Solid–Liquid Reactions of Manganese and Cobalt Carbonyl Anions with Alkyl Halides Containing β-Hydrogens or -Halogens

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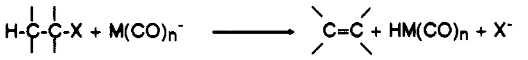
Heterogeneous reactions afforded the first detection (by IR and NMR spectroscopy) of a secondary (η^1-allyl)manganese carbonyl complex, $CH_3CH{=}CHCH(CH_3)Mn(CO)_5$, which results from the reaction of solid $NaMn(CO)_5$ with 4-bromo-2-pentene in benzene or in saturated hydrocarbons at temperatures up to 5 °C. The analogous reaction of $NaCo(CO)_4$ gives $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_4$, the product of CO insertion into $CH_3CH{=}CHCH(CH_3)Co(CO)_4$, which constitutes approximately 10% (by IR spectroscopy) of the equilibrium mixture with $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_4$ under CO at 1 atm and 5 °C. Addition of PPh_3 to this mixture leads to the formation of isolable $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_3PPh_3$. Similar reactions of 4-bromo-2-pentene with $NaMn(CO)_4PPh_3$ and $NaCo(CO)_3PPh_3$ do not give metal–carbon-bonded species, nor do room-temperature reactions of 4-bromo-2-pentene with $NaMn(CO)_5$ and $NaCo(CO)_4$. Instead, the products include 2-pentenes, 1,3-pentadienes, 4,5-dimethyl-2,6-octadiene isomers, $BrMn(CO)_5$, $Mn_2(CO)_{10}$, $Co_2(CO)_8$, and η^3-$(CH_3CHCHCHCH_3)Co(CO)_3$. Reactions of dimethyl chlorosuccinate, ethyl 2-bromopropionate, methyl 3-bromopropionate, and dimethyl dibromosuccinate with $NaMn(CO)_5$ and $NaCo(CO)_4$ give varying amounts of alkylmetal carbonyl compounds and products of β-elimination. The characteristics of these transformations suggest radical mechanisms initiated by single electron transfer (SET). Radical pairs formed by SET are implicated as intermediates in both substitutions and eliminations.

Introduction

In addition to providing syntheses of alkyl-, acyl-, and (π-allyl)metal carbonyls,[1] substitution reactions of alkyl halides RX with carbonyl metalates $M(CO)_n^-$ ($Mn(CO)_5^-$, $Co(CO)_4^-$, etc.) in homogeneous solutions play key roles in catalytic and stoichiometric carbonylations of RX.[2,3]

$$RX + M(CO)_n^- \longrightarrow RM(CO)_n + X^- \qquad (1)$$

Substitution is often accompanied by elimination.



$$H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X + M(CO)_n^- \longrightarrow \;\rangle C{=}C\langle\; + HM(CO)_n + X^- \qquad (2)$$

Consistent with the variety and significance of the applications of $RX/M(CO)_n^-$ reactions, their mechanisms have received considerable attention over the past two decades. Certain kinetic[4] and stereochemical[5] studies support one-step, S_N2 mechanisms,[3] with the carbonyl metalates as nucleophiles,[6] and this view has been widely accepted. Radical pathways initiated by single electron transfer (SET) are also plausible in many cases. Equation 3 represents a simple SET mechanism in which the product $RM(CO)_n$ is formed by geminate recombination, but chain and nonchain mechanisms involving nongeminate radicals are also possible.

$$\begin{tikzcd} RX + M(CO)_n^- \arrow[r, "SET"] & {[RX^{\bullet -}, {}^{\bullet}M(CO)_n]} \arrow[r, "-X^-"] & {[R{\bullet}{\bullet}M(CO)_n]} \arrow[r] \arrow[d, shift left] & RM(CO)_n \\ & & R{\bullet} + {\bullet}M(CO)_n \arrow[u, shift left] \arrow[r] & RR + M_2(CO)_{2n} \end{tikzcd} \qquad (3)$$

The ESR detection of alkyl radicals in the reaction of $Fe(CO)_2Cp^-$ and alkyl iodides,[7] the formation of coupling products of organic and inorganic radicals,[8] and the formation of halometal carbonyls[9] all support radical mechanisms. Such evidence is consistent with SET (eq

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§ Department of Organic Chemistry.

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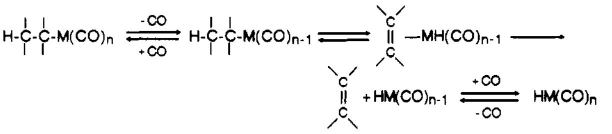
3), but it is also consistent with S_N2 substitution followed by C–M bond homolysis, which has been invoked to account for the formation of coupling products (eq 4).[10]

$$RX + M(CO)_n^- \xrightarrow[-X^-]{S_N2} RM(CO)_n \rightleftharpoons [R\bullet\bullet M(CO)_n] \rightleftharpoons R\bullet + \bullet M(CO)_n \longrightarrow RR + M_2(CO)_{2n} \quad (4)$$

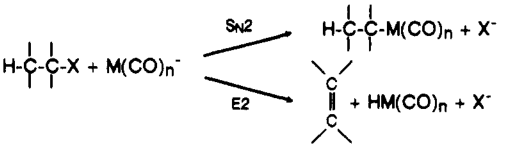
Recent investigations provide an even more complicated picture. Reactions of $NaMn(CO)_5$ with 2-bromoacyl halides, leading to ketenes and $BrMn(CO)_5$, may proceed through enolate intermediates.[11] The formation of manganese enolate and dienolate complexes probably occurs through a carbanion mechanism, but the initial step could be SET.[12] In other studies, benzyl chloride was found to undergo a reversible oxidative addition to $Co(CO)_4^-$ in the presence of a crown ether, giving an $RC(O)Co(CO)_3X^-$ species, complicating what was otherwise considered to be an S_N2 reaction.[13]

β-Eliminations of hydrogen or halogen atoms in metal carbonyl systems have received less mechanistic attention than substitution. Eliminations of hydrogen have often been considered to be unrelated reactions, probably because there is a commonly cited scheme in which a coordinative unsaturated alkylmetal species transforms to a hydrido–olefin complex and subsequently dissociates to the olefin and hydride.[14]



(5)

However, there are possible mechanistic connections between substitutions and eliminations. E2 often accompanies S_N2, providing an alternative to the "classic" mechanism of eq 5.



(6)

It is not the only additional possibility, however. Recent studies provide precedent for radical disproportionations between $R^\bullet$ and $^\bullet M(CO)_n$. The isomerization of tetramethylallene to 2,4-dimethyl-1,3-pentadiene, catalyzed by $HMn(CO)_5$ or $HCo(CO)_4$, appears to proceed through the disproportionation of intermediate radical pairs $[R^{\bullet\bullet}Mn(CO)_5]$.[15] No intermediate $RMn(CO)_5$ is required. In addition, kinetic studies show that $MeOOCCH_2CH(COOMe)Co(CO)_4$ thermally decomposes to $HCo(CO)_4$ and dimethyl fumarate in a completely reversible (radical) process catalyzed by $Co_2(CO)_8$.[16] Most recently, while the manuscript was in preparation, Baird et al. communicated on halogen and β-hydrogen atom abstraction from several alkyl halides by $Cr(CO)_3Cp$ radicals leading to olefins.[17]

There are only sporadic reports in the literature about β-eliminations of halogens.[18] It is evident from these results that elimination of a halogen (fluorine or bromine) is favored over that of hydrogen when both are attached to the same C_β atom. E2 and radical disproportionation pathways were suggested for the reactions of several vicinal dibromides with η^3-$C_3H_5Fe(CO)_3^-$ and η^3-$C_3H_5Fe(CO)_3$ radicals, respectively.[18b]

Our work began in efforts to prepare allylmetal carbonyls that are possible intermediates in reactions between 2,3-pentadiene and $HMn(CO)_5$ or $HCo(CO)_4$ by reactions of $NaMn(CO)_4L$ and $NaCo(CO)_3L$ (L = CO, PPh_3) with 4-bromo-2-pentene.[19] Similarly, manganese analogues of $MeOOCCH_2CH(COOMe)Co(CO)_4$[20] and $MeOOCCH_2CH(COOMe)Co(CO)_3PPh_3$[21] were attempted to be prepared through reactions of $NaMn(CO)_4L$ with dimethyl chlorosuccinate. Prompted by unsatisfactory results obtained in homogeneous reactions 1 in ethereal solvents and by the hope that nonpolar solvents might promote the formation of the desired products by radical mechanisms, we conducted the reactions heterogeneously, using hydrocarbon solvents (benzene, octane, etc.), atmospheres of CO or Ar, and sometimes PPh_3 or $HMn(CO)_3$dppe as an additive. We later broadened the study to include reactions of 1-bromo-2-pentene and α- and β-halo esters ethyl 2-bromopropionate, methyl 3-bromopropionate, and (±)- and *meso*-dimethyl dibromosuccinates.

To the best of our knowledge, all previously reported reactions of alkyl halides with metal carbonyl anions were carried out in homogeneous solutions, most frequently in basic solvents such as tetrahydrofuran (THF) or diethyl ether.

We now report our preparative and mechanistic observations on these reactions under heterogeneous conditions. In this context a new mechanistic pathway for β-eliminations of both hydrogen and halogen, through radical pairs, is discussed.

Results

General Methods. As pure liquids or in nonpolar solvents such as benzene, toluene, and alkanes, several activated primary and secondary alkyl halides, namely 1-bromo-2-pentene, 4-bromo-2-pentene, dimethyl chlorosuccinate, ethyl 2-bromopropionate, methyl 3-bromopropionate, and (±)- as well as *meso*-dimethyl dibromosuccinate, react readily with $M(CO)_nL^-$ (M = Co, Mn; n = 3, 4; L = CO, PPh_3) when stirred with the solid sodium salts $NaM(CO)_nL$ in the "concentration" range 0.01–1 M, using

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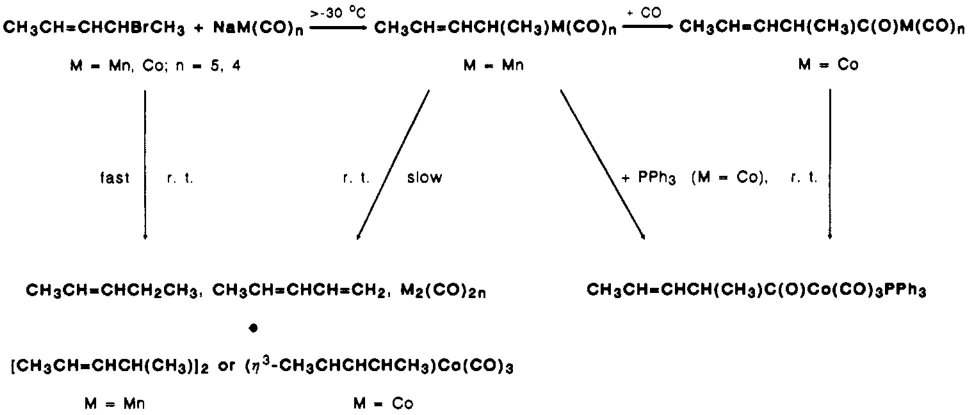
Scheme I



the reactants in ca. 1:1 molar ratio, temperatures in the range −30 °C to rt (rt = room temperature), and atmospheric pressures of CO or Ar. In addition, we note that metal carbonyl halides react with a number of metal carbonyl anions under the same conditions.

Allylic Bromopentenes. Reactions of 4-Bromo-2-pentene with $\mathrm{NaMn(CO)_5}$ and $\mathrm{NaCo(CO)_4}$. The secondary allylic bromide, 4-bromo-2-pentene, reacts readily with $\mathrm{NaMn(CO)_5}$ and $\mathrm{NaCo(CO)_4}$ above 0 °C. With benzene solutions of relatively high halide concentrations (ca. 0.6 M) at room temperature, perceptible heat evolution takes place.

In room-temperature reactions of $\mathrm{NaMn(CO)_5}$ under CO, mixtures of 2-pentene, 1,3-pentadiene, and 4,5-dimethyl-2,6-octadiene isomers[22] are formed. $\mathrm{Mn_2(CO)_{10}}$ and $\mathrm{BrMn(CO)_5}$ are the only metal carbonyl complexes that were detected. Under Ar, traces of η^3-$\mathrm{(CH_3CHCHCHCH_3)Mn(CO)_4}$[23] were also identified.

In room-temperature reactions of $\mathrm{NaCo(CO)_4}$, $\mathrm{Co_2(CO)_8}$ is accompanied by η^3-$\mathrm{(CH_3CHCHCHCH_3)Co(CO)_3}$ isomers,[24] which are the main carbonyl-containing species under Ar (>60%). The organic product mixture consists of 2-pentenes and 1,3-pentadienes.

η^1-$\mathrm{CH_3CH{=}CHCH(CH_3)Mn(CO)_5}$ or η^1-$\mathrm{CH_3CH{=}CHCH(CH_3)Co(CO)_4}$ results when 4-bromo-2-pentene is mixed with $\mathrm{NaMn(CO)_5}$ or $\mathrm{NaCo(CO)_4}$ under CO at about −30 °C and the temperature is allowed to rise slowly to 5 °C. This is the first report of the detection of (*sec*-η^1-allyl)manganese and -cobalt carbonyl complexes.[25]

$\mathrm{CH_3CH{=}CHCH(CH_3)Mn(CO)_5}$,[28] which is formed together with considerable amounts of $\mathrm{Mn_2(CO)_{10}}$, $\mathrm{BrMn(CO)_5}$, and organic decomposition products, even at the beginning of the reaction, undergoes CO insertion very slowly. Only a weak band at 2111 cm^{-1} and a shoulder at 2016 cm^{-1}, representing the acyl complex, appear in the IR spectrum after a prolonged reaction time. The formation of 2-penten-4-al, however, when $\mathrm{CH_3CH{=}CHCH(CH_3)Mn(CO)_5}$ decomposes is more convincing evidence of $\mathrm{CH_3CH{=}CHCH(CH_3)C(O)Mn(CO)_5}$. The aldehyde was identified by high-resolution (300 MHz) ^{1}H NMR spectroscopy[29] and could derive from the cleavage of the acylmanganese complex by $\mathrm{HMn(CO)_5}$, which, in turn, is a product of β-elimination. Added $\mathrm{PPh_3}$ does not promote the incorporation of CO. In fact, there is no substitution of the alkyl complex at all at room temperature. Only the substitution of $\mathrm{BrMn(CO)_5}$ and transient formation of $\mathrm{HMn(CO)_4PPh_3}$ were detected.

$\mathrm{CH_3CH{=}CHCH(CH_3)Co(CO)_4}$ immediately converts to its equilibrium mixture with the more stable acyl derivative $\mathrm{CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_4}$.[30] In this mixture, the acyl/alkyl ratio is ≈9:1.[27] Thus, the alkylcobalt complex is detected only by its characteristic A_1 infrared band at 2092 cm^{-1}. When $\mathrm{PPh_3}$ is added to the cold reaction mixture, both the alkyl- and acylcobalt tetracarbonyl complexes are substituted to $\mathrm{CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_3PPh_3}$, which was isolated.

The alkyl and acyl complexes of both metals, detected in situ, spontaneously decompose or transform to the above mixtures of organic and organometallic products, even in cold solutions, in about 2 h. We were unable to isolate them in pure form. These transformations are summarized in Scheme I.

Reactions of 1-Bromo-2-pentene with $\mathrm{NaMn(CO)_5}$ and $\mathrm{NaCo(CO)_4}$. Room-temperature reactions of $\mathrm{NaMn(CO)_5}$ or $\mathrm{NaCo(CO)_4}$ with the primary allylic bromide 1-bromo-2-pentene give quantitative yields of $\mathrm{CH_3CH_2CH{=}CHCH_2Mn(CO)_5}$[32] or η^3-$\mathrm{(CH_3CH_2CHCHCH_2)Co(CO)_3}$.[24] (Quantitation is based on the complete con-

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[22] The three compounds were identified by GC–MS. Only traces of *cis*-2-pentene and *cis*-1,3-pentadiene could be observed; e.g., the trans isomers dominated in both cases. The concentration of *cis*-1,3-pentadiene was below the sensitivity level of the NMR spectrometer; its characteristic olefinic proton resonances did not appear. Three additional peaks were found in the GC spectra and assigned to the same constitution, 4,5-dimethyl-2,6-octadiene. These peaks probably represent cis,cis, cis,trans, and trans,trans isomers.

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[28] Data for $\mathrm{CH_3CH{=}CHCH(CH_3)Mn(CO)_5}$ are as follows. IR (pentane): ν_{CO} = 2100 w, 2008 vs, 1986 m cm^{-1}. ^{1}H NMR (toluene-d_8, 300 MHz): δ = 1.44 (d, 3H, –CH–C*H*$_3$), 1.54 (d, 3H, =CH–C*H*$_3$), 2.465 (m, 1H, –C*H*–), 5.065 (m, 1H, =C*H*–CH$_3$), 5.79 (m, 1H, –CH–C*H*=) ppm.

[29] Data for $\mathrm{CH_3CH{=}CHCH(CH_3)CHO}$ are as follows. ^{1}H NMR (toluene-d_8, 300 MHz): δ = 1.36 (d, 3H, =CH–C*H*$_3$), 2.385 (m, 1H, –C*H*–), 9.13 (s, 1H, –CO*H*) ppm and two multiplets in the range 4.95–5.23 ppm, partly overlapped with the multiplets of 2-pentene and *trans*-1,3-pentadiene and characteristic of the vinylic protons, as well as a second doublet, completely covered by that of 1,3-pentadiene at 1.44 ppm and attributable to –CH–C*H*$_3$.

[30] Data for $\mathrm{CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_4}$ are as follows. IR (pentane): ν_{CO} = 2103 m, 2044 vs, 2023 vs, 2003 vs, 1746 sh, 1721 w, br, 1685 sh cm^{-1}, identical with that observed in the reaction of $\mathrm{HCo(CO)_4}$ with *trans*-1,3-pentadiene.[31] ^{1}H NMR (toluene-d_8, −10 °C, 80 MHz): δ = 0.90 (d, 3 H, –CH–C*H*$_3$), 1.12 (d, 3H, =CH–C*H*$_3$), 3.50 (m, 1H, –C*H*–CH$_3$), 5.22 (m, 2H, –C*H*=C*H*–) ppm.

[31] Ungváry, F. Unpublished results.

sumption of the bromide and was determined by ^{1}H NMR spectroscopy.)

There is no published example of CO insertion in any of the known primary (η^1-allyl)manganese pentacarbonyls. The evidence that the secondary allyl complex $CH_3CH{=}CHCH(CH_3)Mn(CO)_5$ undergoes CO insertion prompted us to attempt to force insertion in $CH_3CH_2CH{=}CHCH_2Mn(CO)_5$. We therefore added PPh_3 to its benzene solution and heated the mixture to 50 °C, under 1 atm of CO. $CH_3CH_2CH{=}CHCH_2Mn(CO)_5$ is completely consumed within 3 h, giving mostly decomposition products (≈90%) and some η^3-$(CH_3CH_2CHCHCH_2)Mn(CO)_4$[33] (≈10%), according to eq 7. Without PPh_3, there is a very slow loss of CO, leading to the η^3-allyl complex (≈50%) and coupling products (≈50%) in 2 days.[34]

$$CH_3CH_2CH{=}CHCH_2Mn(CO)_5 + PPh_3 \xrightarrow{\Delta} Mn_2(CO)_8(PPh_3)_2 + (CH_3CH_2CH{=}CHCH_2)_2 + \eta^3\text{-}(CH_3CH_2CHCHCH_2)Mn(CO)_4 \quad (7)$$

Reactions of 4-Bromo-2-pentene and 1-Bromo-2-pentene with $NaMn(CO)_5$ and $NaCo(CO)_4$ in the Presence of $HMn(CO)_3$dppe. The persistence of the free radical $Mn(CO)_3$dppe[36] suggests that $HMn(CO)_3$dppe might be a useful trap for alkyl radical intermediates. It can be used sensibly as a radical trap only if it does not otherwise interfere. Control experiments show that $HMn(CO)_3$dppe does not react with any of the reactants and products of the reactions under study. Most important, and unlike $HMn(CO)_5$ and $HMn(CO)_4PPh_3$, $HMn(CO)_3$dppe does not react with 4-bromo-2-pentene or 1-bromo-2-pentene to produce 2-pentenes.

Reactions of $NaMn(CO)_5$ with either 4-bromo-2-pentene or 1-bromo-2-pentene in benzene in the presence of equimolar amounts of $HMn(CO)_3$dppe results in organic product mixtures that are rich in 2-pentenes. In each case, the IR spectrum shows bands characteristic of $Mn(CO)_3$dppe radicals (which is indicated also by a characteristic purple-red color) and $BrMn(CO)_3$dppe. 1-Bromo-2-pentene gives $Mn(CO)_3$dppe, $BrMn(CO)_3$dppe, and 2-pentenes (35%) along with $CH_3CH_2CH{=}CHCH_2Mn(CO)_5$, which is formed quantitatively in the absence of $HMn(CO)_3$dppe. The formation of $BrMn(CO)_3$dppe indicates that $Mn(CO)_3$dppe partly reacts with the starting halides.[36c].

Reactions of 4-Bromo-2-pentene with $NaMn(CO)_4PPh_3$ and $NaCo(CO)_3PPh_3$. $NaMn(CO)_4PPh_3$ and $NaCo(CO)_3PPh_3$, unlike their parent salts, fail to give any alkyl or acyl complexes, even though they react smoothly under the same conditions. Again, decomposition products, among them the organometallics $Co_2(CO)_6(PPh_3)_2$ or $Mn_2(CO)_8(PPh_3)_2$, $BrMn(CO)_4PPh_3$, and $HMn(CO)_4PPh_3$, were identified.

These results may be surprising, since phosphine-substituted derivatives of both alkyl- or acylmanganese and -cobalt carbonyls, once formed, are invariably more stable than their unsubstituted counterparts. This is certainly true for $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_3PPh_3$, which we obtain from its very unstable percursor $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_4$ by PPh_3 substitution. In homogeneous solutions, primary allylic halides, however, are known to react with $NaMn(CO)_4PPh_3$ to form (η^1-allyl)manganese tetracarbonyl phosphine complexes.[9a]

Halo Esters. Reactions of α- and β-Halo Esters with $NaMn(CO)_5$, $NaCo(CO)_4$, $NaMn(CO)_4PPh_3$, and $NaCo(CO)_3PPh_3$. Dimethyl chlorosuccinate reacts less vigorously than 4-bromo-2-pentene, but still at a convenient rate at room temperature, with $NaMn(CO)_5$, $NaCo(CO)_4$, $NaMn(CO)_4PPh_3$, and $NaCo(CO)_3PPh_3$. Our attempts to prepare the corresponding alkyl or acyl complexes succeeded only with $NaMn(CO)_5$.

IR spectroscopy[37] shows that reactions of dimethyl chlorosuccinate with $NaMn(CO)_5$ at 0 °C and in diluted octane solutions give $MeOOCCH_2CH(COOMe)Mn(CO)_5$, along with $Mn_2(CO)_{10}$. Unfortunately, all of our attempts failed to obtain this complex in solvents and concentrations suitable for NMR detection. No signs of spontaneous CO insertion into its C–Mn bond, nor of substitution with PPh_3 when it was present, were detected.

At room temperature, reactions of dimethyl chlorosuccinate with $NaMn(CO)_5$ give $ClMn(CO)_5$, $Mn_2(CO)_{10}$, dimethyl fumarate (dimethyl *trans*-2-butenedioate), and dimethyl succinate. In these and other reactions of dimethyl chlorosuccinate, dimethyl fumarate and dimethyl succinate are formed in ≈1:1 molar ratio.

From reactions in the presence of PPh_3, which might stabilize the alkyl or perhaps an acyl complex as a PPh_3-substituted derivative, only $ClMn(CO)_4PPh_3$, $Mn_2(CO)_{10}$, and $Mn_2(CO)_8(PPh_3)_2$ were detected. Similarly, from reactions of $NaMn(CO)_4PPh_3$, the only metal carbonyl species detected were $ClMn(CO)_4PPh_3$ and $Mn_2(CO)_8(PPh_3)_2$.

The known complex $MeOOCCH_2CH(COOMe)Co(CO)_4$ was not detected from the rection of dimethyl chlorosuccinate with $NaCo(CO)_4$, perhaps because it thermally decomposes as it is formed.[16] The reaction of dimethyl chlorosuccinate with $NaCo(CO)_3PPh_3$ results in the formation of $Co_2(CO)_6(PPh_3)_2$ as the only cobalt carbonyl compound. The absence of $MeOOCCH_2CH(COOMe)Co(CO)_3PPh_3$ is not due to its instability. We have synthesized it in an other way and found that it is quite stable.[16,21]

In contrast to heterogeneous reactions in hydrocarbon solvents, more dimethyl succinate than dimethyl fumarate is formed when a solution of the anions in THF is added to an alkane solution of dimethyl chlorosuccinate. When $NaMn(CO)_5$ reacts in THF without a cosolvent, dimethyl succinate constitutes 95% of the organic products.

We also carried out reactions of $NaMn(CO)_5$, $NaCo(CO)_4$, and $NaCo(CO)_3PPh_3$ with a primary β-bromo ester, methyl 3-bromopropionate, in *n*-octane at rt or at −30 °C under Ar [$NaCo(CO)_4$, $NaCo(CO)_3PPh_3$] and CO [$NaMn(CO)_5$, $NaCo(CO)_4$] at 1 atm total pressure. In each case, the rapid formation of metal carbonyl hydrides [$HMn(CO)_5$, $HCo(CO)_4$, $HCo(CO)_3PPh_3$] and methyl acrylate

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[32] Data for $CH_3CH_2CH{=}CHCH_2Mn(CO)_5$ are as follows. IR(hexane): ν_{CO} = 2104 w, 2010 vs, 1992 s cm^{-1}. ^{1}H NMR (benzene-d_6, 90 MHz): δ = 0.93 (t, 3H, $-CH_3$), 1.70 (d, 2H, Mn$-CH_2-$), 1.92 (m, 2H, $-CH_2-$Me), 5.27 (m, 1H, $=CH-$Et), 5.67 (m, 1H, $=CH-CH_2-$) ppm.

[33] Oudeman, A.; Sorensen, T. S. *J. Organomet. Chem.* **1978**, *156*, 259.

[34] A recent publication describes the similar lack of CO insertion on phosphine substitution of primary (η^1-allyl)cobalt tetracarbonyls.[35] However, some derivatives containing branched carbon chains, such as (3-methyl-2-butenyl)- and (2,3-dimethyl-2-butenyl)cobalt tetracarbonyls, insert CO spontaneously. Even so, these give a considerably smaller acyl/alkyl ratio than the (*sec*-η^1-allyl)cobalt complexes (1-methyl-2-butenyl)- and (3-cyclohexenyl)cobalt tetracarbonyls.[27]

[35] Loubser, C.; Roos, H. M.; Lotz, S. *J. Organomet. Chem.* **1991**, *402*, 393.

[36] (a) Sacco, A. *Gazz. Chim. Ital.* **1963**, *93*, 698. (b) Reimann, R. H.; Singleton, E. *J. Organomet. Chem.* **1972**, *38*, 113. (c) Tyler, D. R.; Goldman, A. S. *J. Organomet. Chem.* **1986**, *311*, 349.

[37] Data for $MeOOCCH_2CH(COOMe)Mn(CO)_5$ are as follows. IR (octane): ν_{CO} = 2117 w, 2024 vs, 2003 s, 1744 w, 1708 w cm^{-1}.

was observed (eq 8). The hydrides subsequently decomposed slowly to the corresponding metal carbonyl dimers, $\mathrm{Mn_2(CO)_{10}}$, $\mathrm{Co_2(CO)_8}$, and $\mathrm{Co_2(CO)_6(PPh_3)_2}$, respectively. In parallel with its decomposition, $\mathrm{HCo(CO)_4}$ adds to methyl acrylate to form some $\mathrm{MeOOCCH(CH_3)Co(CO)_4}$.[38]

$$\mathrm{MeOOCCH_2CH_2Br + NaM(CO)_nL \longrightarrow MeOCCH{=}CH_2 + HM(CO)_nL + NaBr} \qquad (8)$$

There are two especially interesting features of these results. First, $\mathrm{NaMn(CO)_5}$ and methyl 3-bromopropionate do not give the known complex $\mathrm{MeOOCCH_2CH_2Mn(CO)_5}$ even in cold solutions. It can be prepared, however, by decarbonylation of its acylmanganese precursor.[39] Since $\mathrm{MeOOCCH_2CH_2Mn(CO)_5}$ is expected to be stable under forced conditions (90 °C), $\mathrm{HMn(CO)_5}$ could not arise in its fast decomposition. Second, $\mathrm{MeOOCCH_2CH_2C(O)Co(CO)_4}$ was reported to form in a solution reaction of $\mathrm{NaCo(CO)_4}$ with methyl 3-bromopropionate[40] as well as in the thermal rearrangement of $\mathrm{MeOOCCH(CH_3)Co(CO)_4}$[38] under 1 atm pressure of CO. Both processes require the transient formation of $\mathrm{MeOOCCH_2CH_2Co(CO)_4}$, which undergoes CO insertion rather than β-hydride elimination. Consequently, $\mathrm{HCo(CO)_4}$ could not be the product of a fast decomposition of $\mathrm{MeOOCCH_2CH_2Co(CO)_4}$.

Ethyl 2-bromopropionate behaves differently. $\mathrm{EtOOCCH(CH_3)Co(CO)_4}$ and $\mathrm{EtOOCCH(CH_3)Mn(CO)_5}$[5] are formed in good yields (≈60%) with $\mathrm{NaMn(CO)_5}$ and $\mathrm{NaCo(CO)_4}$, respectively. The byproducts in each case include ethyl acrylate, ethyl propionate, diethyl methylmalonate, and diethyl succinate, which were detected by GC–MS analyses.

Reactions of Dimethyl Dibromosuccinates with $\mathrm{NaMn(CO)_5}$, $\mathrm{NaCo(CO)_4}$, and $\mathrm{NaCo(CO)_3PPh_3}$. Both (±)- and *meso*-dimethyl dibromosuccinates undergo apparently instantaneous reactions with $\mathrm{NaMn(CO)_5}$ (CO atmosphere), $\mathrm{NaCo(CO)_4}$ (CO), or $\mathrm{NaCo(CO)_3PPh_3}$ (Ar) at rt. When $\mathrm{NaMn(CO)_5}$ is the limiting reagent, the reactions proceed according to the stoichiometry of eq 9.

$$\mathrm{MeOOCCHBrCHBrCOOMe + NaMn(CO)_5 \longrightarrow MeOOCH{=}CHCOOMe + BrMn(CO)_5 + NaBr} \qquad (9)$$

An excess of $\mathrm{NaMn(CO)_5}$ results in the conversion of the primary product, $\mathrm{BrMn(CO)_5}$, to $\mathrm{Mn_2(CO)_{10}}$ and NaBr under these conditions. $\mathrm{NaCo(CO)_4}$ and $\mathrm{NaCo(CO)_3PPh_3}$ also give the olefins, but the corresponding cobalt carbonyl halides decompose as they are formed, owing to their extreme instability. Nevertheless, CO evolution and precipitation of $\mathrm{CoBr_2}$ give clear signs of their transient formation. Considerable amounts of $\mathrm{Co_2(CO)_8}$ as well as $\mathrm{Co_2(CO)_6(PPh_3)_2}$ and $\mathrm{Co_2(CO)_7PPh_3}$ (a result of CO evolution) are also found.

When the anions are added as stock solutions in diethyl ether or THF, the saturated byproduct, dimethyl succinate, appears in small quantities. Its amount can be reduced by keeping the temperature low. No traces of any carbon–metal-bonded species or partly hydrogenated dimethyl bromosuccinate were identified, even in cold (>−30 °C) mixtures.

meso-Dimethyl dibromosuccinate gives mostly dimethyl fumarate at rt, although traces of dimethyl maleate (dimethyl *cis*-2-butenedioate) are also formed. At −30 °C, only the fumarate is formed—no traces of maleate were detected.

At rt, the racemic bromide also gives dimethyl fumarate but together with a significant amount (at least ≈10%) of dimethyl maleate. In reactions initiated at −30 °C, the cis and trans isomers are formed in about equal ratios.

Discussion

Synthetic Considerations. For syntheses of substitution products and their derivatives, the method described here sometimes has considerable advantages over homogeneous reactions in basic solvents.

(1) In spite of careful purification, THF and ether solvents sometimes lead to unexpected complications and poor yields of metal carbonyl derivatives. In some cases, the use of nonpolar solvents and heterogeneous reactions gives superior results.

(2) Solutions of alkyl-, acyl- or (π-allyl)cobalt and manganese carbonyls in hydrocarbons are often required for further studies. These solutions can be produced directly in heterogeneous reactions, thereby avoiding several workup steps that often lead to decomposition, especially when the product is very unstable.

(3) The probability of undesirable secondary reactions of the halides can be minimized. Because unreacted salts such as $\mathrm{NaMn(CO)_5}$ and $\mathrm{NaCo(CO)_4}$ remain largely in the solid phase, it is not necessary to use the halides in excess. Reactions can be carried nearly to completion, so that in the final solution the halides are not available for secondary reactions. This can be especially important for the less volatile halides.

(4) With either nonpolar or polar solvents, the presence of some $\mathrm{Co_2(CO)_8}$ and $\mathrm{Mn_2(CO)_{10}}$ in the product cannot be avoided. However, alkane solvents offer the advantage that $\mathrm{Co_2(CO)_8}$ precipitates almost quantitatively from chilled solutions. $\mathrm{Mn_2(CO)_{10}}$ can be removed only by chromatography if the desired product is stable enough to tolerate this procedure.

Mechanistic Considerations. Our data certainly do not permit us to sort out all of the previous suggestions concerning the mechanism of substitution and elimination in $\mathrm{RX/M(CO)}_n$ reactions, and we make no such attempt, but we are led to several conclusions. (1) Radicals are intermediates in many, perhaps all, of our reactions. (2) In some cases, at least, the radicals are formed in processes that precede carbon–metal bond formation. They do not arise in homolyses of alkylmetal carbonyl complexes (eq 4) but may be formed by SET (eq 3). (3) β-Elimination of hydrogen or bromine can occur by radical disproportionation in the same radical-pair intermediate as substitution. A vacant coordination site in an alkyl complex (eq 5) is not required.

The formation of both organic and inorganic radicals in the course of our reactions is suggested by the following observations:

(1) Coupling products, RR and $\mathrm{M_2(CO)_{2n}L_2}$, are formed in several reactions. They could be the products of dimerization of radicals escaped from a radical pair.

(2) Halomanganese carbonyls, $\mathrm{XMn(CO)_4L}$, are formed in reactions of $\mathrm{NaMn(CO)_5}$ and $\mathrm{NaMn(CO)_4PPh_3}$ with monohalides. $\mathrm{XMn(CO)_4L}$ complexes could be formed by halide atom abstraction of $\mathrm{Mn(CO)_4L}$ radicals from RX.[41]

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[38] Ungváry, F.; Markó, L. *Organometallics* **1986**, *5*, 2341.

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[40] Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1962**, *84*, 2499.

(3) $Mn_2(CO)_8(PPh_3)_2$, formed in the reactions of $NaMn(CO)_5$ when added PPh_3 was present, could arise by facile PPh_3 substitution for CO in $Mn(CO)_5$ radicals.[42]

(4) Dimethyl succinate, which is formed in large amounts, exceeding those of dimethyl fumarate, in reactions of dimethyl chlorosuccinate in the presence of THF or diethyl ether, could be a product of the reaction of the intermediate $MeOOCCH_2CHCOOMe$ radical with the solvent.

These observations point to radicals, but they do not exclude the possibility of radical formation exclusively from homolytic dissociations of metal–carbon bonds following S_N2 reactions (eq 4), for which there is ample evidence and precedent in analogous systems. There is kinetic evidence for the thermal homolysis of the C–M bond of alkylmetal carbonyl complexes.[43] In agreement with these results, we find that the products of the thermolysis of $CH_3CH_2CH{=}CHCH_2Mn(CO)_5$ are those expected from such homolysis. In addition, this kind of decomposition of $EtOOCCH(CH_3)Co(CO)_4$, leading to coupling products and three times as much ethyl propionate as ethyl acrylate, has been proposed in connection with the homogeneous reactions (thought to be S_N2) of $NaCo(CO)_4$ with secondary α-halo carboxylates.[44]

Mechanisms of radical formation that are formally related to S_N2/homolysis are supported by strong evidence found in recent studies of the annihilation of metal carbonyl anions and metal carbonyl cations. Radicals are formed by additions of the anions $^-M(CO)_n$, with the metal as nucleophilic site, to C≡O or C≡C bonds of ligands L in the cations $^+M'(CO)_mL$, followed by C–M bond homolyses.[45,46] For example, Kochi et al. reports[46] that the formally (η^1-allyl)molybdenum carbonyl complexes, which are intermediates in each of the reactions studied, undergo thermal homolysis. The radicals subsequently couple to dimers or $^\bullet Mo(CO)_3Cp$ reacts with added PPh_3 and alkyl halides to give products similar to those we obtained. It is also evident that primary complexes are much more stable than secondary ones. In both Kochi's work and ours, primary η^1-allyl complexes are formed at room temperature but secondary ones are not.

Even so, no direct analogy can be drawn between the mechanisms of cation–anion annihilation and those of the anion/halide reactions considered here, and we think it unlikely that the initial steps of our reactions are nucleophilic additions. In fact, for some of our cases, an S_N2 reaction followed by the homolysis of a carbon–metal bond can be excluded.

(1) We find that alkylmetal carbonyl complexes cannot be intermediates in the formation of radicals.

The products of reactions of PPh_3-substituted anions, both manganese and cobalt, do not include carbon–metal-bonded species, even at low temperatures, despite the fact that PPh_3 ligands generally stabilize carbon–metal bonds. Indeed, $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_3PPh_3$ and $MeOOCCH_2CH(COOMe)Co(CO)_3PPh_3$,[21] which were synthesized through alternative routes, decompose too slowly to account for their absence from reactions of $NaCo(CO)_3PPh_3$ with 4-bromo-2-pentene and dimethyl chlorosuccinate, respectively.

In addition, $MeOOCCH_2CH_2Mn(CO)_5$ and $MeOOCCH_2CH_2C(O)Co(CO)_4$ are known to be thermally stable,[38–40] yet neither could be prepared in a heterogeneous reaction of methyl 3-bromopropionate with $NaMn(CO)_5$ or $NaCo(CO)_4$. The intermediates $CH_3CH{=}CHCH(CH_3)Mn(CO)_5$ and $MeOOCCH_2CH(COOMe)Mn(CO)_5$ are formed in low yields in heterogeneous reactions of the corresponding halides with $NaMn(CO)_5$ below room temperature. Even at room temperature, they decompose relatively slowly in solution for that process to be responsible for the other products.

(2) For some reactions, giving stable organometallic products, radical intermediates can be trapped.

Although heterogeneous reactions of 1-bromo-2-pentene with $NaMn(CO)_5$ and $NaCo(CO)_4$ at room temperature give (η^1- or (η^3-allyl)metal complexes cleanly, the addition of $HMn(CO)_3dppe$ to the reaction mixture of $NaMn(CO)_5$ diverts ≈35% of the product to 2-pentenes and $Mn(CO)_3dppe$ radicals or $BrMn(CO)_3dppe$. Since $HMn(CO)_3dppe$ does not react with any of the reactants or products, it apparently scavenges intermediate 1-ethylallyl radicals that escape geminate reaction.

The yield of 2-pentenes, however, may not be an exact measure of escape, because $Mn(CO)_3dppe$ radicals could initiate a chain reaction leading to the formation of $BrMn(CO)_3dppe$. In turn, it is known that $Mn(CO)_3dppe$ radicals are not reactive enough to complete a chain reaction initiated by only trace amounts of escaped, or adventitous, radicals.[36c] In accordance with that, we observed the formation of free $Mn(CO)_3dppe$ radicals in substantial concentrations. Consequently, it is reasonable to assume that still significant, but less than 35%, amounts of 2-pentenes could derive from the trapping of allylic radicals by $HMn(CO)_3dppe$, which is a plausible extent of escape.

Assuming that a radical mechanism describes reactions of both primary and secondary allylic bromides, steric effects can explain the much larger extent of radical combination of primary allylic radicals with $^\bullet M(CO)_n$.

Taken all together, the data discussed above support the conclusion that radicals are formed first and then carbon–metal bonds, when the latter are formed at all.

The stereochemistries of reactions of (±)- and *meso*-dimethyl dibromosuccinates with metal carbonyl anions are also consistent with radical mechanisms. Heterolytic substitutions and eliminations tend to be highly stereospecific, but in our cases the reactions give mixtures of trans and cis products dimethyl fumarate and dimethyl maleate, respectively, in which the trans isomer is predominant. S_N2 reactions occur with inversion of configuration,[5] and the elimination of $DCo(CO)_4$ from $MeOOCCH_2CH(COOMe)Co(CO)_4$ is syn.[16,47] If the elimination of $BrM(CO)_nL$ from a hypothetic intermediate $MeOOCCHBrCH(COOMe)M(CO)_nL$ were also syn, then an S_N2 reaction of a metal carbonyl anion with (±)-dimethyl dibromosuccinate, followed by the elimination of $BrM(CO)_nL$, would give dimethyl maleate, contrary to what is found. The observed stereochemistries are consistent with radical intermediates. Indeed, a radical pathway has been suggested previously to explain the sole formation of *trans*-stilbene from both *meso*- and (±)-dibromostilbene in

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(41) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* **1985**, *4*, 42.

(42) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095.

(43) (a) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34. (b) Mancuso, C.; Halpern, J. *J. Organomet. Chem.* **1992**, *428*, C8.

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(47) Csizmadia, J.; Ungváry, F.; Markó, L. *Transition Met. Chem.* **1976**, *1*, 170.

reactions analogous to ours.[8a] In our cases, some cis product is formed along with the trans.

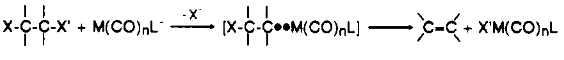
S_N2 processes are counterindicated also by weak nucleophilicities of $Mn(CO)_5^-$ and $Co(CO)_4^-$ [6] and the vigor of their reactions (as solids) with solutions of alkyl halides in hydrocarbon solvents. Since S_N2 reactions are often fastest in dipolar aprotic solvents, such facile reactions (of weak nucleophiles) with halides in nonpolar medium might be more consistent with single electron transfer (SET), which would explain the formation of radical intermediates. A caveat to this reasoning is that the initial steps of the reactions probably occur at the interface between the ionic solid and the nonpolar solvent. It is not clear how polar the interfacial environment is.

However, there is a plausible scenario for SET and radical formation at this interface. SET might be favored by a bridging sodium ion, as in $[M]^-{-}CO\cdots Na^+\cdots X{-}R$. Such an oxygen–sodium interaction is clearly present in the crystal structure of $NaCo(CO)_4$[48] and can be presumed for salts of this class on the basis of solution ion-pairing studies.[4b] The driving force for SET at the surface of the ionic solid could be the formation of Na^+X^- there, where its ions are attracted to those of the lattice as well as one another, along with two relatively stable, nonpolar free radicals. The SET transition state could be stabilized similarly.

These considerations may apply generally to reactions of solutes at interfaces between ionic solids and nonpolar solvents. Juaristi and Jiménez-Vázquez argue similarly in connection with observations that support SET from solid 1,3-dithianyllithium to 2-iodooctane in hexane.[49]

A correlation between charge delocalization and electron-transfer ability also has been pointed out and applied to the dehalogenation of halides, somewhat similar to those considered here, by $HFe(CO)_4^-$.[50]

If radicals form in a SET process, before that of carbon–metal bonds, then they are available for reactions leading to net elimination, that is, the formation of new carbon–carbon double bonds and metal carbonyl hydrides (from monohalides) or halides (from vicinal dihalides). This provides a new, radical mechanism for β-elimination.



$$X{-}C{-}C{-}X' + M(CO)_nL^- \xrightarrow{-X^-} [X{-}C{-}C{\bullet\bullet}M(CO)_nL] \longrightarrow C{=}C + X'M(CO)_nL \qquad (10)$$

We note that a similar disproportionation step was suggested recently for the reactions of tetramethylallene with $HMn(CO)_5$ and $HCo(CO)_4$,[15] but SET followed by this step has not been proposed previously as a mechanism of elimination of either HX or X_2 in reactions with $M(CO)_nL^-$.

We observed, furthermore, in accordance with earlier reports,[18] that if there are hydrogen and bromine atoms present in the C_β position, elimination of bromine is always favored over that of hydrogen, even when it takes place through radical intermediates.

Summary. Heterogeneous reactions of solid $NaMn(CO)_5$ and $NaCo(CO)_4$ with allylic bromides in hydrocarbon solvents sometimes offer significant synthetic advantages over similar reactions in homogeneous solutions in ethers. Heterogeneous reactions of 4-bromo-2-pentene give secondary allylmetal carbonyl complexes, the detection of which is reported here for the first time. There is substantial evidence that heterogeneous substitution and elimination reactions of allylic bromides and of certain halo esters appear to proceed through radical, not S_N2/E2, mechanisms. In some cases, it is clear that radicals are not formed through homolytic bond cleavage of intermediate alkylmetal carbonyls $RM(CO)_n$.

Experimental Section

General Methods. All manipulations were carried out under anaerobic conditions, using standard Schlenk technique.[51] Gastight Hamilton syringes were used for sample transfers.

Solvents and gases were carefully deoxygenated and dried prior to use. Solvents were freshly distilled from benzophenone ketyl under CO or Ar and stored in a sealed flask under the appropriate atmosphere in the dark. The gases were passed through columns filled with KOH, silica gel, P_2O_5, and an oxygen-scavenging BTS contact (BASF). Deuterated solvents were purchased from Aldrich. 4-Bromo-2-pentene (cis and trans, Wiley), ethyl 2-bromopropionate, and methyl 3-bromopropionate (Fluka) were obtained commercially and used without further treatment. 1-Bromo-2-pentene,[52] dimethyl chlorosuccinate,[53] and dimethyl dibromosuccinates[54] were prepared by literature methods.

IR spectra were recorded on Perkin-Elmer 599B (0.1-mm NaCl cuvettes) and Specord IR 75 (Zeiss, Jena, Germany; 0.057- and 0.21-mm CaF_2 cuvettes) spectrophotometers. The spectra were calibrated by CO,[55] benzene (1959.4 cm^{-1}), and polystyrene (1601.5 cm^{-1}). ^1H NMR spectra were recorded on 300-MHz Varian Unity 300, 90-MHz Varian EM-390, and 80-MHz BS-487 (Tesla, Brno, Czechoslovakia) spectrometers, using TMS as an internal standard. Gas chromatographic analyses were performed on a Hewlett-Packard 5830A chromatograph equipped with FID and capillary columns (1) SP-2330, 25 m (for maleates, fumarates, and succinates) and (2) SPB-1, 30 m. GC–MS spectra were obtained on a HP 5890 II gas chromatograph equipped with a 12-m HP-1 capillary column and a HP 5971A mass-selective detector.

Preparation of (2-Methyl-3-pentenoyl)cobalt Tricarbonyl Triphenylphosphine. $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_3PPh_3$ was prepared according to our general method. To a stirred suspension of solid $NaCo(CO)_4$ (290 mg, 1.5 mmol) in 10 mL of *n*-pentane under CO (1 atm total pressure) at −20 °C, 180 μL (223 mg, 1.5 mmol) of 4-bromo-2-pentene was injected. The temperature was allowed to rise slowly, over about 30 min, to 5 °C. During this time the mixture turned brown. Stirring was stopped, and after the solid phase had settled, a sample was taken for IR analysis, which showed the presence of $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_4$, along with some η^1-alkyl and η^3-allyl complexes. The solution was decanted and transferred to a second Schlenk tube containing 3 mL of a 0.5-M ethereal solution of PPh_3. This mixture was stirred at rt, and a voluminous ocher precipitate appeared instantly. It was filtered out, washed with 3 × 5 mL of *n*-pentane and then dried in vacuo. Yield: 600 mg (80%). The product, $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_3PPh_3$, was characterized by spectroscopic means.[56]

Although no decomposition was observed on exposure of $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_3PPh_3$ to air or on keeping the sample at rt for a short time, it can be stored for long periods only

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(53) Karrer, P.; Reschofsky, H.; Kaase, W. *Helv. Chim. Acta* **1947**, *30*, 271. Methanol and chlorosuccinic acid were esterified directly.

(54) *Organikum*; VEB Deutscher Verlag der Wissenschaften: Berlin, 1977; p 321.

(55) *IUPAC Commission on Molecular Structure and Spectroscopy: Tables of Wavenumbers for the Calibration of Infrared Spectrometers*; Butterworths: London, 1961; p 581.

(56) Data for $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_3PPh_3$ are as follows. IR (pentane): ν_{CO} = 2045 m, 1980 vs, 1959 vs, 1708 sh, 1676 w cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): δ = 1.06 (d, 3H, $-CH-CH_3$), 1.58 (d, 3H, $=CH-CH_3$), 3.95 (m, 1H, $-CH-$Me), 5.44 (m, 2H, $-CH{=}CH-$), 7.26 (m, 15H, PPh_3) ppm.

at dry ice temperature. In contrast, $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_4$ readily decomposes in solution (benzene or chlorinated hydrocarbons), even at low temperatures.

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