_2$C*H*$_3$]. – ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz, 223 K): δ = 227.5, 226.4 (MnCO), 138.1 (C^5), 132.2 (C^1), 134.8, 128.8, 128.4, 126.9 (Ph), 125.4 (C^4), 105.9, 90.9, 90.8, 89.5, 89.2 (Me*Cp*), 77.3 (C^2), 72.6 (O*C*H$_2$CH$_3$), 62.2 (C^3), 14.1 (OCH$_2$*C*H$_3$), 12.2 (*Me*Cp).

3. Typical Procedure for the Synthesis of the Aldehyde Complexes [Cp′(CO)$_2$Mn(η^2-RCH=CHCHO)] (5) as Illustrated for 5c [R = (*E*)-PhCH=CH]: TfOH (0.180 mL, 2.0 mmol) was added to a solution of [Cp′(CO)$_2$Mn=C(OEt)CH=CHCH=CHPh] (**3c**, 0.750 g, 2.0 mmol) in dichloromethane (15 mL) at -80°C. The cooling bath was removed to allow the reaction medium to reach room temperature. An excess of water (5 mL) was added. After stirring for 30 min, the organic phase was separated and the volatiles were removed under vacuum. The brownish oily residue was purified by column chromatography on alumina. Elution with a diethyl ether/pentane (1:1) mixture gave a brown band, which was discarded. Elution with pure dichloromethane released [Cp′(CO)$_2$Mn(η^2-PhCH=CHCH=CHCHO) (**5c**), isolated as an orange solid after evaporation of the solvent (0.610 mg, 1.76 mmol, 88% yield). – $C_{19}H_{17}MnO_3$ (348.28): calcd. C 65.51, H 4.88; found C 65.68, H 4.81. – Mp 136°C (dec.). – IR (ν_{CO}, CH$_2$Cl$_2$): $\tilde{\nu}$ = 1965, 1904, 1675 cm^{-1}. – ^{1}H NMR (C_6D_6, 250 MHz, 298 K): δ = 8.32 (d, 1

H, H^1, J_{H1H2} = 7 Hz), 7.26−7.05 (Ph), 6.67 (d, 1 H, H^5, J_{H5H4} = 16 Hz), 5.55 (dd, 1 H, H^4, J_{H4H3} = 10 Hz), 3.83, 3.79, 3.75, 3.60 (m, 4 H, Me*Cp*), 4.05 [AB(X) pattern, 2 H, H^2 and H^3, J_{H2H3} = 11 Hz], 1.47 (s, 3 H, *Me*Cp). − $^{13}C\{^1H\}$ NMR (C_6D_6, 63 MHz, 298 K): δ = 233.0, 229.8 (MnCO), 192.2 (C^1), 131.9 (C^5), 131.8−125.0 (Ph), 129.9 (C^4), 103.2, 86.2, 85.8, 85.5, 84.3 (Me*Cp*), 67.8 (C^3), 60.5 (C^2), 12.8 (*Me*Cp). − MS (EI); *m/z*: 348 [M^+].

4. Typical Procedure for the Demetallation of α,β-Unsaturated Aldehydes RCH=CHCHO (6) as Illustrated for (*E*,*E*)-PhCH=CHCH=CHCHO [6c (≡ 2h)]: Complex [Cp′(CO)$_2$Mn(η^2-PhCH=CHCH=CHCHO)] (**5c**, 0.610 g, 1.76 mmol) was dissolved in degassed acetonitrile (15 mL) and then heated under reflux for 1 h. After cooling, acetonitrile was removed under vacuum. The oily yellow residue was chromatographed on an alumina column. Elution with a pentane/diethyl ether (1:1) mixture afforded a yellow band containing [Cp′(CO)$_2$Mn(NCMe)]. A second elution with pure diethyl ether afforded (*E*,*E*)-5-phenyl-2,4-pentadienal [**6c** (≡ **2h**)], which was isolated as a yellow solid (0.255 g, 1.62 mmol, 95% yield).

5. One-Vessel Vinylogation of Aldehydes as Illustrated for Formylferrocene (2b) To Give (3-Oxo-1-propenyl)ferrocene [6b (≡ 2g)]: The carbene anion [Cp′(CO)$_2$Mn=C(OEt)CH$_2$]$^-$ [**1**]$^-$ was generated in situ by addition of *n*BuLi (1.25 mL of a 1.6 M solution in hexanes, 2.0 mmol) to a solution of [Cp′(CO)$_2$Mn=C(OEt)CH$_3$] (**1**, 525 mg, 2.0 mmol) in THF (15 mL) at −60 °C in a two-necked flask fitted with a reflux condenser. After stirring for 20 min, the solution was cooled to −80°C and formylferrocene was added as a powder (430 mg, 2.0 mmol). The cooling bath was removed to allow the reaction medium to reach room temperature gradually, and the solution was stirred for an additional 1 h. THF was evaporated under vacuum and replaced by degassed acetonitrile (30 mL). Hydrochloric acid (0.330 mL of a 10 M solution in water) was added dropwise, and the mixture was heated under reflux for 1 h. After cooling, the volatiles were removed under vacuum. The oily residue was purified by column chromatography on alumina. Elution with a pentane/diethyl ether (1:1) mixture afforded a yellow band containing traces of [Cp′(CO)$_3$Mn], traces of **1**, and [Cp′(CO)$_2$Mn(NCMe)], which was discarded. A second elution with pure diethyl ether gave a purple band followed by an orange one. The first one contained (3-oxo-1-propenyl)ferrocene [**6b** (≡ **2g**)], isolated as a microcrystalline purple material (360 mg, 1.5 mmol, 75% yield), whereas the second one contained traces of unchanged formylferrocene.

Acknowledgments

We wish to thank the CNRS for financial support, the French Ministère de l'Education Nationale, de la Recherche et de la Technologie for a fellowship to C. M. and Y. O., and Dr. Guy Lavigne for helpful discussions.

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[12] Complete spectroscopic data for all the new complexes are available as Supporting Information.

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Received December 3, 1998
[I98410]