of NEt_3 having no σ donor ability through the introduction of a correction factor D, i.e., by plotting δ vs. $\chi/(D + (\pi - \sigma))$. A linear correlation line (correlation coefficient 0.95 for an empirically optimized $D = 6.5$) is obtained (Figure 5). The deviations for some of the ligands (NCPh, CN^-, $S(O)R_2$, $TePh_2$) should be a measure for the difference between the effective χ_L and the Pauling values of the ligating atoms.

Conclusion

It has been shown, for $[V(CO)_5L]^-$ complexes, that the IR and ^{51}V NMR spectroscopic series of ligand strengths can be matched if the ligand field splitting parameter $\Delta\bar{E}$ as one of the factors influencing the shielding constant is interchanged with the quantity $\chi/(6.5 + (\pi - \sigma))$, where π and σ are the Graham parameters calculated from the $\nu(CO)$. The electronegativity χ is a suitable measure for the contributions arising from the covalency of the V–L bond (C_{3d}^2) and the polarizability of L (or its nephelauxetic effect; $\langle r^{-3}\rangle$). A straight correlation is thus obtained for $\delta(^{51}V)$ as the parameter quantifying overall shielding.

The magnetochemical series of ligands as depicted by decreasing ^{51}V shielding are as follows: group 14 ligands, $SnPh_3^- > PbPh_3^- > CO > CNR > CN^- > \eta^2$-C=C > η^2-C≡C; group 15 ligands, $SbR_3 > PR_3 > AsR_3 > BiEt_3 > N_2 > NCR > NH_3 > NR_3$, NC_5H_4R, NO^+;[54] group 16 ligands, $TePh_2 > S(O)R_2 > SePh_2 > SR_2 > SO_2 >$ {O}; second period, {C} > {N} > {O}; third period, $PR_3 >$ {S}; fourth period, $AsR_3 > SePh_2$; fifth period, $SnPh_3^- > SbPh_3 > TePh_2$. Closely related trends have been reported for, inter alia, $\delta(^{51}V)$ of $[CpV(NO)_2L]$[55] and $[V(NO)_2L_4]X$[34,35] and $\delta(^{95}Mo)$ of $[Mo(CO)_5L]$.[56,57] The orderings represent counteracting effects arising from $\Delta\bar{E}$ (dominated by the $A_1(b_2^2e^4) \rightarrow E(b_2^2e^3a_1^1)$ transition) related to the strength of the ligand and the quantity $\langle r^{-3}\rangle_{3d}C_{3d}^2$. The importance of the ligand polarizability as a factor responsible for variations in metal shielding is evidenced by a comparison of η^1 and η^2 coordination, the additional deshielding contribution observed with side-on bonded ligands being a consequence of the low polarizability perpendicular to the backbone axis.

Registry No. $[V(CO)_5py]^-$, 82887-76-1; $[V(CO)_5CN]^{2-}$, 45047-39-0; $[V(CO)_5(2\text{-CN-py})]^-$, 96427-93-9; $[V(CO)_5(4\text{-CN-py})]^-$, 86638-29-1; $[V(CO)_5(2\text{-}NH_2\text{-py})]^-$, 86638-26-8; $[V(CO)_5THF]^-$, 86638-25-7; $[V(CO)_5(2\text{-Me-THF})]^-$, 34089-14-0; $[V(CO)_5(Te(P\text{-}t\text{-}Bu_2)_2)]^-$, 96427-94-0; $[V(CO)_5S(O)Me_2]^-$, 96427-95-1; $[V(CO)_5CS_2]^-$, 96427-96-2; $[V(CO)_5(1\text{-hexyne})]^-$, 95974-55-3; $[V(CO)_5N_2]^-$, 95974-51-9; $[V(CO)_5(\text{cyclopentene})]^-$, 95974-61-1; $[V(CO)_5(1\text{-pentene})]^-$, 95974-59-7; $[Et_4N][V(CO)_6]$, 13985-78-9; $[Et_4N][V(CO)_5CN\text{-}i\text{-}Pr]$, 96427-67-7; $[Et_4N][V(CO)_5CN\text{-}t\text{-}Bu]$, 78954-02-6; $[Et_4N][V(CO)_5CNCy]$, 78954-04-8; $[Et_4N][V(CO)_5CNCH_2CO_2Et]$, 96427-69-9; $[Et_4N][V(CO)_5NCMe]$, 96444-39-2; $[Et_4N][V(CO)_5NCPh]$, 96427-70-2; $[Et_4N][V(CO)_5OCMe_2]$, 95974-68-8; $[Et_4N][V(CO)_5OPh_2]$, 96427-72-4; $[Et_4N][V(CO)_5SPh_2]$, 96427-74-6; $[Et_4N][V(CO)_5SMePh]$, 96427-76-8; $[Et_4N][V(CO)_5SePh_2]$, 96427-78-0; $[Et_4N][V(CO)_5TePh_2]$, 96427-80-4; $[Et_4N][V(CO)_5SO_2]$, 95998-43-9; $[Et_4N][V(CO)_5X(O)Ph_2]$, 96427-82-6; $[Et_4N][V(CO)_5NEt_3]$, 96427-84-8; $[Et_4N][V(CO)_5NHEt_2]$, 96427-86-0; $[Et_4N][V(CO)_5NH_2Ph]$, 96427-88-2; $[Et_4N][V(CO)_5NHPh_2]$, 96427-90-6; $[Et_4N][V(CO)_5NEt_2Ph]$, 96427-92-8.

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Kinetic Investigation of the Mixed-Metal Bimolecular Reductive Eliminations in the Reactions of $EtOC(O)CH_2M(CO)_n$ or $EtOC(O)M(CO)_n$ (M = Co, n = 4; M = Mn, n = 5) with $HCo(CO)_4$ or $HMn(CO)_5$

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The alkyl- and acylmetal carbonyls $EtOC(O)CH_2M(CO)_n$ and $EtOC(O)M(CO)_n$ (M = Co, n = 4; M = Mn, n = 5) react with $HCo(CO)_4$ or $HMn(CO)_5$ to yield ethyl acetate or ethyl formate and the corresponding binuclear metal carbonyl. Kinetic experiments support a mechanism according to which the reaction between a coordinatively unsaturated alkyl- or acylmetal carbonyl (formed by CO loss) and the metal carbonyl hydride is rate determining. The rate of this bimolecular reductive elimination step varies strongly and unexpectedly in the mixed-metal systems.

Introduction

High activities and selectivities with homogeneous mixed-metal catalysts have been reported for aminomethylation,[1] carbonylation,[2] glycol formation from synthesis gas,[3] hydrogenation,[4] hydroformylation,[5] methanol homologation[6] and water gas shift reaction.[7] Very little

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is known, however, about the origin of the beneficial effect of the second metal. The comparison of reaction rates involved in the catalytic cycle with homometal and mixed-metal complexes would help to localize the kinetic differences.

We report now such a comparison for reductive bimolecular eliminations related to the product formation steps of olefin hydroformylation and hydrogenation.

Results

Ethyl formate and ethyl acetate were formed smoothly at 25 °C from (ethoxycarbonyl)- and (ethoxycarbonyl)methyl complexes of cobalt and manganese carbonyls using both $HCo(CO)_4$ and $HMn(CO)_5$ (reactions 1–8).

$$\underset{1}{EtOC(O)Co(CO)_4} + \underset{3}{HCo(CO)_4} \xrightarrow{r_1} EtOC(O)H + Co_2(CO)_8 \quad (1)$$

$$\underset{2}{EtOC(O)CH_2Co(CO)_4} + \underset{3}{HCo(CO)_4} \xrightarrow{r_2} EtOC(O)CH_3 + Co_2(CO)_8 \quad (2)$$

$$\underset{1}{EtOC(O)Co(CO)_4} + \underset{4}{HMn(CO)_5} \xrightarrow{r_3} EtOC(O)H + \underset{5}{MnCo(CO)_9} \quad (3)$$

$$\underset{2}{EtOC(O)CH_2Co(CO)_4} + \underset{4}{HMn(CO)_5} \xrightarrow{r_4} EtOC(O)CH_3 + \underset{5}{MnCo(CO)_9} \quad (4)$$

$$\underset{6}{EtOC(O)Mn(CO)_5} + \underset{3}{HCo(CO)_4} \xrightarrow{r_5} EtOC(O)H + \underset{5}{MnCo(CO)_9} \quad (5)$$

$$\underset{7}{EtOC(O)CH_2Mn(CO)_5} + \underset{3}{HCo(CO)_4} \xrightarrow{r_6} EtOC(O)CH_3 + \underset{5}{MnCo(CO)_9} \quad (6)$$

$$\underset{6}{EtOC(O)Mn(CO)_5} + \underset{4}{HMn(CO)_5} \xrightarrow{r_7} EtOC(O)H + Mn_2(CO)_{10} \quad (7)$$

$$\underset{7}{EtOC(O)CH_2Mn(CO)_5} + \underset{4}{HMn(CO)_5} \xrightarrow{r_8} EtOC(O)CH_3 + Mn_2(CO)_{10} \quad (8)$$

The rate of these reactions could be followed spectroscopically by the decrease of reactant concentration and by the increase of the product concentration in a way similar as described recently for the reactions 1[8] and 2.[9] As shown in Figure 1, first order in **1**, **2**, **6**, and **7**, less than first order in **3** and **4**, and less than negative first order in CO were found. These latter apparent reaction orders decreased by increasing the concentrations of the corresponding reactants.

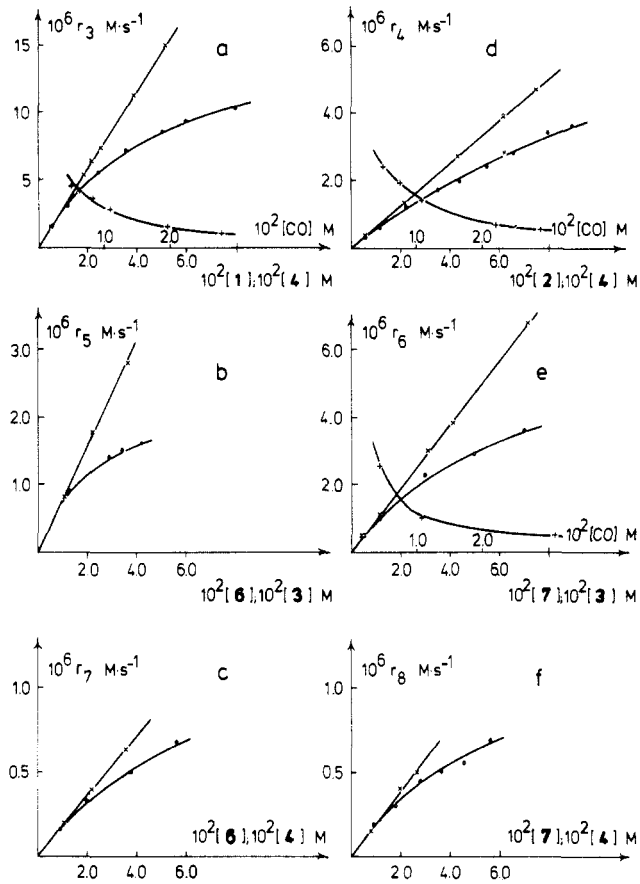

Figure 1. Influence of concentrations on rates of ethyl formate (r_3, r_5, r_7) and ethyl acetate (r_4, r_6, r_8) formation in *n*-heptane solution at 25 °C. The concentration of CO was calculated from p_{CO} and the solubility of CO in *n*-heptane[10] (a) (+) experiments at constant [1] = [4] = 0.012 M, (○) experiments at constant [CO] = 0.0108 M and [1] = 0.012 M, and (×) experiments at constant [CO] = 0.0108 M and [4] = 0.012 M; (b) (○) experiments at constant [CO] = 0.0107 M and [6] = 0.012 M and (×) experiments at constant [CO] = 0.0107 M and [3] = 0.012 M; (c) (○) experiments at constant [CO] = 0.0107 M and [6] = 0.012 M and (×) experiments at constant [CO] = 0.0107 M and [4] = 0.012 M; (d) (+) experiments at constant [2] = 0.024 M and [4] = 0.012 M, (○) experiments at constant [CO] = 0.0108 M and [2] = 0.012 M, and (×) experiments at constant [CO] = 0.0108 M and [4] = 0.012 M; (e) (+) experiments at constant [7] = [3] = 0.012 M, (○) experiments at constant [CO] = 0.0108 M and [7] = 0.012 M, and (×) experiments at constant [CO] = 0.0108 M and [3] = 0.012 M; (f) (○) experiments at constant [CO] = 0.0107 M and [7] = 0.012 M and (×) experiments at constant [CO] = 0.0107 M and [4] = 0.012 M.

The mixed-metal carbonyl **5** is the only organometallic product of the reactions 3–6. From the reaction mixtures **5** could be isolated in good yields.

Discussion

The kinetics of the reactions 1–8 are closely similar and support the general picture depicted in Scheme I.

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Scheme I

$$RM(CO)_n \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} RM(CO)_{n-1} + CO$$

$$RM(CO)_{n-1} + HM'(CO)_m \xrightarrow{k_b} RH + MM'(CO)_{m+n-1}$$

$$MM'(CO)_{m+n-1} + CO \xrightarrow{fast} MM'(CO)_{m+n}$$

R = EtOC(O), $EtOC(O)CH_2$; if M or M' = Co, n or m = 4; if M or M' = Mn, n or m = 5

The kinetic behavior is in accordance with a reversible dissociation of CO from $RM(CO)_n$ followed by a fast reaction between $HM'(CO)_n$ and the intermediate $RM(CO)_{n-1}$. Assuming steady-state concentration for this intermediate, the rate (r) can be described by eq 9 or after

$$r = k_a k_b [RM(CO)_n] \times [HM'(CO)_m]/(k_b[HM'(CO)_m] + k_{-a}[CO]) \quad (9)$$

$$[RM(CO)_n]/r = k_{-a}[CO]/k_a k_b [HM'(CO)_m] + 1/k_a \quad (10)$$

arrangement by eq 10, and k_a and the ratio of k_b to k_{-a} can be calculated from the intercept and the slope by plotting $[RM(CO)_n]/r$ against $[CO]/[HM'(CO)_m]$. The plots for reactions 1–8 can be seen in Figure 2. The constants derived in this way for reactions 1–8 are compiled in Table I.[11]

The k_a values for reactions 3 and 4 showed good agreement with the values derived earlier for the reactions 1 and 2. This supports the assumption that k_a is indeed the rate constant of CO dissociation from the alkyl or acyl complex. Manganese in place of cobalt in the alkyl or acyl complex results in a 10–20-fold slower rate of CO dissociation. This is in accordance with the well-known significantly higher stability of alkyl- and acylmanganese carbonyls as compared to their cobalt analogues.

Remarkable, the highest (0.67) and also the lowest (0.021) k_b/k_{-a} values—which reflect the relative reactivities of the coordinatively unsaturated acyl- or alkylmetal carbonyls toward the metal carbonyl hydride and CO—were found with the mixed-metal systems (reactions 3–6). On the other hand, the homometallic systems showed rather similar k_b/k_{-a} values (reactions 1, 2, 7, and 8) ranging between 0.078 and 0.13. In addition, the k_b/k_{-a} values of the mixed-metal systems were in three out of four cases higher, than those of their homometallic counterparts. Especially reaction 3 deserves attention in this respect, since comparing it with reaction 1 it is apparent that in this case $HMn(CO)_5$ was found to be more reactive than $HCo(CO)_4$.

A further conclusion which can be reached from these data is that the rates of product formation in the manganese-containing homometallic systems are only by about 1 order of magnitude smaller than in the corresponding cobalt-containing ones. If we compare this result with the very low catalytic activity of manganese in hydroformylation[14,15] and hydrogenation, it becomes evident that the bottleneck is not in this part of the catalytic cycle.

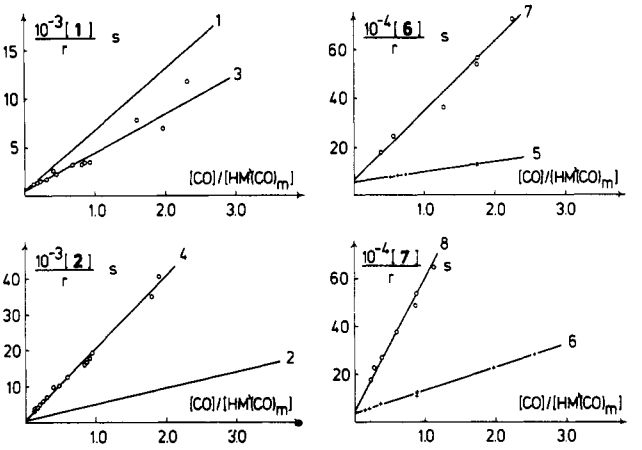

Figure 2. Plots of $[RM(CO)_n]/$rate against $[CO]/[HM'(CO)_m]$ for reactions 1–8 (R = EtOC(O), $EtOC(O)CH_2$; M, M' = Co, Mn; $m = n = 5$ for mN and 4 for Co). Curves 1[8] and 2[9] represent literature data.

Experimental Section

General Techniques. Infrared spectra were recorded on a Carl Zeiss Jena IR 75 spectrophotometer using a Carl Zeiss Jena low-temperature thermostated KBr cuvette. Analysis of the volatile compounds was performed on an analytical Hewlett-Packard Model 5830A gas chromatograph using 30-m glass capillary column with 0.15-μm OV-1 or SP 2100 stationary phase. All manipulations involving air-sensitive organometallic compounds were carried out by using anaerobic techniques.[17]

Materials. All solvents were dried on sodium wire and were freshly distilled under a CO atmosphere. Stock solutions of $HCo(CO)_4$ were prepared in n-heptane from $Co_2(CO)_8$, DMF, and concentrated HCl.[18] The concentration of $HCo(CO)_4$ was determined by titration with 0.1 N NaOH at 0 °C under CO in the presence of phenolphthalein as indicator. In some cases the concentration of $HCo(CO)_4$ in the reaction mixtures was checked also by using the value of $\epsilon_M(HCo(CO)_4) = 330 \pm 10$ cm² mmol⁻¹[19] for its highest energy infrared absorption band at 2116 cm⁻¹.

Almost colorless pale yellow 0.3 M stock solutions of $HMn(CO)_5$ in n-heptane were freshly prepared from $Mn_2(CO)_{10}$ in a fashion similar to that reported by King.[20] Instead of the difficult purification procedure using a vacuum line, $HMn(CO)_5$ was extracted with n-heptane after the addition of H_3PO_4 to $NaMn(CO)_5$, and then this solution was distilled in vacuo. The concentration of $HMn(CO)_5$ was determined after its infrared spectrum was checked, by manganese analysis. In order to control the $HMn(CO)_5$ concentration independently, we used the stoichiometric hydrogenation of α-methylstyrene which was reported to proceed quantitatively in benzene solution between 40 and 75 °C[21] according to reaction 11.

$$PhC(CH_3)=CH_2 + 2HMn(CO)_5 \rightarrow PhCH(CH_3)_2 + Mn_2(CO)_{10} \quad (11)$$

To aliquots of the $HMn(CO)_5$ stock solution (1 mL) were added n-heptane–benzene mixture (2 mL, 1:1), α-methylstyrene (0.082 mL, 0.63 mmol), and mesitylene (0.010 mL, 0.07 mmol) as internal standard at room temperature. After the solution was heated (4 h at 75 °C), the quantity of cumene was measured by GLC analysis. The $HMn(CO)_5$ concentration calculated on the basis of cumene formed was 95% of that found by Mn analysis.

(11) The same kinetic picture has been found for the reaction between p-$CH_3OC_6H_4CH_2Mn(CO)_5$ and $HMn(CO)_5$ in nonpolar solvents.[12] The kinetics of the reaction between *cis*-p-$CH_3OC_6H_4CH_2C(O)Mn(CO)_4(PMe_2Ph)$ and $HMn(CO)_5$ is somewhat more complex because of the simultaneous decarbonylation to *cis*-p-$CH_3OC_6H_4CH_2Mn(CO)_4(PMe_2Ph)$ but may also be explained by the formation of a coordinatively unsaturated intermediate by CO loss and the oxidative addition of $HMn(CO)_5$ to this intermediate.[13]

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Table I. Rate Constants[a] for the Reactions in Scheme I at 25 °C

reactn	M in $EtOC(O)M(CO)_n$	M in $EtOC(O)CH_2M(CO)_n$	M′ in $HM'(CO)_m$	$10^5 k_a$, s^{-1}	k_b/k_{-a}
1[8]	Co		Co	1.73 ± 0.07	0.084 ± 0.006
3	Co		Mn	1.57 ± 0.17	0.171 ± 0.027
2[9]		Co	Co	2.86 ± 0.43	0.078 ± 0.014
4		Co	Mn	2.53 ± 0.39	0.020 ± 0.001
7	Mn		Mn	0.14 ± 0.06	0.131 ± 0.078
5	Mn		Co	0.18 ± 0.01	0.671 ± 0.081
8		Mn	Mn	0.20 ± 0.01	0.095 ± 0.006
6		Mn	Co	0.26 ± 0.04	0.375 ± 0.074

[a] Deviations represent 95% confidence level.

The compounds $EtOC(O)Co(CO)_4$[8] (1) and $EtOC(O)CH_2Co(CO)_4$[22] (2) were prepared by published procedures.

Preparation of (Ethoxycarbonyl)manganese Pentacarbonyl (6) Stock Solution. To a solution of $NaMn(CO)_5$ (15.4 mmol) in THF (60 mL) was added ethyl chloroformate (1.50 mL, 15.4 mmol) at −10 °C. When the mixture was stored overnight, a red-orange solution and a white precipitate (NaCl) was formed. After filtration and removal of THF in vacuo the orange oil was dissolved in *n*-heptane (40 mL), washed with water (20 mL), and filtered through a mixture of activated carbon and anhydrous $MgSO_4$. On the basis of manganese analysis, the yield of 6 was 20%: IR (heptane) ν(CO) 2125 (w), 2059 (sh), 2030 (vs), 2007 (s), 1653 (w) cm^{-1}.

To prepare 6 by thermal decarbonylation of (ethoxyoxalyl)manganese pentacarbonyl (8) failed. Instead of a facile decarbonylation as could be observed in the case of pyruvoylmanganese pentacarbonyl[23] or (alkoxyoxalyl)cobalt tetracarbonyls,[8,24] the manganese complex 8[25] decomposed according to reaction 12.

$$2\underset{8}{EtOC(O)C(O)Mn(CO)_5} \xrightarrow{80\ °C} [EtOC(O)]_2 + Mn_2(CO)_{10} + 2CO \quad (12)$$

Thermal Decomposition of (Ethoxyoxalyl)manganese Pentacarbonyl (8). The complex 8 (0.2 mmol) dissolved in *n*-heptane (5 mL) was heated at 80 °C under CO atmosphere. CO evolution started immediately with an initial rate of 9×10^{-6} M s^{-1} and ceased after 4 h releasing 0.19 mmol of CO. IR spectra showed the presence of 0.09 mmol of diethyl oxalate (absorbancies: 1750 (ϵ_M([EtOC(O)]$_2$) 445) and 1775 cm^{-1} (ϵ_M([EtOC(O)]$_2$) 848 cm^2 $mmol^{-1}$)) and $Mn_2(CO)_{10}$ as the only complex in the solution.

Preparation of [(Ethoxycarbonyl)methyl]manganese Pentacarbonyl (7) Stock Solution. To a solution of $NaMn(CO)_5$ (15.4 mmol) in THF (60 mL) was added ethyl bromoacetate (1.78 mL, 16 mmol) at 0 °C. Immediately a yellow solution and a white precipitate were formed. A stock solution of 7 in *n*-heptane was prepared in the same way as in the case of 6. Yield based on manganese analysis was 30%. IR (heptane): ν(CO) 2117 (w), 2050 (m), 2027 (sh), 2022 (vs), 1996 (s), 1957 (w), 1720 (w) cm^{-1}.

Preparation of Manganese Cobalt Nonacarbonyl (5). To a solution of 1 (1.2 mmol) in *n*-heptane (96 mL) under carbon monoxide atmosphere (752 mmHg) was added a solution of 4 (1.2 mmol) in *n*-heptane (4 mL) at 25 °C. The color of the reaction mixture changed slowly from pale yellow to red orange. Monitoring the reaction by IR spectra showed the gradual decrease of the concentrations of 1 and 4 parallel to the increase of the concentration of 5 which was the only new complex in the solution. Complex 5 was identified by its known infrared spectrum (heptane): ν(CO) 2117 (w), 2056 (s), 2026 (vs), 2004 (sh), 1996 (m), 1981 (br) cm^{-1}.[26] After 24 h 5 was practically the only complex in the reaction mixture which could be isolated after removing 90% of the solvent in vacuo at 0 °C and crystallizing at −79 °C: orange red needles (310 mg); 71% yield. Similar yields of 5 could be achieved in reactions 4–6 by using the above procedure.

Kinetic runs were performed under CO in a thermostated (25 °C) reaction vessel connected to a 5-L buffer flask in order to maintain the pressure constant. The actual total pressure was determined in milimeters of Hg by using an open mercury manometer measuring the pressure difference between the atmosphere and the reaction vessel. The reactions were started by injecting 0.2–0.3 M solutions of 3 or 4 in *n*-heptane into vigorously stirred solutions of 1, 2, 6, or 7 in *n*-heptane. The change of IR spectra was followed from samples withdrawn by a gas-tight syringe and filled through a three-way Hamilton valve and Teflon tubing into the thermostated (25 °C) 0.11- or 0.25-mm KBr cuvette. Initial rates were calculated from graphical plots below 20% conversions.

Reaction of 1 with $HMn(CO)_5$. The change of IR spectra was followed at 1692 (ϵ_M(1) 1266)[8] and 1737 cm^{-1} (ϵ_M(EtOC(O)H) 1050 cm^2 $mmol^{-1}$).[8]

Reaction of 2 with $HMn(CO)_5$. The change of IR spectra was followed at 1717 cm^{-1} (ϵ_M(2) 820)[9] and 1752 cm^{-1} (ϵ_M(EtOC(O)CH_3) 740 cm^2 $mmol^{-1}$).[9]

Reaction of 6 with $HCo(CO)_4$ and $HMn(CO)_5$. The change of IR spectra was followed at 2125 (ϵ_M(6) 477), 1653 (ϵ_M(6) 657 cm^2 $mmol^{-1}$), and 1737 cm^{-1}.

Reaction of 7 with $HCo(CO)_4$ and $HMn(CO)_5$. The change of IR spectra was followed at 2117 (ϵ_M(7) 557), 1720 (ϵ_M(7) 475 cm^2 $mmol^{-1}$), and 1752 cm^{-1}.

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Registry No. 1, 86970-72-1; 2, 79170-75-5; 3, 16842-03-8; 4, 16972-33-1; 5, 35646-82-3; 6, 28300-66-5; 7, 96504-49-3; 8, 71147-64-3; $Co_2(CO)_8$, 10210-68-1; $Mn_2(CO)_{10}$, 10170-69-1; *cis*-*p*-$CH_3OC_6H_4CH_2(CO)Mn(CO)_4(PMe_2Ph)$, 96612-34-9; *cis*-*p*-$CH_3OC_6H_4CH_2Mn(CO)_4(PMe_2Ph)$, 96612-35-0; $NaMn(CO)_5$, 13859-41-1; EtOC(O)H, 109-94-4; $EtOC(O)CH_3$, 141-78-6; $[EtOC(O)]_2$, 95-92-1; ethyl chloroformate, 541-41-3; ethyl bromoacetate, 105-36-2.

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