The $M(\eta\text{-}C_5H_5)$ unit, where M = Rh and Ir, shows a preference for complexing to non-conjugated dienes rather than conjugated dienes;[10-12,36-38] in the case of cobalt, however, this preference is not paticularly marked. Thus 1,3,5-cyclooctatriene can bond either as a 1,2,5,6 or a 1-4 ligand to $Co(\eta\text{-}C_5H_5)$.[39] This behavior contrasts with that of the $M(CO)_3$ unit of Fe, Ru, and Os and CoL_3^+; These d^8 ML_3 fragments prefer to bind conjugated dienes.[40] Elian and Hoffman[14] have discussed the preference of the $M(CO)_3$ unit and concluded that the frontier orbitals consist of an empty σ acceptor orbital and two π orbitals occupied by two electrons. The conjugated diene provides a good donor orbital, ψ_2, of the right symmetry to interact with one of the π components and a good acceptor orbital, ψ_3, to interact with the other. In a nonconjugated diene both the donor and acceptor properties would be expected to be poorer. As the $M(\eta\text{-}C_5H_5)$ fragment is claimed to be isolobal with $M(CO)_3$ and in the case of Co, Rh, and Ir the electron occupancy is similar to that described above, the absence of preference for conjugated dienes is rather surprising.

It is difficult to ascertain from our studies whether the ionization energy data bear out the relative acceptor properties of the two types of diene. The ionization energy of the $2\pi_+$ band is very sensitive to substituent effects, for example, it shifts 0.1 eV to lower IE on the introduction of one methyl group on the diene (II and III) and 0.7 eV on permethylation of the ring (V and Va). Comparable substituent effects might be envisaged for VII and V, and in these cases the nonconjugated diene complex V does show a lower (0.1 eV) $2\pi_+$ band than the conjugated diene complex VII. However the difference is not striking.

What is apparent from the ionization energy pattern, is that there appears to be substantially more mixing in the $1\pi_-$ and $2\pi_-$ orbitals in the nonconjugated diene complexes than the conjugated diene complexes. This is because the π_- orbital of the nonconjugated dienes lies closer in energy to the metal-ring e_1 orbital. It may well be that the resulting delocalization of electrons is the important stabilizing force.

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Reactions of Coordinatively Unsaturated Cobalt-Alkene Complexes Generated by Metal Atom Condensation Techniques

Susan A. Locke and Philip B. Shevlin*

Department of Chemistry, Auburn University, Auburn, Alabama 36849

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The cocondensation of cobalt atoms with ethylene at 77 K generates a labile cobalt-ethylene complex. Addition of either acetaldehyde or formaldehyde to this complex brings about insertion of the ethylene into the aldehydic C-H bond and reduction of the aldehyde. Thus, the products of the reaction of acetaldehyde with the $Co\text{-}C_2H_4$ complex are 2-butanone, 2-butanol, ethanol, ethyl acetate, and methane. Addition of CO and H_2 to the $Co\text{-}C_2H_4$ complex results in the hydroformylation of the ethylene and reduction of the CO. Substitution of propylene for ethylene generates a complex that mainly effects reduction of the added aldehyde.

Introduction

There have been numerous investigations of the cocondensation of metal atoms with organic ligands in which coordinatively unsaturated organometallic intermediates have been implicated chemically[1] and identified spectroscopically.[2] An interesting example of the latter is the low-temperature matrix reaction of metal atoms with ethylene in which the formation of mono-, bis-, and tris(ethylene) complexes of general formula $M_n(C_2H_4)_m$ (n, m = 1, 2, 3, 4; M = Co, Ni, Pd, Cu) have been reported.[2,3] In the case of cobalt, complexes of the formula $Co_n(C_2H_4)_m$ (n, m = 1, 2, 3, or 4) have been observed spectroscopically either in an inert argon matrix or in a pure ethylene matrix.[3a] In analogy with other unsaturated organometallic intermediates, it is expected that species generated in this manner should be capable of effecting novel transformations of added substrates. In this connection, we report the reaction of the coordinatively unsaturated cobalt-ethylene intermediates, which have been observed spectroscopically,[3a] with simple aldehydes. The result of this

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reaction is to effect the insertion of ethylene into the aldehydic carbon–hydrogen bond and to reduce the aldehyde. Such ethylene insertion reactions are important in both the stoichiometric and catalytic hydroformylation[4] and hydroacylation reactions.[5] Although both of these well-studied reactions involve unsaturated organometallic intermediates, this report is the first example of a system in which such an intermediate is generated by a metal atom cocondensation technique.

Results and Discussion

Reaction of Cobalt Atoms with Acetaldehyde. The reactions of metal atoms with carbonyl compounds to form acetylacetonates[6] and to generate aldol and pinacol type products[7] have been reported. However in the present case, the cocondensation of cobalt atoms with acetaldehyde alone is disappointing in that only low yields of methane are produced. The yield of methane can be improved by decomposing the nonvolatile residue with either distilled water or concentrated hydrochloric acid to give 4.1% and 10.3% methane, respectively. The formation of methane can be rationalzied by assuming insertion of cobalt into the aldehydic carbon–hydrogen bond followed by methyl migration and reductive elimination (eq 1). This mechanism is consistent with the fact that reaction of cobalt with acetaldehyde-2,2,2-d_3 yields methane-d_3.

$$\mathrm{Co} + \mathrm{CH_3CHO} \xrightarrow[77\ \mathrm{K}]{\text{cocondense}} \mathrm{CH_3C({=}O){-}Co{-}H} \rightarrow \mathrm{CH_3Co(H){-}CO} \xrightarrow{\text{elimination}} \mathrm{CH_4} \quad (1)$$

Reactions of Cobalt, Ethylene, and Acetaldehyde. Cocondensation of cobalt and ethylene at 77 K followed by the addition of acetaldehyde to the cobalt–ethylene matrix gives a dramatically different result. After the solution was warmed to room temperature and left standing for 24 h, the products in eq 2 are identified. Typical yields are shown in Table I.

$$\mathrm{Co} + \mathrm{C_2H_4} \xrightarrow[77\ \mathrm{K}]{\text{cocondense}} \mathrm{Co}_n(\mathrm{C_2H_4})_m \xrightarrow[\text{(2) warm to room temp and stand for 24 h}]{\text{(1) CH}_3\text{CHO at 77 K}} \mathrm{CH_4} + \mathrm{CH_3CH_2OH} + \mathrm{CH_3C({=}O)CH_2CH_3} + \mathrm{CH_3C(OH)HCH_2CH_3} + \mathrm{CH_3C({=}O)OCH_2CH_3} \quad (2)$$

Perhaps the most interesting of these products is 2-butanone which may be rationalized by the sequence of reactions in eq 3 in which initial reaction of cobalt with ethylene is postulated to yield cobalt–ethylene complex **1**. The spectroscopic investigations of Ozin, Hanlan, and Power[3a] show that such a complex will not be mononuclear in cobalt at 77 K, and these workers postulate a binuclear complex of the formula $\mathrm{Co_2(C_2H_4)_2}$.

We propose that the reaction of acetaldehyde with **1** proceeds via insertion of the cobalt into the aldehydic C–H bond to give acyl complex **2**. Subsequent insertion of an ethylene molecule into the cobalt–hydrogen bond of **2**

Table I. Products of the Reactions of Cobalt–Alkene Complexes with Aldehydes

reactants (mmol)			products (% based on Co evaporated)					
Co	alkene	substrate						
11.1		$\mathrm{CH_3CHO}$ (100)	$\mathrm{CH_4}$[a] (trace)					
4.0		$\mathrm{H_2C{=}O}$ (50)	$\mathrm{HCO_2Me}$ (2.87)	MeOH (trace)				
14.7	$\mathrm{CH_2{=}CH_2}$ (141)	$\mathrm{CH_3CHO}$ (88.9)	$\mathrm{CH_4}$ (3.29)	$\mathrm{CH_3CH_2OH}$ (13.43)	$\mathrm{CH_3C({=}O)CH_2CH_3}$ (7.32)	$\mathrm{CH_3C(OH)HCH_2CH_3}$ (3.59)		EtOAc (4.19)
9.4	$\mathrm{CH_2{=}CH_2}$ (25)	$\mathrm{H_2C{=}O}$ (100)	$\mathrm{HCO_2Me}$ (24.12)	MeOH (7.76)	$\mathrm{CH_3CH_2CH_2OH}$ (5.13)	$\mathrm{CH_3CH_2CHO}$ (27.03)		
10.2	$\mathrm{CH_2{=}CH_2}$ (50)	$\mathrm{H_2C{=}O}$ (50)	$\mathrm{HCO_2Me}$ (6.04)	MeOH (1.13)	$\mathrm{CH_3CH_2CH_2OH}$ (4.51)	$\mathrm{CH_3CH_2CHO}$ (18.61)		
6.6	$\mathrm{CH_2{=}CH_2}$ (50)	CO (18) + $\mathrm{H_2}$ (18)	$\mathrm{HCO_2Me}$ (0.52)	MeOH (0.23)	$\mathrm{CH_3CH_2CH_2OH}$ (9.63)	$\mathrm{CH_3CH_2CHO}$ (9.45)		
7.5	$\mathrm{CH_2{=}CH_2}$ (257.9)	PhCHO (49)	PhH (trace)[b]	$\mathrm{PhCH_2OH}$ (trace)[b]				
8.1	$\mathrm{CH_2{=}CH_2}$ (255.5)	$\mathrm{CH_3CH_2CHO}$ (69.4)		$\mathrm{CH_3CH_2CH_2OH}$ (12.20)	$\mathrm{CH_3CH_2C({=}O)CH_2CH_3}$ (2.06)	$\mathrm{CH_3CH_2C({=}O)OPr}$ (0.51)		
9.5	$\mathrm{CH_3CH{=}CH_2}$ (141)	$\mathrm{CH_3CHO}$ (88.9)	$\mathrm{CH_4}$ (5.4)	$\mathrm{CH_3CH_2OH}$ (75.61)	$\mathrm{CH_3C({=}O)CH_2CH_2CH_3}$ (2.09)	$\mathrm{CH_3C({=}O)CH(CH_3)_2}$ (0.67)	$\mathrm{CH_3C(OH)HCH_2CH_2CH_3}$ (0.36)	EtOAc (0.90)

[a] Hydrolysis of resulting matrix increased the yield of methane produced to 4.1% using $\mathrm{H_2O}$ and 10.3% using concentrated HCl. [b] Identified by GC/MS.

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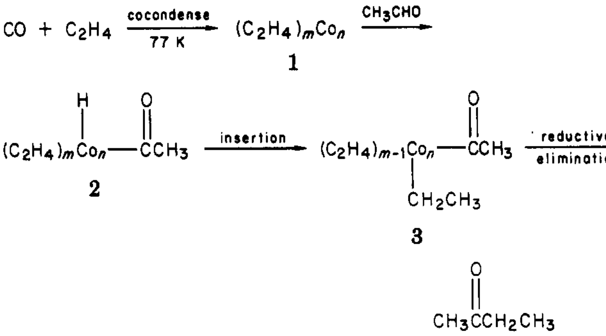
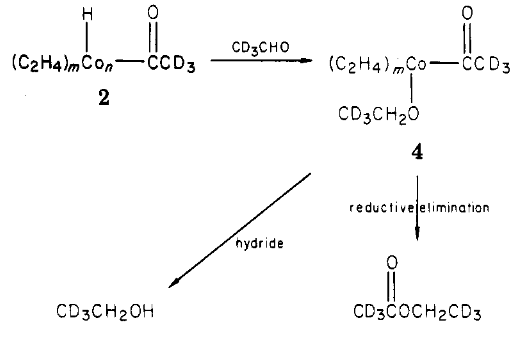


(3)

yields the alkylcobalt acyl compound **3** which can undergo reductive elimination of 2-butanone. The role of ethylene in 2-butanone formation is demonstrated by the use of 1,2-dideuterioethylene in a cocondensation reaction with cobalt followed by the addition of acetaldehyde. The methane, ethanol, and ethyl acetate products are deuterium free, while both the 2-butanone and 2-butanol contain two deuteriums. In the case of 2-butanone, the mass spectrum is sufficient to show that the acyl group (m/e 43) is deuterium free and that the ethyl group (m/e 31) contains two deuteriums. In another labeling experiment, the cobalt–ethylene-d_0 matrix is reacted with acetaldehyde-*2,2,2*-d_3 to generate CD_3H, $CD_3CH_2OH(D)$, $CD_3COCH_2CH_3$, and $CD_3COOCH_2CD_3$. Small amounts of 2-butanol are also shown to be present by GC; however, the yields are too low to allow ^1H NMR analysis of the deuterium distribution. Thus in both labeling experiments, 2-butanone is labeled in the manner expected from the process in eq 3. A number of the reactions postulated in eq 3 have recently been observed upon treatment of $RhCl(PMe_3)_3$ with aldehydes.[5g] This rhodium complex inserts in aldehydic C–H bonds to generate hydridoacylrhodium complexes which effect the hydroacylation of ethylene.

The use of acetaldehyde-*2,2,2*-d_3 also allows an evaluation of the mechanism of formation of the other products. It is reasonable to postulate that the ethanol arises from the reduction of acetaldehyde by a cobalt hydride such as **2**. As shown in eq 4, this process would result in the observed ethanol-*2,2,2*-d_3. The deuterium distribution in the ethyl acetate is consistent with a mechanism in which this species is generated by reductive elimination on acylcobalt ethoxide, **4**.[8] The 2-butanol is postulated to result from the reduction of 2-butanone by hydride **2**.



(4)

Further evidence for the intermediacy of acylcobalt complex **2**, from which all the products can be formed, is obtained by the addition of n-propyl alcohol (0.5 mmol) to the reaction mixture. This experiment results in the formation of n-propyl acetate (0.64%) as well as products normally obtained. In this case, the n-propyl alcohol reacts with intermediate cobalt acyl **2** to produce propyl acetate. The reaction of acylcobalt complexes with alcohols to produce esters (eq 5) has been previously reported.[8]

$$L_n\text{—Co—C(=O)-CH}_3 + \text{ROH} \rightarrow \text{CH}_3\text{—C(=O)-OR} \quad (5)$$

From the mechanisms in eq 3 and 4, it is clear that there are two types of products formed in the reaction between cobalt, ethylene, and acetaldehyde. Equation 3 postulates a mechanism in which 2-butanone arises from a reaction between cobalt, ethylene, and acetaldehyde and is thus an "ethylene-derived" product. However, the products shown in eq 4 and methane result only from the interaction of cobalt and acetaldehyde and are "non-ethylene-derived" products. It should be noted, however, that it is essential that the cobalt be present as a cobalt–ethylene species in order for ethanol and ethyl acetate to form. The reaction of cobalt with acetaldehyde alone produces neither ethanol nor ethyl acetate (vide supra).

Table II shows that the ratio of "ethylene derived" products to "non-ethylene-derived" products decreases when the cobalt–ethylene matrix is allowed to warm before the addition of acetaldehyde. Allowing the matrix to warm to 156 K before addition of acetaldehyde brings about a fourfold decrease in the 2-butanone yield as compared to the case in which acetaldehyde is added at 77 K. The "non-ethylene-derived" product yields are unaffected. Increasing the temperature of the matrix to 195 K before addition of acetaldehyde brings about a more dramatic decrease in the yield of 2-butanone with the yields of the "non-ethylene-derived" products staying approximately constant over the temperature range. If the excess ethylene is removed at 156 or 195 K before acetaldehyde is added to the matrix, the yields of all products are reduced. The decrease in "ethylene-derived" product yields is almost complete when the matrix is warmed to 195 K and the excess ethylene removed before addition of acetaldehyde.

We have also examined the effect of the concentration of ethylene on the product yields as shown in Table II. Decreasing the ethylene:cobalt ratio from 125:1 to 9.6:1 decreases the ratio of "ethylene-derived" products to "non-ethylene-derived" products without any significant change in the total yield of products. Decreasing the ethylene:cobalt ratio further to 0.7:1, while maintaining an eightfold excess of acetaldehyde, reduces the "ethylene-derived" products markedly. However, the total yield is only decreased from 31.8% to 25.9%. Changing the cobalt:ethylene:acetaldehyde ratio further to 1:1.4:1.4 reduces the product yield drastically to 2% ethanol and no "ethylene-derived" products. These observations demonstrate that, when acetaldehyde is added at 77 K, the yield of "ethylene-derived" products is dependent on the concentration of ethylene. These results are in accord with a mechanism in which there is competition between the processes shown in eq 3 and 4. As the concentration of ethylene decreases, the process in eq 4 becomes more important.

Attempts To Trap Low-Temperature Intermediates by Ligand Addition. Since the intermediacy of a Co–C_2H_4 complex at 77 K is implied by these experiments and such intermediates have been observed spectroscopically, we have attempted to trap this complex by the addition of carbon monoxide to the low-temperature matrix. However, the only isolable products are $Co_2(CO)_8$ (1.0%) and $Co_4(CO)_{12}$ (3.7%) as determined by IR spectroscopy. Although these experiments do not result in the trapping of the Co–C_2H_4 species, they do serve to further confirm the intermediacy of an active cobalt species in these systems. Addition of CO to a matrix of deposited Co metal at 77 K gives no cobalt carbonyls upon warming.

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Table II. Products of the Reactions of Cobalt-Ethylene Complex with Acetaldehyde

reactants, mmol					products, % based on Co evaporated						
cobalt	C_2H_4	C_2H_4/Co	CH_3CHO	T,[a] K	CH_4	EtOH	$CH_3C(=O)CH_2CH_3$	$CH_3C(OH)HCH_2CH_3$	EtOAc	total	$CH_3C(=O)CH_2CH_3$ + $CH_3C(OH)HCH_2CH_3$/CH_4 + EtOH + EtOAc
8.0	1000	125.0	88.9	77		9.62	15.00	1.62	4.41	30.65	1.18
14.7	141	9.6	88.9	77	3.29	13.43	7.32	3.59	4.19	31.82	0.52
12.2	9	0.7	88.9	77	7.55	14.32	1.11	0.55	2.43	25.96	0.07
7.2	10	1.4	10	77		2.20				2.02	
21.2	141[c]	6.7	88.9	156	3.74	17.07	1.82	2.27	1.66	26.56[c]	0.18
9.4	10.8[b]	1.1	35.6	156	10.51	5.97	1.15	0.81	1.56	20.00[b]	0.11
4.0	255.6[c]	63.9	88.9	195	8.82	18.41	0.24	0.53	0.24	28.24[c]	0.03
7.1	255.6[b]	36.0	88.9	195	14.25	1.14	0.03	0.13	0.002	15.55[b]	0.01

[a] All cocondensations of cobalt and ethylene were carried out at 77 K. T is the temperature to which the cobalt/ethylene matrix was warmed before addition of acetaldehyde. [b] The cobalt-ethylene complex was warmed to T under dynamic vacuum, and any excess ethylene not bound to the cobalt was removed. [c] The cobalt-ethylene complex was warmed to T, and the excess ethylene was not removed.

At attempt to trap the acylcobalt complex in this system was also made. It was expected that addition of CO to the low-temperature matrix after the addition of acetaldehyde would result in the formation of acylcobalt tetracarbonyl, **5**. However **5** is reported to decompose at 253 K[9] and can itself be trapped as the stable triphenylphosphine complex **6**.[10] Accordingly, we have added CO to the matrix at 77

$$(C_2H_4)_mCo_n(H){-}C(=O){-}CH_3 \xrightarrow{CO} \underset{\mathbf{5}}{(CO)_4Co{-}C(=O){-}CH_3} \rightarrow \underset{\mathbf{6}}{(CO)_3(PPh_3)Co{-}C(=O){-}CH_3}$$

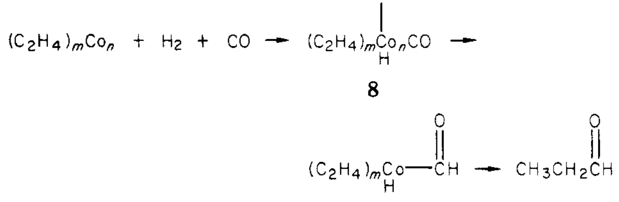
K and allowed the mixture to warm in the presence of triphenylphosphine. Although this procedure did yield a residue whose mass spectrum showed a parent ion at m/e 448 and carbonyl IR absorptions at 1978 and 1958 cm^{-1}, no evidence for the acyl methyl group could be detected in the ^1H NMR spectrum. Hence we conclude that a complex mixture of products is obtained in which traces of **6** may be present.

Reaction of the Cobalt-Ethylene Complex with Other Aldehydes. The products of the reaction of the cobalt-ethylene complex with formaldehyde (eq 6) are analogous to those observed in the acetaldehyde reaction.

$$Co + C_2H_4 \xrightarrow[\text{(2) } H_2CO\text{, warm to room temp and stand 24 h}]{\text{(1) cocondense 77 K}} CH_3OH + HCO_2Me + CH_3CH_2CHO + CH_3CH_2CH_2OH \quad (6)$$

The yields in Table I demonstrate that the ratio of "ethylene-derived" products to "non-ethylene-derived" products is larger in the case of formaldehyde than in the acetaldehyde reaction. This may simply be due to the fact that the smaller formaldehyde molecule becomes mobile on the matrix at a lower temperature than does acetaldehyde and is thus better able to undergo reaction before the cobalt-ethylene complex can decompose. A steric effect may also slow the reaction of larger aldehydes with the cobalt-ethylene complex. Table I demonstrates a reduced reactivity of the cobalt-ethylene complex as the size of added aldehyde is increased and its mobility is decreased.

One drawback to these ethylene insertion reactions is the fact that excess aldehyde is always reduced in a competing reaction. In the case of formaldehyde a simply way to avoid this may be to react the cobalt-ethylene complex with a mixture of carbon monoxide and hydrogen rather than with formaldehyde. If the hydridoformyl complex **7** were to form in the absence of excess aldehyde, little reduction of formaldehyde could occur. Table I demonstrates that, when CO and H_2 are substituted for formaldehyde in this system, the ratio of "ethylene-derived" products to "non-ethylene-derived" products increases dramatically. It is logical to postulate that this reaction proceeds via the dihydride species **8**. Interconversion of



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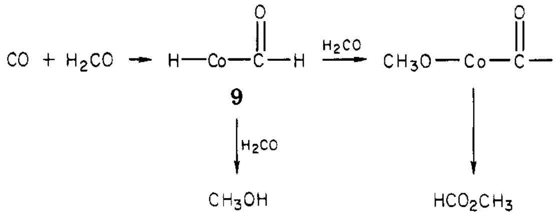
hydrido carbonyl complexes and formyl complexes has been previously postulated in the hydrogenation of Co.[12-18] An alternate mechanism for propanol formation involves initial insertion of ethylene into the Co–H bond of 8 followed by CO insertion and reductive elimination.

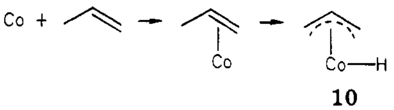
Cocondensation of cobalt directly with formaldehyde in the absence of ethylene produces methanol and methyl formate as shown in Table I. These products can easily arise from an intermediate hydridoformyl complex, 9 as shown in eq 7. A similar disprortionation of formaldehyde to methyl formate has been observed by Caulton and Goeden[19] with use of the soluble copper hydride $(HCuPPh_3)_6$ as a catalyst.



(7)

Reaction of Cobalt with Propene and Acetaldehyde. Attempts to extend the olefin insertion reaction to propene, an alkene with allylic hydrogens, lead to the products shown in eq 8. The main course of this reaction is reduction of the acetaldehyde to ethanol (75% yield, Table I). This fact may be rationalized if one assumes that the major reaction occurring upon cocondensation of cobalt with propene is the formation of η^3-allyl hydride 10 which acts to reduce the acetaldehyde. Evidence supporting the formation of (η^3-allyl)metal hydrides in the cocondensation of metal atoms with propene has been reported.[20] Timms[20a] has demonstrated that (η^3-allyl)tris(trifluorophosphine)cobalt is produced when cobalt, propene, and trifluorophosphine are cocondensed.

$$\mathrm{Co} + \mathrm{CH_3CHCH_2} \xrightarrow[\text{(2) } \mathrm{CH_3CHO}\text{, warm to room temp and stand for 24 h}]{\text{(1) cocondense 77 K}} \mathrm{CH_4} + \mathrm{EtOH} + \mathrm{CH_3C({=}O)CH_2CH_2CH_3} + \mathrm{H_2CH_2CH_3CH_3C(OH)HC} + \mathrm{CH_3C({=}O)CH_2C(CH_3)HCH_3} \quad (8)$$



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(9)

Insertion of propene into the aldehydric carbon–hydrogen bond of acetaldehyde gives a ratio of straight chain ketone to branched chain ketone of 3:1 (Table I). This result may be compared to the hydroformylation reaction, which, although temperature dependent, gives a straight to branched chain ratio of 1.6:1 (using $Co_2(CO)_8$ for hydroformylation of propene at P_{CO} = 2.5 atm).[4] It is possible that some of the processes we observe may involve free radical addition of the acyl radical to the alkene.[21] If this is the case however, one would expect higher yields going from unactivated ethylene to propene and perhaps more stereoselective addition of the acyl radical to propene.

Conclusion

These investigations demonstrate that labile cobalt–ethylene complexes, generated by metal atom deposition techniques, may be used to effect chemical transformation of added substrates. In this case, the high reactivity of the $Co–C_2H_4$ complex renders an ethylene insertion facile at low temperatures. However, the lability of the complex allows reactions only with those substrates whose melting points are low enough to bring about mobility on the matrix before the decomposition temperature of the $Co–C_2H_4$ complex is reached. Metal atom reactions, which by their nature involve stepwise addition of ligands and the intermediacy of unsaturated centers, should readily lend themselves to a variety of similar processes. Reactions of this type that have been reported include initiation of polymerization,[22] dimer and trimer formation,[23] hydrogenations with reactive hydrides,[24] and the production of hydrogenation catalysts.[25] Although there are a number of reactions with utilize an unsaturated metal center to effect the stoichiometric and catalytic insertion of an alkene into an adehydic C–H bond,[5] this is the first example of such a reaction in which the unsaturated complex is generated by a metal atom condensation. We are currently investigating systems in which we hope to modify the ligand in such a way as to decrease the lability of the initial complex while maintaining its high reactivity.

Experimental Section

Cobalt vapor was produced by resistively heating (6 V, 45 A) pieces of cobalt metal (Ventron, Alfa Division) in an alumina crucible (G.T.E. Sylvania Emissive Products) supported between two water-cooled brass electrodes in an apparatus based on designs by Skell, Timms, and Klabunde.[26] The substrate inlet tube was designed in such a way that the substrate and metal vapor cocondensed in the same region on the cold (77 K) vessel walls. A glass heat shield was suspended from the electrodes between the crucible and inlet tube. This served the dual purpose of (a) keeping the electrodes rigid and preventing the breaking of the crucible during the reaction due to vibration and (b) protecting the incoming substrate from pyrolysis on the hot crucible.

Cobalt was typically evaporated at a rate of 0.5–1 g in 0.5 h under vacuum of 2×10^{-5} torr. Of the cobalt evaporated, 14.8% was determined to be coated on the heat shield and inlet tube. All the yields of products reported are based on the remaining 85% cobalt. However, although all of the yields have been calculated by the same method and can thus be used for comparison with one another, they are lower than the actual yield because the cobalt condensing on the brass electrodes was not measured and is included with the weight of cobalt reacting with the substrate.

Reaction of Cobalt, Ethylene, and Acetaldehyde. In a typical experiment cobalt (14.7 mmol) was cocondensed with degassed ethylene (141 mmol) on a cold (77 K) surface. The

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reactor was sealed off, and acetaldehyde (88.9 mmol) was cocondensed on top of the cobalt–ethylene matrix. The reactor was allowed to warm to room temperature and stand under static vacuum for 24 h. The products were fractionated through traps at 195 K (dry ice/acetone) and 77 K (liquid N_2) and an activated charcoal trap at 77 K. The activated charcoal trapped the methane which was identified and quantitated by IR spectroscopy. Traces of carbon monoxide were also sometimes observed in the 77 K charcoal trap. The contents of 195 K trap were analyzed by gas chromatography/mass spectrometry (GC/MS), using Propack Q and Graphpac C columns, with toluene as an internal standard. Retention times and mass spectra agreed with those of authentic samples. Products and yields are shown in Table I. In addition to the products in Table I, ethane was generated in 7.4% yield. However ethane (3.1%) was also produced in the reaction between Co atoms and ethylene.

Reaction of Cobalt, Ethylene-d_2, and Acetaldehyde. 1,2-Dideuterioethylene was prepared by the reduction of acetylene-d_2 using a freshly prepared aqueous solution of Cr^{II}.[27] The product alkene was shown by mass spectral analysis to contain 17% unreacted acetylene-d_2. The mixture (8 mmol) was reacted with cobalt (9.3 mmol) followed by the addition of acetaldehyde (35.6 mmol) as above. The mass spectrum of unlabeled 2-butanone showed *m/e* (90 eV, relative intensity) 43.0 (100 CH_3CO^+), 72.0 (21.3, M^+), and 73.0 (2.0, M + 1), while that of the 2-butanone from this reaction showed *m/e* (90 eV, relative intensity) 43.0 (100, CH_3CO^+, 74.1 (15.9, M^+), 75.1 (8.3, M + 1), 76.1 (1.9, M + 2), and 31.1 (12.7, M − 43). Thus is was concluded that the 2-butanone produced contained 100% deuterium uncoporation in the ethyl group.

Reaction of Cobalt, Ethylene, and Acetaldehyde-*2,2,2-d*$_3$. Acetaldehyde-*2,2,2-d*$_3$ (92.9% d_3, 88.9 mmol), prepared by the method of Baldwin and Pudussery,[28] was added to a matrix consisting of cobalt (11.7 mmol) and ethylene 48.8 mmol) at 77 K. Products were identified by GC retention times and by ^1H NMR (90 MHz). The ^1H NMR analysis showed deuterium distribution in the products as follows: CD_3CH_2OH (D), $CD_3CO_2CH_2CD_3$, and $CD_3COCH_2CH_3$. IR spectroscopy showed CD_3H but no CD_2H_2 or CDH_3.

Reaction of Cobalt, Ethylene, and Acetaldehyde Followed by Addition of *n*-Propyl Alcohol to Nonvolatile Residue. Cobalt (12.2 mmol), ethylene (9 mmol), and acetaldehyde (88.9 mmol) were reacted in the usual manner. The reaction mixture was allowed to stand for 1 h before the products were pumped out and fractionated as described above, to produce methane (3.7%), ethanol (3.17%), and 2-butanone (0.05%). *n*-Propyl alcohol (0.5 mmol) was added to the nonvolatile residue that was then allowed to stand for 24 h before working up in the usual manner. Yields of products were methane (3.48%), ethanol (11.15%), 2-butanone (1.0%), 2-butanol (0.55%), ethyl acetate (2.43%), and propyl acetate (0.64%). All products were identified by GC/MS.

Reaction of Cobalt, Ethylene, and Formaldehyde. The reaction was carried out as above with cobalt, (10.2 mmol, ethylene (50 mmol), and formaldehyde (100 mmol). Formaldehyde was prepared by the decomposition of paraformaldehyde and passed through a 195 K trap before being added on top of the cobalt–ethylene matrix. Products and yields are listed in Table I.

Reaction of Cobalt, Ethylene, Carbon Monoxide, and Hydrogen. Cobalt (6.6 mmol) and ethylene (50 mmol) were cocondensed as above. An equimolar mixture of carbon monoxide and hydrogen (18 mmol) was added to the reactor, and the cobalt-ethylene matrix was allowed to warm up in the usual way. Products and yields are shown in Table I.

Reaction of Cobalt, Ethylene, and Propanal. The reaction was carried out as above with cobalt (8.15 mmol), ethylene (255.5 mmol), and propanal (69.4 mmol). Products and yields are shown in Table I.

Reaction of Cobalt, Ethylene, and Benzaldehyde. The reaction was carried out as above with cobalt (7.55 mmol), ethylene (257.9 mmol), and benzaldehyde (49.0 mmol). Products and yields are shown in Table I.

Reaction of Cobalt, Propene, and Acetaldehyde. The reaction was carried out as above with cobalt (9.5 mmol), propene (141 mmol), and acetaldehyde (88.9). Products and yields are shown in Table I.

Reactions of Cobalt with Acetaldehyde. In these experiments cobalt (11.1 mmol) and acetaldehyde (100 mmol) were cocondensed at 77 K and treated as above. A trace of methane was observed at the 77 K charcoal trap, and only acetaldehyde was present in the 195 K trap. Hydrolysis of nonvolatile residue in the reactor with water or concentrated hydrochloric acid increased the yields of methane to 4.1% and 10.3%, respectively.

Reaction of Cobalt with Formaldehyde. Formaldehyde (50 mmol) was cocondensed with cobalt (4.0 mmol) at 77 K. Products and yields are shown in Table I.

Control Experiments. Cocondensation of cobalt (21.4 mmol) with acetaldehyde (178 mmol) followed by the addition of ethylene (10.6 mmol) gave only methane (2.25%).

Cobalt (7.7 mmol) was deposited alone on a cold (77 K) surface and allowed to warm to room temperature. After the solution was cooled to 77 K, an equimolar mixture of ethylene and acetaldehyde (178 mmol) was added. The only product observed was methane (0.19%).

Cocondensation of cobalt with an equimolar mixture of alkene and acetaldehyde at 77 K produced methane (1.10%), using ethylene (50 mmol), and methane (2.45%) and ethanol (3.03%) using propylene (141 mmol).

Addition of Ligands to the Low-Temperature Matrix. Carbon Monoxide Trapping Experiments. Cobalt and ethylene were cocondensed at 77 K, and the reactor was sealed off. Carbon monoxide (equimolar to the amount of ethylene used) was added to the reactor that was then warmed to room temperature and allowed to stand for 0.5 h. The volatile contents of the reactor were pumped out, and $Co_2(CO)_8$ (0.12 mmol, 1.0%) was collected in a 195 K trap. After the reactor was filled with nitrogen, the top was removed and replaced by a sublimator head. The reactor was evacuated and heated gently (below 323 K) to sublime $Co_4(CO)_{12}$ (0.44 mmol, 3.7%) onto the cold finger at 195 K. The $Co_2(CO)_8$ and the $Co_4(CO)_{12}$ were identified by IR spectroscopy.

Attempts To Trap the Cobalt Acetyl Complex as Acetylcobalt Tricarbonyl Triphenylphosphine, 6. Triphenylphosphine (11.5 mmol) was placed in the bottom of the metal atom reactor and the crucible positioned in such a manner that Co could not condense on triphenylphosphine. Ethylene (100 mmol) and Co (22.2 mmol) were cocondensed in the usual manner at 77 K, and acetaldehyde (88.9 mmol) was added. Reactants were warmed to 195 K and allowed to stand for 0.5 h. The reactor was cooled to 77 K, and 10 mL of sodium-dried THF was condensed in to act as a solvent for the reaction. Carbon monoxide (50 mmol) and argon (1 atm) were added, and the reactor was allowed to warm to 273 K and finally to room temperature over a 24-h period. Volatiles were pumped out, and the reactor was opened under argon. THF (10 mL) was added to extract products. The IR spectra of the THF solution shows carbonyl absorbtion bands at 1978 and 1958 cm^{-1} which were also present in the IR spectrum of a THF solution of an authentic sample of **6**. However no ν(C=O) acyl stretch was observed in the IR, and no signal for the acyl methyl could be detected by ^1H NMR in $CDCl_3$ solutions. The residue from this reaction did show a peak in the mass spectrum at *m/e* 448. The major product from this reaction was insoluble THF and appears to be a cluster of high nuclearity.

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Registry No. Co, 7440-48-4; ethylene, 74-85-1; acetaldehyde, 75-07-0; formaldehyde, 50-00-0; carbon monoxide, 630-08-0; hydrogen, 1333-74-0; propanal, 123-38-6; benzaldehyde, 100-52-7; propene, 115-07-1; triphenylphosphine, 603-35-0.

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