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# SYNTHESIS GAS INCORPORATION INTO ACYLMANGANESE PENTACARBONYLS

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## Summary

The reaction of $p$-$CH_3C_6H_4{}^{13}C(O)Mn(CO)_5$ with $H_2/CO$ at 2400 psi in hexane solvent leads to incorporation of 1/1 $H_2/CO$ and essentially exclusive production of the oxycarbonyl, $p$-$CH_3C_6H_4{}^{13}CH_2OC(O)Mn(CO)_5$. The success of this unusual reaction appears to depend on the dihaptocarbonyl nature of an intermediate acylmanganese tetracarbonyl as well as on the use of a hydrocarbon solvent. The reaction is quite general and has even been extended to acylmanganese compounds derived from dibasic acids. In the initial stage of the reaction it seems likely that a carbenic intermediate arising from the dihapto structure is involved but attempts to trap such a species were unsuccessful. The possibility that the reaction proceeds by initial hydrogenolysis of the acylmanganese compound to aldehyde and $HMn(CO)_5$, followed by reaction of these two species with each other to give product, has been ruled out.

## Introduction

We recently reported [1] on the unusual reaction of the acylmanganese pentacarbonyl, $PhCH_2C(O)Mn(CO)_5$, with $CO + H_2$ (2200 psi, 70°C, hexane solvent) to give the alkoxycarbonyl, $PhCH_2CH_2OC(O)Mn(CO)_5$. This product was particularly surprising because we have found that the same reaction in sulfolane gives only the aldehyde, $PhCH_2CHO$. Hydrogenolysis of an analogous acylmanganese complex in sulfolane has been observed previously [2].

In an extension of this reaction we have now varied the nature of the R group in $RC(O)Mn(CO)_5$ and found the titled reaction to be quite general. Furthermore, a labelling study demonstrates that the original acyl carbon in the reactant is exclusively reduced to the methylene group of the product.

The mechanism of the reaction is not well understood and a variety of valence electron-deficient species are probably involved. Experiments to trap intermediates were investigated and these and other facets of the reaction are discussed below.

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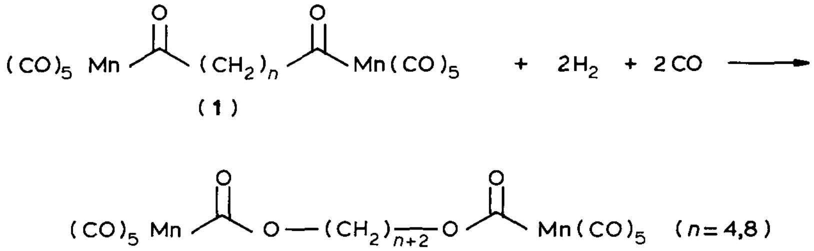
## Results and discussion

In the original report [1], acylmanganese pentacarbonyls, $RC(O)Mn(CO)_5$, ($R = C_6H_5CH_2$, $C_6H_5CH_2CH_2$), were shown to undergo conversion into the corresponding alkoxycarbonylmanganese pentacarbonyls (eq. 1).

$$RC(O)Mn(CO)_5 + H_2 + CO \rightarrow RCH_2OC(O)Mn(CO)_5 \qquad (1)$$

The reaction appears to be quite general. Thus, the following acyls where R is equal to $CH_3$, $CH_3(CH)_2)_5$, and $p$-$CH_3C_6H_4$ were prepared and successfully converted to the corresponding alkoxycarbonylmanganese pentacarbonyls under the oxo conditions indicated above. The reaction has also been successfully extended to two bis-acylmanganese carbonyls (eq. 2):



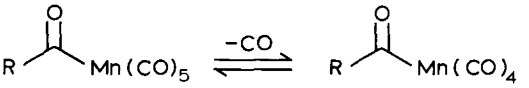
$$(CO)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5 + 2H_2 + 2CO \longrightarrow (CO)_5MnC(O)O{-}(CH_2)_{n+2}{-}OC(O)Mn(CO)_5 \quad (n=4,8) \qquad (2)$$

(1)

(2)

The reaction of $p$-toluoylmanganese pentacarbonyl was studied in detail. The reaction of $^{13}C$ labelled $p$-toluoylmanganese pentacarbonyl (prepared from $^{13}C$ labelled $p$-toluoyl chloride and $[Mn(CO)_5]^-$) was carried out under the same conditions employed for the unlabelled compound. $^1H$ NMR examination of the resulting oxycarbonyl, $p$-$CH_3C_6H_4{}^\star CH_2OC(O)Mn(CO)_5$ showed no unlabelled $CH_2$ present.

It seems reasonable to assume that the reaction is initiated by dissociation of CO (eq. 3).



$$RC(O)Mn(CO)_5 \underset{}{\overset{-CO}{\rightleftharpoons}} RC(O)Mn(CO)_4 \qquad (3)$$

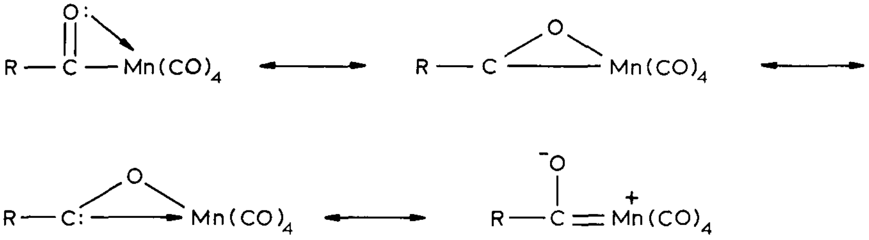
(3)

The absence of unlabelled $CH_2$ suggests that the coordinatively unsaturated tetracarbonyl is not involved in a competitive R migration (CO deinsertion) [3] (eq. 4),

$$R^\star C(O)Mn(CO)_4 \rightleftharpoons cis\text{-}RMn(CO)_4{}^\star CO \rightleftharpoons RC(O)Mn(CO)_3{}^\star CO \qquad (4)$$

during the conversion to the oxycarbonyl product. The $^1H$ NMR spectrum of the product from the labelled acyl shows only a doublet ($^1J$(C–H) 148 Hz) centered at 5.1 ppm which corresponds to the resonance of the newly formed methylene group. In the unlabelled sample a singlet at 5.1 ppm is observed; no such absorption is observed in the labelled product. Furthermore, if the alkyl did form, its cleavage might be expected to yield some RH [2], but no toluene is observed among the reaction products (GC/MS).

The intermediate acylmanganese tetracarbonyl may owe its stabilization to the interaction of the acyl oxygen with the metal center; the formation of such an $\eta^2$-carbonyl is a distinct possibility:



$\eta^2$-Acyls are known for both the oxophilic early transition metals and some actinide metals [4,5]. In the case of low valent manganese such interaction seems unusual. However, there is both theoretical and experimental support for the formation of $\eta^2$-acylmanganese carbonyls [6,7]. The IR matrix isolation study of acetylmanganese tetracarbonyl provides rather convincing evidence; the carbonyl absorption is shifted to 50 $cm^{-1}$ lower energy compared to the parent acetylmanganese pentacarbonyl [7].

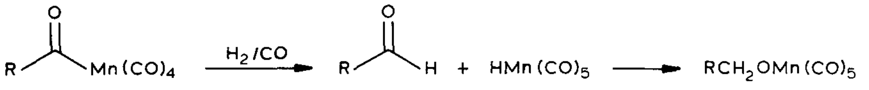
The canonical forms of the $\eta^2$-carbonyl indicate a considerable amount of carbenic character on the acyl carbon. However, trapping experiments with cyclohexene, 1-pentene, and dimethyl maleate under oxo conditions at 70°C yield only the alkoxycarbonyl, and in the latter case a small amount of dimethyl fumarate was formed.

The complete hydrogenation of the acyl carbon to $CH_2$, implies the formation of an intermediate manganese alkoxide (**4**) (eq. 5), which presumably undergoes rapid insertion of CO to yield the final isolated product.

$$\underset{(\mathbf{4})}{RCH_2OMn(CO)_5} \xrightarrow{CO} RCH_2OC(O)Mn(CO)_5 \qquad (5)$$

Surprisingly, the reaction terminates at this point; the alkoxycarbonyl appears to be inert to further incorporation of $CO + H_2$. Phenethoxycarbonylmanganese pentacarbonyl was subjected to oxo conditions at 200°C in hexane but the only observed reaction was a small amount of cleavage to form phenethyl formate [1].

An alternative route to the formation of an intermediate manganese alkoxide (and subsequently the alkoxycarbonyl product) could conceivably involve the reaction between $HMn(CO)_5$ and the aldehyde produced from the hydrogenolysis reaction (eq. 6).



(6)

It is known that formates are formed from the reaction of $HMn(CO)_5$ and aldehydes under oxo conditions at temperatures of 200°C [8] and so it was important to rule out the reaction represented by eq. 6.

The possible participation of $HMn(CO)_5$ in the reaction with aldehyde was examined in two ways. $HMn(CO)_5$ (sealed ampoule) was reacted with benzaldehyde under the desired oxo conditions by breaking the ampoule under a $CO/H_2$

atmosphere (2400 psi) and heating to 70°C. After 3 h, analysis of the reaction mixture showed only $Mn_2(CO)_{10}$ and a small trace, $<1\%$, of benzyl alcohol (GC/MS). No other products were observed that would be indicative of the formation of the manganese alkoxide (benzyl formate, benzylalkoxycarbonylmanganese pentacarbonyl). The reason for conducting the reaction using a sealed ampoule of $HMn(CO)_5$ was to make certain that this sensitive compound was intact under reaction conditions and was not inadvertently destroyed by exposure to air during prior manipulation.

In a second experiment, diphenylethylene was placed in the reaction mixture in order to trap any $HMn(CO)_5$ that may have been formed. The hydrogenation of diphenylethylene by $HMn(CO)_5$ is facile [9] and the reaction is stoichiometric (eq. 7):

$$Ph_2C{=}CH_2 + 2HMn(CO)_5 \rightarrow Ph_2CHCH_3 + Mn_2(CO)_{10} \qquad (7)$$

Placing diphenylethylene along with *p*-toluoylmanganese pentacarbonyl in an autoclave and conducting the reaction as described above yielded only a very small amount of diphenylethane (GLC).

Although it appears that reaction 6 does not occur as shown, one may suggest that an undissociated aldehyde-Mn complex may be an intermediate which proceeds to give the manganese alkoxide. Conceivably this complex could undergo aldehyde exchange. When reaction 6 was attempted with R′CHO in the presence of $RC(O)Mn(CO)_5$, no $R'CH_2C(O)Mn(CO)_5$ was detected in the product ($^1H$ NMR).

Because it seems most reasonable that a $RCH_2OMn(CO)_5$ intermediate species is involved, considerable effort was devoted to attempts to prepare such a manganese alkoxide or to generate it in the presence of $H_2/CO$, but with no success.

The exact intermediate steps in the incorporation of 1/1 $H_2/CO$ during the conversion of $RC(O)Mn(CO)_5$ to $RCH_2OC(O)Mn(CO)_5$ remain obscure and speculation beyond that previously proposed [1] is not justified at this time.

## Experimental

### *General*

All reactions were carried out in Schlenk ware under an inert atmosphere. THF and petroleum ether (40–60°C) were freshly distilled under argon from potassium benzophenone ketyl. Ether and dodecane were degassed prior to use. $Mn_2(CO)_{10}$ was obtained from either Pressure Chemical or Strem and used as received. Adipoyl choride was purified by distillation under reduced pressure. All other acid chlorides were used as received. Infrared spectra were recorded on a PE 599 IR spectrometer. Both $^1H$ and $^{13}C$ NMR spectra were obtained using an IBM NR 80 instrument. Chemical shifts are referenced to TMS in the proton spectra, whereas the solvent signal ($CDCl_3$) was used as a reference in the carbon spectra and the chemical shifts adjusted accordingly. Mass spectral data were obtained using a HP5995A quadrupolar GC/MS system. Reaction mixtures were generally analysed by GC/MS (OV-101, 12 m capillary column) and pure solids were analysed by direct inlet. High resolution mass spectra were obtained on a Kratos MS-80 instrument. Reaction mixtures were also examined by GLC (HP-5890, 3% OV-17, 1/8″ × 6′, temperature programming). Melting points were obtained in open capillaries using a Mel-Temp apparatus and are uncorrected.

*Synthesis of the acylmanganese pentacarbonyls*

All of the acyl complexes were prepared from $[Mn(CO)_5]^-$ and the appropriate acyl halide using a modified literature procedure [10]. The anion, $[Mn(CO)_5]^-$, was generated from $Mn_2(CO)_{10}$ by either Na/Hg or K/Hg reduction in either THF or ether. In our hands, K/Hg reduction in ether gave the most satisfactory results, principally because the slow settling of suspended Hg in the Na/Hg preparation is avoided. A typical preparation of *p*-toluoylmanganese pentacarbonyl was conducted as follows: Potassium metal (1 g, 26 mmol) was cut up, rinsed with pentane and added to 15 ml Hg with vigorous stirring. After the potassium had reacted completely, the amalgam was stirred an additional 10 min. $Mn_2(CO)_{10}$ (1.88 g, 4.8 mmol) was added along with 50 ml of ether. The mixture was stirred for 1 h. The formation of $[Mn(CO)_5]^-$ was indicated by the color of the reaction mixture (pale green) and by the IR spectrum: 1910, 1890, 1820 $cm^{-1}$ in ether, or 1890, 1865 $cm^{-1}$ in THF [11]. The anion solution was transferred to a second flask, equipped with stirrer, via a transfer needle. The amalgam was washed with 15 ml fresh ether and this was transferred to the second flask as well. The anion solution was cooled to 0°C and the acyl halide (1.3 ml, 9.6 mmol) was added dropwise via syringe. Immediate precipitation of both KCl and acyl complex occurred. The mixture was stirred for 0.5 h at 0°C and warmed to room temperature and stirred an additional 0.5 h. The product was collected by filtration and KCl was separated by extraction of the solids with $CH_2Cl_2$. Recrystallization (−78°C, $CH_2Cl_2$/ether) afforded the product (lemon yellow). Additional product could be obtained by evaporation of the original filtrate and recrystallization of the residual solids as above. Obtained: 1.62 g (5.15 mmol), 54%. M.p. 89–90°C (lit. [12] 98°C). IR ($CH_2Cl_2$): $\nu$(C≡O) 2111(m); 2048(sh); 2010(s); $\nu$(C=O) 1606 (w) $cm^{-1}$. $^{13}C$ NMR ($CDCl_3$): 248.6 (acyl C); 211.6 (C≡O); 130.3, 129.6, 125.3 (ArC); 21.89 ($CH_3$) ppm. Mass spectrum: $M^+ =$ 314.

Acetylmanganese pentacarbonyl was prepared in 42% yield from $[Mn(CO)_5]^-$ and acetyl chloride. M.p. 52–54°C. IR (pentane): $\nu$(C≡O) 2108(m), 2045(s), 2000(vs), 1975(m,sh); $\nu$(C=O) 1658(s) $cm^{-1}$.

Hexanoylmanganese pentacarbonyl was prepared in 38% yield essentially as described above. The pure white compound was isolated by preparative TLC (silica gel G, 99/1 40–60°C petroleum ether/ether); it appears to melt at about room temperature but is difficult to keep solid and readily turns into a yellow-green oil. IR $(CH_2Cl)_2$: $\nu$(C≡O) 2110(m), 2040(sh), 2005(vs); $\nu$(C=O) 1635 $cm^{-1}$ (m,br). $^1H$ NMR ($CDCl_3$): 2.67 (2H, $\alpha$-$CH_2$); 1.43 (2H, $\beta$-$CH_2$); 1.10 (4H, $\gamma$-and $\delta$-$CH_2$); 0.79 (3H, $CH_3$) ppm. Mass Spectrum $M^+ = 294$.

Adipoylmanganese pentacarbonyl (**1**, $n = 4$) was prepared as above except that only one equivalent of adipoyl chloride was added to the etheral solution containing $[Mn(CO)_5{}^-]$ (22%). M.p. 118–121°C (dec.) (lit. [13] 119–120°C). IR ($CHCl_3$): $\nu$(C≡O) 2102(m), 2038(m), 2000(s); $\nu$(C=O) 1632 (m,br) $cm^{-1}$.

Sebacoylmanganese pentacarbonyl (**1**, $n = 8$) was prepared as above using only one equivalent of sebacoyl chloride. M.p. 95–97°C. IR ($CHCl_3$): $\nu$(C≡O) 2105(m), 2043(sh), 2008(vs); $\nu$(C=O) 1635 (m,br) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): 2.88 (4H, t, $\alpha$, $\alpha'$ $CH_2$); 1.40 (12H, m) ppm.

*p*-Toluoylmanganese pentacarbonyl $^{13}C$: The Grignard of *p*-bromotoluene (Aldrich) was prepared in THF. The system was sealed (septa) and a stoichiometric amount of $^{13}CO_2$ (Cambridge Isotopes, 99%) was added over the course of several hours from a gas buret. To facilitate $CO_2$ absorption, the reaction was carried out at about 0°C although an optimal temperature was not investigated. The labelled *p*-toluic acid was converted to *p*-toluoyl chloride by refluxing with a slight excess of thionyl chloride in benzene (4 h). Both the residual thionyl chloride and solvent were removed by water aspirator, and the labelled acyl halide was used directly (> 95% pure by GLC). Labelled *p*-toluoylmanganese pentacarbonyl was obtained in 41% yield. M.p. 86–89°C, $^{13}C$ NMR ($CDCl_3$): 248.6 (acyl-$^{13}C$); 212.6 (CO,br); 130.3,129.6,125.8 (ArC); 21.9 ($CH_3$) ppm.

$HMn(CO)_5$ was prepared in 45% yield as previously described [14] but utilizing dodecane to extract $HMn(CO)_5$ from the aqueous $H_3PO_4$ layer instead of heptane [15]. The organic layer was carefully removed by transfer needle to a second flask. The aqueous layer was washed with 2 × 15 ml portions of dodecane, and the organic layers were again transferred as described above. $HMn(CO)_5$ was separated from the dodecane by fractionation in a high vacuum line. In the final fractionation $HMn(CO)_5$ was collected in an ampoule (−196°C) which was then sealed and used in the high pressure reactions described below.

### *High pressure reactions*

All high pressure reactions were carried out in an Autoclave Engineers 300 ml magnedrive autoclave. In a typical reaction, the autoclave was charged with the acyl (1–3 mmol) and 100 ml of hydrocarbon solvent (40–60°C petroleum ether, pentane, or hexane) and sealed. After appropriate flushing, the autoclave was pressurized with $H_2$ to 1200 psi followed by CO until a total pressure of 2400 psi was reached. The mixture was heated to 70°C for 3 h, cooled, and the autoclave vented and the contents removed and examined.

4-Methylbenzyloxycarbonylmanganese pentacarbonyl; in a typical preparation 316 mg (1 mmol) of *p*-toluoylmanganese pentacarbonyl was subjected to the high pressure $H_2/CO$ reaction. The resulting yellow solution was filtered. The GC/MS showed the presence of 4-methylbenzyl alcohol, 4-methylbenzyl formate and $Mn_2(CO)_{10}$ but the alkoxycarbonyl product was not observed. It was subsequently shown that the alkoxycarbonyl product decomposes to *p*-methylbenzyl alcohol, *p*-methylbenzylformate and $Mn_2(CO)_{10}$ under these conditions. Solvent removal gave a yellow solid (475 mg) which was dissolved in a minimum amount of $CH_2Cl_2$, pentane was added to the cloud point, and on cooling to −78°C, 193 mg (0.561 mmol) off-white crystals of 4-methylbenzyloxycarbonylmanganese pentacarbonyl was obtained. A second recrystallization gave pure white material which slowly decomposed over several weeks. M.p. 118–120°C (dec.). IR ($CH_2Cl_2$): $\nu$(C≡O) 2120(w), 2030(s), 2010(sh,s); $\nu$(C=O) 1638(m,br) $cm^{-1}$; $^1H$ NMR ($CDCl_3$): 7.29 (4H,s,ArH); 5.17 (2H,s,oxy-$CH_2$); 2.46(3H,s,$CH_3$) ppm. The remaining solids (246 mg) were shown by IR to be a mixture of $Mn_2(CO)_{10}$ and 4-methylbenzyl alcohol.

4-Methylbenzyloxycarbonylmanganese pentacarbonyl-$^{13}C$ was prepared by $H_2/CO$ insertion into the acylmanganesepentacarbonyl-$^{13}C$. A 38% yield of pure material was obtained. IR ($CHCl_3$): $\nu$(C≡O) 2118(w), 2022(s); $\nu$(C=O) 1632(m,br) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): 7.29 (4H,s,ArH); 5.1(2H,d,$^1J$(C–H) 148 Hz, oxy-$CH_2$); 2.46 (3H,s,$CH_3$) ppm. $^{13}C$ NMR ($CDCl_3$): 222.7 (C≡O); 137.7, 133.8, 129.6, 129.4, 128.3 (ArC); 66.5 (oxy $^{13}CH_2$); 21.6 ($CH_3$) ppm.

Ethoxycarbonylmanganese pentacarbonyl was prepared from acetylmanganese pentacarbonyl (329 mg, 1.30 mmol) under the described oxo conditions (90 mg, 0.35

mmol). $^1$H NMR ($CDCl_3$): 4.15 (2H,br,q, oxy-$CH_2$); 1.23 (3H, br, t, $CH_3$) ppm. This spectrum is identical to the $^1$H NMR spectrum of an authentic sample of ethoxymanganese pentacarbonyl prepared from $[Mn(CO)_5]^-$ and ethylchloroformate.

n-Heptoxycarbonylmanganese pentacarbonyl was obtained from n-hexanoylmanganese pentacarbonyl (599 mg, 2 mmol) by autoclave treatment under the usual oxo conditions. The product was isolated from the crude reaction mixture by recrystallization from petroleum ether at −78°C (124 mg, 0.55 mmol). M.p. 42–44°C. IR (40–60°C petroleum ether): $\nu$(C≡O) 2120(w); 2020(vs), 2000(s), 1988(m); $\nu$(C=O) 1654(m) $cm^{-1}$. $^1$H NMR ($CDCl_3$): 4.00 (2H, t, oxy-$CH_2$); 1.1–1.8 (8H, br m); 0.82 (3H, t, $CH_3$) ppm. Mass Spectrum: $M^+ = 224$

The bis-oxycarbonyl, **2** ($n = 6$), was obtained from the high pressure reaction of adipoylmanganese pentacarbonyl, **1** ($n = 4$). IR ($CHCl_3$): $\nu$(C≡O) 2120(w); 2010(s); $\nu$(C=O) 1635(m,br) $cm^{-1}$. $^1$H NMR ($CDCl_3$): 4.08 (4H, t, $\alpha,\alpha'$ oxy-$CH_2$); 1.2–1.9 (8H, m) ppm.

The bis-oxycarbonyl, **2** ($n = 8$), was prepared from the high pressure reaction of sebacoylmanganese pentacarbonyl, **1** ($n = 6$). M.p. 115–120°C (dec.). IR ($CHCl_3$): $\nu$(C≡O) 2120(w), 2022(s); $\nu$(C=O) 1630 (m,br) $cm^{-1}$. $^1$H NMR ($CDCl_3$): 4.1 (4H,t,$\alpha,\alpha'$ oxy-$CH_2$); 1.32 (16H,m,br) ppm.

The bis-oxycarbonyls were difficult to handle and to purify and were isolated in less than 15% yields.

$HMn(CO)_5$ and benzaldehyde; $HMn(CO)_5$ (50.0 mg, 2.9 mmol) in a sealed small diameter glass tube ampoule was placed in the autoclave with benzaldehyde (200 μl, 1.89 mmol) and mesitylene (200 μl, 1.44 mmol, internal standard) in 100 ml 40–60°C petroleum ether. The autoclave was sealed, and after appropriate flushings the autoclave was pressurized to 1200 psi with $H_2$. CO was then added to a total pressure of 2400 psi. The stirrer was then started, breaking the ampoule of $HMn(CO)_5$. Analysis of the reaction mixture (GLC) indicated the aldehyde and internal standard only and in the same ratio as the original. GC/MS indicated the presence of a very small quantity of benzyl alcohol.

*p*-Toluoylmanganese pentacarbonyl and diphenylethylene. The autoclave was charged with 339 mg (1.08 mmol) of *p*-toluoylmanganese pentacarbonyl along with 200 μl (1.1 mol) of diphenylethylene in 100 ml of 40–60°C petroleum ether. The reaction was carried out under 2400 psi $H_2$/CO and 70°C for 3 h. After cooling to room temperature and venting the autoclave, the mixture was examined by GLC. A small amount of diphenylethane (0.15 mmol) was present.

*p*-Toluoylmanganese pentacarbonyl and alkenes (1-pentene, cyclohexene, and dimethyl maleate): these attempted carbene trapping reactions were carried out using the acceptor compounds noted. In a typical reaction, the autoclave was charged with the acyl (328 mg, 1 mmol) and 100 ml of cyclohexene. The reaction was performed under the usual oxo conditions. No products corresponding to reaction between a carbene and the alkene were observed. *p*-Methylbenzyloxycarbonylmanganese pentacarbonyl was isolated in 19% yield; the remaining manganese was present as $Mn_2(CO)_{10}$.

Attempted aldehyde exchange. $PhCH_2C(O)Mn(CO)_5$ (321 mg, 1 mmol) was placed in an autoclave along with *p*-tolualdehyde (120 μl, 1 mmol) in 100 ml petroleum ether. The reaction was carried out under the usual hydroformylation conditions. After the reaction, the resulting solution was evaporated to dryness, and the product examined by $^1H$ NMR in $CDCl_3$. Only resonances corresponding to $PhCH_2CH_2OC(O)Mn(CO)_5$ [1] and unconverted *p*-tolualdehyde were observed. A benzylic singlet at 5.1 ppm characteristic of authentic $CH_3C_6H_4CH_2OC(O)Mn(CO)_5$ was absent. When the reaction was repeated with a 10 fold excess of aldehyde similar results were obtained.

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