HCo(CO)$_4$, the Quintessential Catalyst
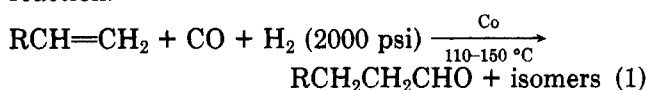
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HCo(CO)$_4$ secured its place in chemical history because of its role in the commercially important oxo reaction:

$$RCH{=}CH_2 + CO + H_2 \text{ (2000 psi)} \xrightarrow[110\text{-}150\,°C]{Co}$$
$$RCH_2CH_2CHO + \text{isomers} \quad (1)$$

The reaction was discovered by Otto Roelen of Ruhrchemie A.G. in the late 1930s and, although he used a standard Fischer–Tropsch catalyst (33% Co, 2% ThO$_2$, 2% MgO, and 65% kieselguhr) in a fixed bed, he believed that the reaction mechanism involved formation of HCo(CO)$_4$.[1] This prediction was substantiated by a comparison of the products of the catalytic oxo reaction produced from a variety of substrates with those obtained when the same substrates were treated with stoichiometric amounts of HCo(CO)$_4$.[2] The prediction was verified by the isolation of HCo(CO)$_4$ under the standard catalytic oxo conditions and the demonstration that under these conditions Co$_2$(CO)$_8$ is readily converted to HCo(CO)$_4$.[3]

The catalytic cycle in the oxo reaction involves the formation and regeneration of HCo(CO)$_4$; the olefin receives both the hydrogen and the carbon monoxide it requires for aldehyde formation from this catalyst. Of course, in the stoichiometric reaction (eq 2),

$$2HCo(CO)_4 + RCH{=}CH_2 + CO \rightarrow$$
$$RCH_2CH_2CHO \text{ (+isomers)} + Co_2(CO)_8 \quad (2)$$
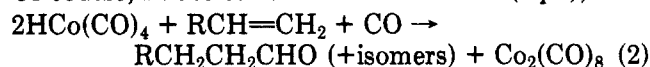
HCo(CO)$_4$ is the only source of hydrogen as well as CO since the reaction can be carried out under nitrogen. In this case the principal cobalt carbonyl product is the tricarbonyl, Co$_4$(CO)$_{12}$, rather than the tetracarbonyl, Co$_2$(CO)$_8$, which is formed under 1 atm of CO.[4]

Equations 1 and 2 representing respectively the catalytic and stoichiometric hydroformylation of terminal alkenes are deceptively simple. The catalytic hydroformylation of 2-pentene produces almost as much 1-hexanal as does 1-pentene under identical conditions, yet little or no 1-pentene is formed during the course of the reaction.[5] When the stoichiometric

reaction is carried out with 1-pentene in excess, the unconverted olefin is largely 2-pentene and the yield of aldehydes is about 40–60%.[6] No conclusive rate expression for the reaction has been published, and it is likely that at least 15 rate constants are involved in separate reactions leading to product.

HCo(CO)$_4$ is a very light yellow, almost colorless, solid, mp –30 °C. The five ligands surrounding Co are arranged in a trigonal-bipyramidal geometry, and the molecule possesses C_3 symmetry. Recent estimates indicate that HCo(CO)$_4$ boils at about 47 °C.[7] Although HCo(CO)$_4$ has only limited solubility in water (5.6 × 10^{-2} mol L^{-1}),[8a] it is much more soluble in organic solvents. It is a protic acid in water with a pK_a between that of HNO$_3$ and HCl.[8a,b]

Stoichiometric Hydroformylation of Alkenes with HCo(CO)$_4$

The overall reaction of eq 2 may be written in stepwise fashion as in Scheme I. Evidence bearing on each of these reactions will be discussed in detail. (In equilibrium reactions, the reverse reaction will be indicated by a minus sign in front of the reaction in question.)

The tricarbonyl 2 is almost always postulated[9] to exist in equilibrium with the tetracarbonyl 1 because 2 is coordinatively unsaturated (16 valence electrons surrounding cobalt) and can thus π-complex with an olefin. Only recently has 2 been successfully identified and its IR spectrum determined by matrix isolation techniques.[10] The tricarbonyl has also been postulated to be the key intermediate in the decomposition of HCo-

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(1) Quoted in I. Wender and M. Orchin, Report of Investigations, 4270, Bureau of Mines, June 1948.
(2) I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, 75, 3041 (1953).
(3) L. Kirch, I. J. Goldfarb, and M. Orchin, *J. Am. Chem. Soc.*, 78, 5450 (1956).
(4) L. Kirch and M. Orchin, *J. Am. Chem. Soc.*, 81, 3597 (1959).
(5) I. J. Goldfarb and M. Orchin, *Adv. Catal.*, 14, 1 (1957).
(6) G. L. Karapinka and M. Orchin, *J. Org. Chem.*, 26, 4187 (1961).
(7) J. A. Roth and M. Orchin, *J. Organomet. Chem.*, 187, 103 (1980).
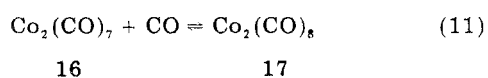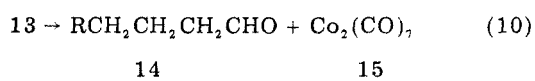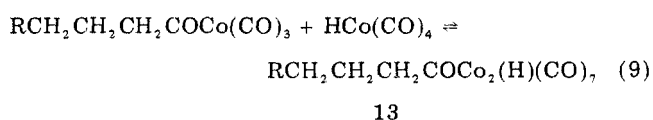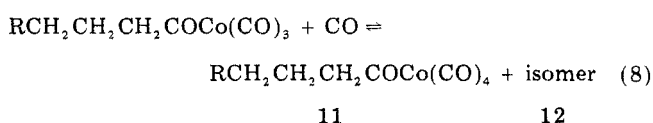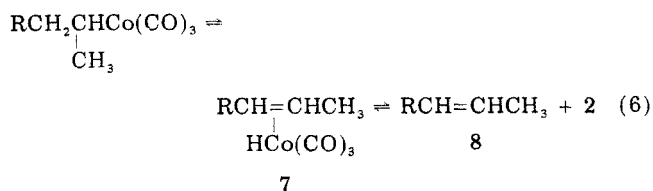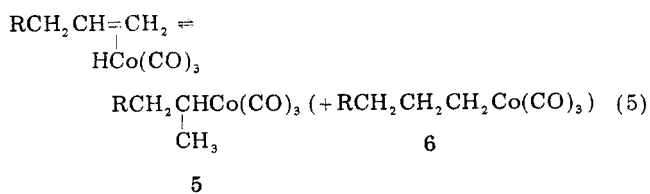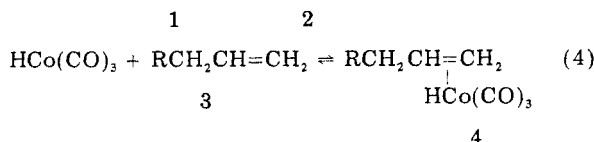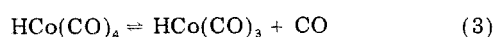(8) (a) H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, 75, 2718 (1953); (b) W. Reppe, *Liebigs Ann. Chem.*, 582, 116 (1952); (c) F. Ungvary and L. Marko, *J. Organomet. Chem.*, 20, 205 (1969).
(9) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, 83, 4023 (1961).
(10) P. Wermer, B. A. Ault, and M. Orchin, *J. Organomet. Chem.*, 162, 189 (1978).

Scheme I

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \qquad (3)$$
$$\quad 1 \qquad\qquad 2$$

$$HCo(CO)_3 + RCH_2CH{=}CH_2 \rightleftharpoons RCH_2CH{=}CH_2 \qquad (4)$$
$$\qquad\qquad\qquad 3 \qquad\qquad\qquad\qquad\overset{|}{HCo(CO)_3}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 4$$

$$\begin{array}{c} RCH_2CH{=}CH_2 \rightleftharpoons \\ \overset{|}{HCo(CO)_3} \end{array}$$

$$\qquad RCH_2\overset{|}{C}HCo(CO)_3 \; (+RCH_2CH_2CH_2Co(CO)_3) \quad (5)$$
$$\qquad\qquad \overset{|}{CH_3} \qquad\qquad\qquad\qquad\qquad 6$$
$$\qquad\qquad 5$$

$$RCH_2\overset{|}{C}HCo(CO)_3 \rightleftharpoons$$
$$\quad \overset{|}{CH_3}$$

$$\qquad\qquad RCH{=}\overset{|}{C}HCH_3 \rightleftharpoons RCH{=}CHCH_3 + 2 \quad (6)$$
$$\qquad\qquad \overset{|}{HCo(CO)_3} \qquad\qquad 8$$
$$\qquad\qquad\qquad 7$$

$$RCH_2CH_2CH_2Co(CO)_3 + CO \rightleftharpoons$$

$$\qquad\qquad RCH_2CH_2CH_2COCo(CO)_3 + \text{isomer} \quad (7)$$
$$\qquad\qquad\qquad\qquad 9 \qquad\qquad\qquad 10$$

$$RCH_2CH_2CH_2COCo(CO)_3 + CO \rightleftharpoons$$

$$\qquad\qquad RCH_2CH_2CH_2COCo(CO)_4 + \text{isomer} \quad (8)$$
$$\qquad\qquad\qquad\qquad 11 \qquad\qquad\qquad 12$$

$$RCH_2CH_2CH_2COCo(CO)_3 + HCo(CO)_4 \rightleftharpoons$$

$$\qquad\qquad RCH_2CH_2CH_2COCo_2(H)(CO)_7 \quad (9)$$
$$\qquad\qquad\qquad\qquad 13$$

$$13 \rightarrow RCH_2CH_2CH_2CHO + Co_2(CO)_7 \quad (10)$$
$$\qquad\quad 14 \qquad\qquad\qquad 15$$

$$Co_2(CO)_7 + CO \rightleftharpoons Co_2(CO)_8 \quad (11)$$
$$\qquad 16 \qquad\qquad\qquad 17$$

$(CO)_4$ to $Co_2(CO)_8$. The decomposition is second order in $HCo(CO)_4$ in both the gas phase[8a] and in solution[8c] and has an inverse dependence on [CO]. The presence of 1 atm of CO in place of an inert gas has a very large retarding effect on the overall rate of the stoichiometric hydroformylation.[6] It thus appears that eq 3 is important even though the equilibrium constant for the reaction may be quite small.

Equation 4 in Scheme I is postulated; it is generally accepted that such complexation occurs prior to a 1,2 addition of metal hydride (M–H) to an olefin.

Equation 5 is an example of olefin insertion into a M–H bond, and eq –5 is an example of β-hydrogen elimination.

Isomerization

The catalytic hydroformylation of 2-pentene leads predominantly to hexanal, yet little or no 1-pentene appears to be formed during the course of the reaction.[5] The appearance of the formyl group at a carbon atom other than at the carbons involved in the π bond of the original olefin cannot be explained by formation of free isomerized olefin (eq 6, Scheme I) followed by hydroformylation of it. In the catalytic reaction, under the high partial pressure of CO, little of complex 7 disso-

ciates. The work performed, first on $(+)$-(S)-3-methyl-1-hexene[11] and subsequently on 3-methyl-1-hexene-3-d,[12] demonstrates the reaction sequence by which the isomeric aldehydes are formed, Scheme II. The nondeuterated olefin gave a 3% yield of (R)-3-ethylhexanal having 70% optical purity.[11] The subsequent investigation[12] on the deuterated olefin showed that the deuterium in this aldehyde is in the 2-position rather than in the original 3-position. These data indicate that π complexes do not dissociate to any appreciable extent under catalytic conditions for if they did the stereochemistry at the chiral center would be lost and racemic product would be formed. Isomeric aldehydes result because the cobalt has wandered down the chain without departing from it.

In the stoichiometric reaction, however, the π complexes may readily dissociate. When such reactions (eq 2) are performed in the presence of substantial excess of olefin and when the reactions are complete as measured by the consumption of all the $HCo(CO)_4$, the recovered olefin is found to be substantially isomerized.[6] Such isomerization is obviously catalytic and obviously occurs very much faster than the hydroformylation since the latter reaction consumes $HCo(CO)_4$ irreversibly. When the stoichiometric reaction is carried out with less than the stoichiometric quantity of olefin, isomerization is the major reaction[13a] because π complexes of internal olefins do not readily undergo olefin insertion, but dissociate under these conditions instead.

A study of the isomerization of allylbenzene by $HCo(CO)_4$ and by $DCo(CO)_4$ shows that both reactions proceed at exactly the same rate;[13b] clearly breaking the H–M bond is not rate determining. Analysis of the *trans*-propenylbenzene obtained in the reaction with $DCo(CO)_4$ is instructive; only about 5% D is present. Assuming a 1,2-addition mechanism,[14] the reaction may be represented[15] as shown in Scheme III where MD and MH are respectively $DCo(CO)_3$ and $HCo(CO)_3$. The fact that only 5% D is incorporated into the product may be interpreted as meaning that CO dissociation from $DCo(CO)_4$ is rate determining and that the $HCo(CO)_3$ formed in the first cycle is responsible for 19 isomerizations before the allylbenzene is able to capture another $DCo(CO)_3$. Only the first cycle incorporates D into the product. At first it was thought[13b] that in view of the very small D incorporation, the mechanism of allylbenzene isomerization involved a 1,3 sigmatropic shift. Although a ground-state suprafacial disrotatory 1,3 shift is symmetry forbidden, a transition-metal catalyst on complexing to the allyl system can theoretically[16] make such a process allowed. However, when $PhCD_2CH{=}CH_2$ is used for the isomerization, it has been shown[17] that indeed the isomerization is best explained by the 1,2-addition–elimination mechanism.

(11) F. Piacenti, S. Pucci, M. Bianchi, R. Lazzaroni, and P. Pino, *J. Am. Chem. Soc.*, **90**, 6847 (1968).

(12) C. P. Casey and C. R. Cyr, *J. Am. Chem. Soc.*, **93**, 1280 (1971); **95**, 2240 (1973).

(13) (a) M. V. McCabe, J. F. Terrapane, and M. Orchin, *Ind. Eng. Chem. Prod. Res. Develop.*, 14, 281 (1975); (b) L. Roos and M. Orchin, *J. Am. Chem. Soc.*, 87, 5502 (1965).

(14) R. Cramer and R. V. Lindsay, *J. Am. Chem. Soc.*, 88, 3534 (1966).

(15) W. E. McCormack and M. Orchin, *J. Organomet. Chem.*, 129, 127 (1977).

(16) F. D. Mango, *Adv. Catal.*, 20, 291 (1969).

(17) Reference 15 and W. T. Hendrix and J. L. von Rosenberg, *J. Am. Chem. Soc.*, 98, 4850 (1976); see also the isomerization of allyl alcohol to propionaldehyde: R. W. Goetz and M. Orchin, *ibid.*, 85, 1549 (1963).

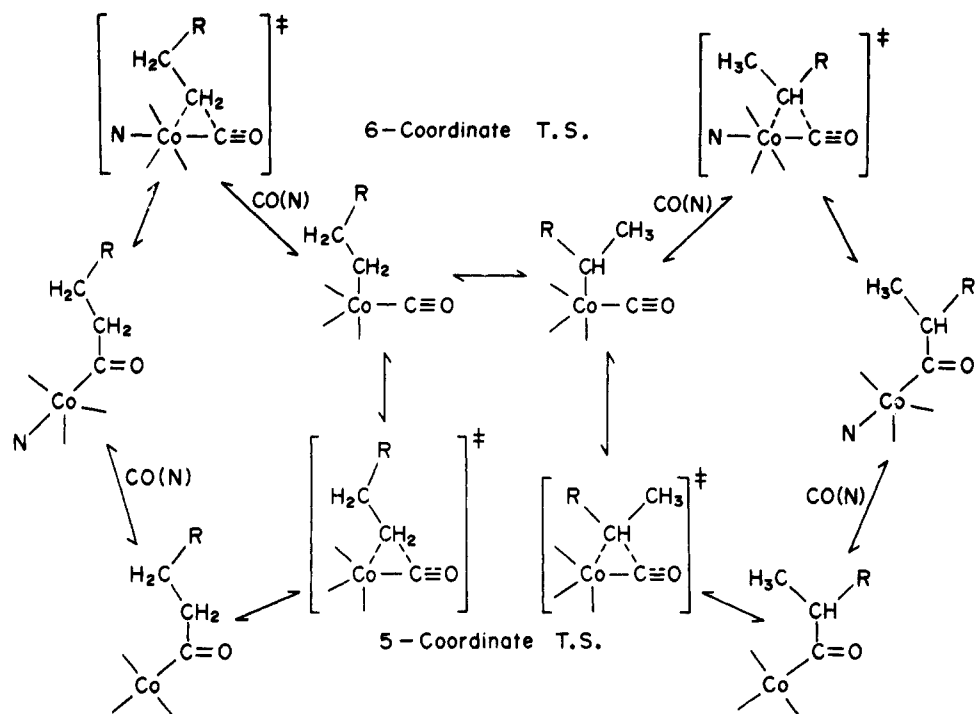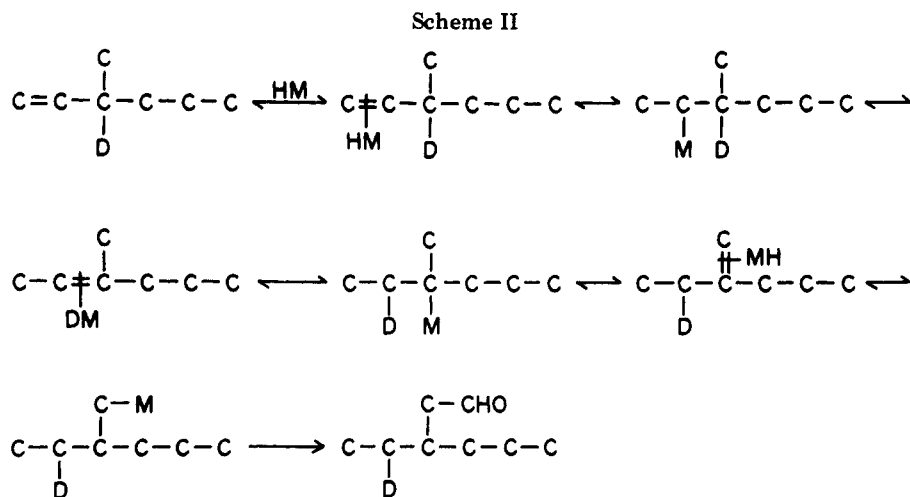**Figure 1.** Transition states for migratory insertion.

Scheme II

Migratory Insertion and Product Control in Hydroformylation

Studies on the vapor-phase isomerization of CD_2= $CDCD_3$ with $HCo(CO)_4$[18] in the absence of CO show that the addition of the $HCo(CO)_4$ to the olefin proceeds in an orientation corresponding to about 70% Markownikoff addition. Analysis of the C_4 aldehydes produced is consistent with such partitioning: 70% isobutyraldehyde and 30% n-butyraldehyde are formed. When CO is added, so that the vapor-phase composition of $HCo(CO)_4$:C_3H_6:CO corresponds to 1:22:5, n-butyraldehyde accounts for 60% of the aldehydes formed.[19] In the catalytic hydroformylation of terminal olefins where high partial pressures of CO are present, yields of straight-chain aldehydes are about 70–80% and are only slightly less when straight-chain alkenes with the double bond in the 2-position are hydroformylated. Clearly the initial addition of HM does not determine the product composition. In Scheme I, the only reaction

Scheme III

Allylbenzene Isomerization
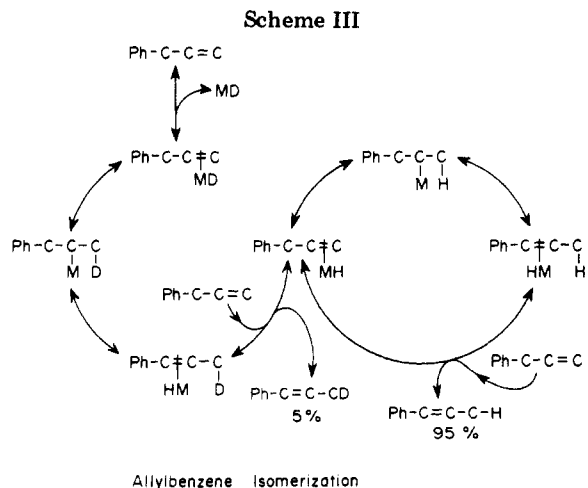
which is not an equilibrium reaction is the final conversion of the acyl complex to an aldehyde. The equilibrium involving the migratory insertion step, i.e., the conversion of alkyl- to acylcobalt carbonyls, apparently controls product distribution.

(18) P. Taylor and M. Orchin, *J. Am. Chem. Soc.*, **93**, 6504 (1971).
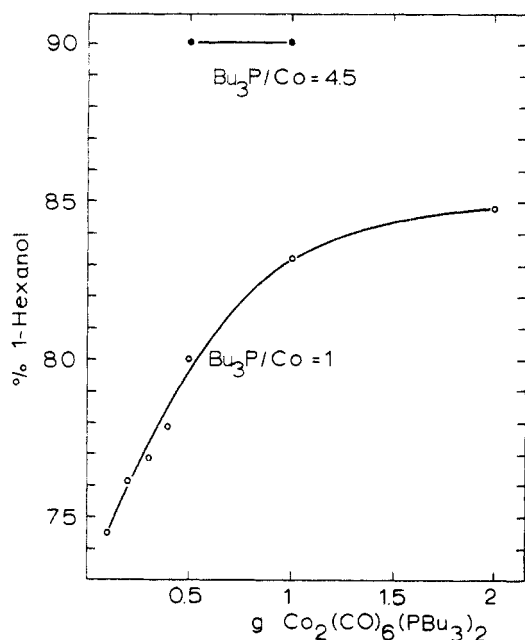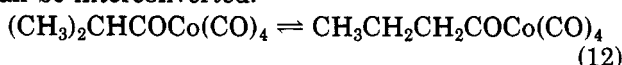(19) M. Orchin and W. Rupilius, *Catal. Rev.*, **6**, 85 (1972).

Figure 2. Effect of phosphine concentration on products from
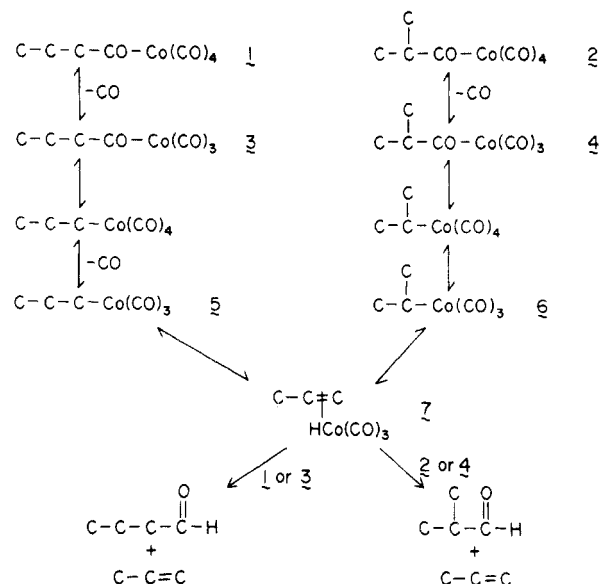1-pentene (170 °C).

Figure 3. Isomerization and disproportionation of butyrylcobalt
tetracarbonyls.

Table I
Stoichiometric Hydroformylation of 1-Pentene[a]

reaction time	yield of hexanals, %	composition of hexanals, %	
		straight	branched
16	60.5	78.2	21.8
24[b]	77.5[b]	69.1[b]	30.9[b]

[a] 1.8 mmol of $HCo(CO)_4$, 10 mmol of 1-pentene, 13 mL
of pentane. [b] Carbon monoxide atmosphere replaced by
nitrogen.

In the absence of substantial amounts of CO or other
nucleophiles, the migratory insertion step may involve
proceeding from a ground-state 5-coordinate alkylcobalt
to a 5-coordinate transition state (Figure 1). Accord-
ingly, the greater steric requirement of the branched
isomer does not greatly affect the transition-state energy
relative to that of the 5-coordinate transition state of
the straight-chain isomer, and, because Markownikoff
orientation is preferred, the branched-chain product
predominates. However, when a high partial pressure
of CO (or other nucleophile) is present, such nucleo-
philes coordinate simultaneously with the CO migra-
tion, and only 6-coordinate transition states are likely.
In such a situation, the greater steric requirement of
the transition state formed from the branched-chain
isomer increases the energy of this transition state
relative to that of the straight-chain isomer. The overall
result is that in the presence of nucleophiles one may
expect the product to be the straight-chain isomer. This
explanation is consistent with most of the known facts
concerning product distribution, including the well-
known enhancement of straight-chain product by using
phosphine-modified cobalt catalysts such as [Co$_2$-
(CO)$_6$(PBu$_3$)$_2$].[20] The effect that phosphine concen-
tration can have on the partitioning between straight-
and branched-chain product derived from 1-pentene[21]
is shown in Figure 2. The lower curve shows that at
a constant Bu$_3$P/Co ratio increasing the concentration
of catalyst increases selectivity to straight-chain prod-
uct. The upper curve shows that at low catalyst con-
centration, addition of excess Bu$_3$P gives very high se-
lectivity.

Skeletal Rearrangements

It has been shown that isomeric acylcobalt carbonyls
can be interconverted:[22]

$$(CH_3)_2CHCOCo(CO)_4 \rightleftharpoons CH_3CH_2CH_2COCo(CO)_4$$
$$(12)$$

In a study of the mechanism of this reaction it was
discovered[23] that not only do the acylcobalt carbonyls
isomerize spontaneously, but they also produce olefins
and aldehydes as well. Thus, when isobutyrylcobalt
tetracarbonyl is prepared at room conditions under 1
atm of CO and then the CO is replaced by nitrogen and
the solution stirred for 24 h, propylene, n-butyr-
aldehyde, and isobutyraldehyde are formed. The series
of reactions which explains the reaction is shown in
Figure 3. The overall reaction thus constitutes a dis-
proportionation of acylcobalt tetracarbonyls:

$$2RCH_2CH_2COCo(CO)_4 \rightarrow$$
$$RCH_2CH_2CHO^* + RCH=CH_2 + Co_2(CO)_8 + CO$$
$$(13)$$
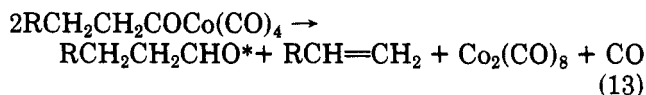
*plus branched chain isomer

When a large (10-fold) excess of olefin is used in the
stoichiometric reaction of eq 2, only about a 50–60%
yield of aldehydes is obtained even though all the
$HCo(CO)_4$ disappears. The balance of the potential
aldehyde remains as the precursor acylcobalt tetra-
carbonyl. If the CO is then removed from over the
solution and replaced by N$_2$, the results[23] shown in
Table I are obtained. These results are completely
rationalized by the scheme shown in Figure 3, the dis-
proportionation being initiated by the decomposition
of the acyltetracarbonyl to the acyltricarbonyl. Note

(20) L. Slaugh and R. Mullineaux, *J. Organomet. Chem.*, 13, 469
(1968); R. Tucci, *Ind. Eng. Chem. Prod. Res. Develop.*, 7, 32 (1968).
(21) W. Rupilius, J. J. McCoy, and M. Orchin, *Ind. Eng. Chem. Prod.
Res. Develop.*, 10, 142 (1971).

(22) Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada, and Y.
Okuda, *Bull. Chem. Soc. Jpn.*, 37, 1190 (1964); Y. Takegami, Y. Watan-
abe, H. Masada, and T. Mitsudo, *ibid.*, 42, 206 (1969).
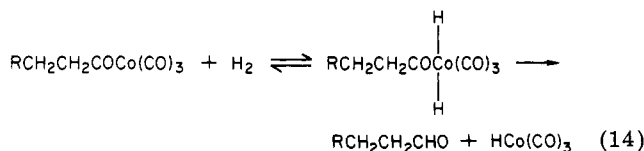(23) W. Rupilius and M. Orchin, *J. Org. Chem.*, 37, 936 (1972).

also from Table I that the distribution of aldehydes produced by the disproportionation favors the branched-chain aldehyde; as a matter of fact, the incremental aldehyde produced is approximately 70:30 branched:straight chain, as might have been predicted from preferred Markownikoff orientation discussed earlier.

Cleavage of Acylcobalt Carbonyls

In the stoichiometric reaction, the acylcobalt carbonyls must be converted to aldehydes by reaction with $HCo(CO)_4$ (eq 9 and 10, Scheme I) since this is the only source of the aldehydic hydrogen. This step(s) must be considerably faster than earlier steps; otherwise, in the presence of excess olefin, all the $HCo(CO)_4$ would have been consumed and none of it would be available for the conversion of acylcobalt carbonyls to aldehyde. Obviously the cleavage of the acylcobalt carbonyls is very fast relative to their formation. Although the cleavage is shown in Scheme I as an oxidative addition followed by a reductive elimination, it is possible that the acylcobalt tricarbonyl (or the tetracarbonyl as well) can undergo direct protonolysis with the strongly acidic $HCo(CO)_4$.

In the catalytic hydroformylation, there is the possibility of oxidative addition of molecular hydrogen to the acylcobalt tricarbonyl followed by reductive elimination (eq 14).[24] This may be competitive with the

$$RCH_2CH_2COCo(CO)_3 + H_2 \rightleftharpoons RCH_2CH_2CO\overset{\displaystyle H}{\underset{\displaystyle H}{Co}}(CO)_3 \longrightarrow$$

$$RCH_2CH_2CHO + HCo(CO)_3 \quad (14)$$

cleavage of acylcobalt carbonyls by $HCo(CO)_4$, but IR studies under reaction conditions[25] seem to indicate that cleavage with $HCo(CO)_4$ is preferred. It has also been shown that the conversion of $Co_2(CO)_8$ to $HCo(CO)_4$ under catalytic conditions is rather rapid.[3] A review of all the steps proposed in Scheme I suggests that the generation of $HCo(CO)_3$ is the rate-limiting step. Other steps involving coordinatively unsaturated species may also be implicated, but the importance of $HCo(CO)_3$, for both the stoichiometric and catalytic hydroformylation, is convincing.

Acid-Catalyzed Reactions Mediated by $HCo(CO)_4$

When the conversion of benzyl alcohol to β-phenylethanol was first reported,[26] it was suggested that this homologation was an acid-catalyzed [$HCo(CO)_4$] reaction. Subsequently, it was found that methanol can be converted to ethanol under catalytic conditions.[27] This reaction has stimulated a great deal of current interest[28] as an alternate nonpetroleum route to C_2 chemicals. A detailed study of the homolgation reaction with substituted benzyl alcohols, particularly those showing that

electron-releasing substituents in the para position accelerate the rate,[29] indicate that carbocations are generated as intermediates. Treatment of pinacol under catalytic oxo conditions gives pinacolone and three other products, all of which can be rationalized[30] on the basis of conventional carbocation chemistry. Other evidence of acid catalysis by $HCo(CO)_4$ consists of the formation and hydrolysis of acetals,[31] the cyclization of a product formed during the hydroformylation of saffrole,[32] and the course of the reaction of $HCo(CO)_4$ with cyclohexene oxide.[33]

All of these reactions were carried out under catalytic hydroformylation conditions, but there is evidence that comparable reactions occur under stoichiometric conditions. Thus, treatment of triphenylcarbinol with $HCo(CO)_4$ in acetone solution at room conditions gives a 100% yield of triphenylmethane.[2,34]
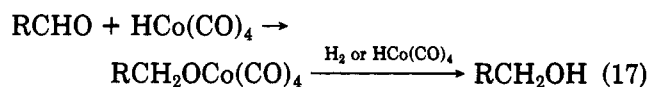
$$Ph_3COH + 2HCo(CO)_4 \rightarrow$$
$$Ph_3CH + H_2O + Co_2(CO)_8 \quad (15)$$
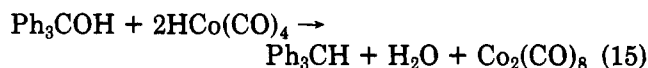
A convincing demonstration[35] of the electrophilic character of $HCo(CO)_4$ is the following reaction, carried out in CH_2Cl_2:
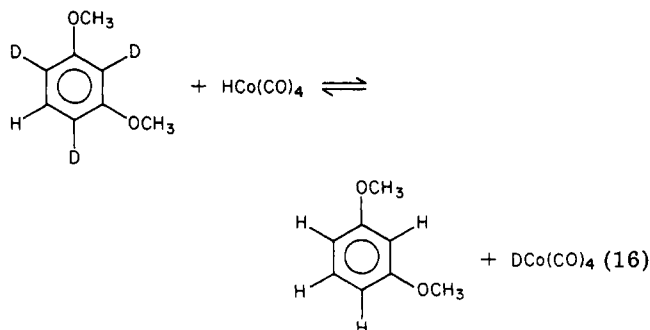
Hydrogenations with $HCo(CO)_4$

When the catalytic hydroformylation of alkenes is conducted at about 185 °C, the product consists principally of alcohols.[36] Obviously, aldehydes are reduced by $HCo(CO)_4$ under these conditions. Aldehydes are also reduced, although slowly, under stoichiometric conditions.[37a] Both the catalytic[37b] and the stoichiometric reactions have been suggested as proceeding through the formation of an intermediate possessing an O–Co bond:

$$RCHO + HCo(CO)_4 \rightarrow$$
$$RCH_2OCo(CO)_4 \xrightarrow{H_2 \text{ or } HCo(CO)_4} RCH_2OH \quad (17)$$

Part of the evidence for such an intermediate is based

(24) L. Markó, G. Bor, G. Almasy, and P. Szabó, Brennst. Chem., 44, 184 (1963).

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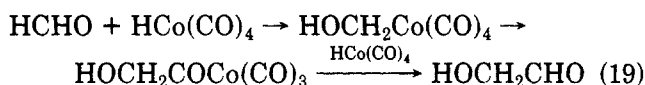(26) I. Wender, R. Levine, and M. Orchin, J. Am. Chem. Soc., 71, 4160 (1949).

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on the fact that formates are frequently found as side products. Their formation can be rationalized on the basis of the intermediate undergoing migratory insertion of CO:

$$RCH_2OCo(CO)_4 \rightarrow RCH_2OCOCo(CO)_3 \xrightarrow{HCo(CO)_4} RCH_2OCOH \quad (18)$$
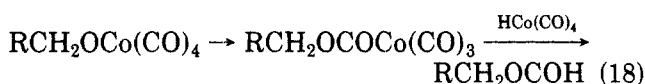
However, the stoichiometric reaction of formaldehyde with $HCo(CO)_4$ leads to glycolaldehyde,[38] and this must involve C–Co bonding:

$$HCHO + HCo(CO)_4 \rightarrow HOCH_2Co(CO)_4 \rightarrow$$
$$HOCH_2COCo(CO)_3 \xrightarrow{HCo(CO)_4} HOCH_2CHO \quad (19)$$

Certain olefin substrates react by hydrogenation rather than by hydroformylation under catalytic hydroformylation conditions.[34] Thus, compounds possessing a double bond conjugated to the carbonyl group of an aldehyde or ketone are reduced to the saturated aldehyde or ketone at temperatures of about 125 °C; however, aliphatic α,β-unsaturated esters undergo hydroformylation. A similar difference in the behavior of α,β-unsaturated aldehydes and ketones as contrasted to α,β-esters seems to hold true of the stoichiometric reaction as well.[39] The one well-documented exception is the behavior of diethyl fumarate. Like other α,β-unsaturated esters, under catalytic conditions it undergoes hydroformylation, but under stoichiometric conditions, exclusive and rapid reduction to diethyl succinate occurs.[40] When the isomeric diethyl maleate is treated under stoichiometric conditions, it is first rapidly isomerized to the fumarate which is then hydrogenated. It has been proposed[39] that the hydrogenation of α,β-unsaturated ketones and aldehydes proceeds by 1,4-addition to form an intermediate π-


16   17 (anti)   18 (syn)
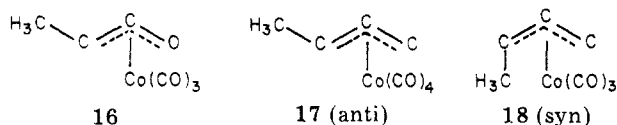
oxapropenyl complex, 16, analgous to the isolable and well-characterized iso-π-electronic complexes 17 and 18 prepared from 1,3-butadiene[41] and $HCo(CO)_4$.

α,β-Unsaturated esters, for both steric and electronic reasons, do not form such complexes. Small structural changes in a substrate can steer reactions with $HCo(CO)_4$ from complete hydroformylation to complete hydrogenation. As might be expected, there are many substrates that undergo both reactions competitively. Even the products of the catalytic hydroformylation of simple alkenes contain alkanes as a minor product, and indeed with some tetrasubstituted alkenes relatively high yields of alkanes are obtained. It thus appears that hydrogenation may always be competitive with hydroformylation under both catalytic and stoichiometric conditions.

Stereochemistry

Surprisingly, there are relatively few studies dealing with the stereochemistry of the stoichiometric hydro-

formylation reaction, probably because the required prochiral olefins, if they react at all, mostly undergo hydrogenation rather than hydroformylation. However, treatment of norbornene with $DCo(CO)_4$ followed by oxidation gave the *exo*-norbornane-2-carboxylic acid (19), indicating cis addition.[42] Also, although under

19
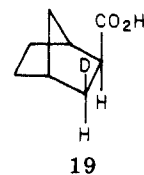
stoichiometric conditions stilbene reacts only very slowly to give a small quantity of 1,2-diphenylethane, the related cyclopropene derivative 20, in addition to giving a mixture of hydrogenated products, gives only one hydroformylated product, 21, corresponding to cis

20   21   (20)
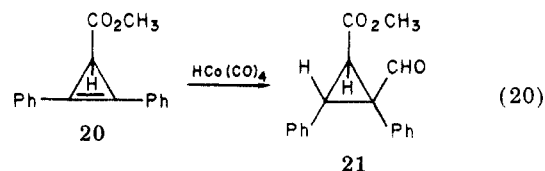
addition to the more hindered face of 20.[43] Treatment of 1,2-diphenyl-1-cyclobutene (22) with stoichiometric

22   23

24   25   (12)

(21)
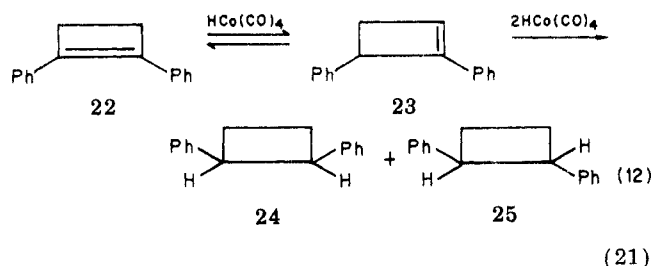
amounts of $HCo(CO)_4$ gives about 30% conversion to 1,2-diphenylcyclobutanes consisting of about 96% cis (24) and 4% trans (25).[44] Under catalytic conditions there is complete conversion to the 1,2-diphenylbutanes, about 90% cis and 10% trans. The large preponderance of cis was taken to indicate essentially complete cis addition, the small amount of trans product arising from prior isomerization to 23 followed by cis addition of HM to 23 from either face.

The stoichiometric hydrogenation of 9,10-dimethylanthracene gives 35% *cis*- and 65% *trans*-9,10-dihydro-9,10-dimethylanthracene.[45a] It is possible to again explain the formation of trans product by 1,4-cis addition of $HCo(CO)_4$ followed by 1,2 elimination and cis addition. However, it has been suggested[45b] that the loss of stereochemistry in this case is due to the formation of a trigonal radical intermediate. Radical intermediates have been suggested[46] in hydrogenation reactions with the isoelectronic $[HCo(CN)_5]^{3-}$ and with $HMn(CO)_5$; in the latter case,[47] a geminate radical pair

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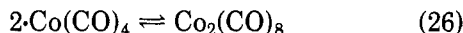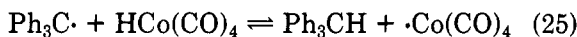(39) R. W. Goetz and M. Orchin, *J. Am. Chem. Soc.*, **85**, 2782 (1962).
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was shown to be present by use of CIDNP measurements during the reduction of α-methylstyrene.

Possible Radical Intermediates

The question of radical involvement in reactions with $HCo(CO)_4$ is of considerable current interest. As early as 1953, the sequence shown in eq 22–26 was written

$$Ph_3COH + HCo(CO)_4 \rightleftharpoons Ph_3COH_2^+ + {}^-Co(CO)_4 \quad (22)$$

$$Ph_3COH_2^+ \rightleftharpoons Ph_3C^+ + H_2O \quad (23)$$

$$Ph_3C^+ + {}^-Co(CO)_4 \rightleftharpoons Ph_3C\cdot + \cdot Co(CO)_4 \quad (24)$$

$$Ph_3C\cdot + HCo(CO)_4 \rightleftharpoons Ph_3CH + \cdot Co(CO)_4 \quad (25)$$

$$2\cdot Co(CO)_4 \rightleftharpoons Co_2(CO)_8 \quad (26)$$
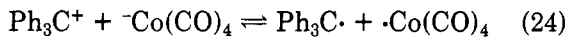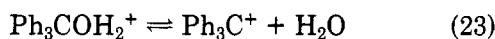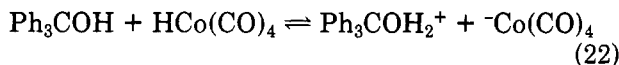
for the reaction of triphenylcarbinol with $HCo(CO)_4$.[48] This sequence still appears essentially correct, especially if eq 24 is regarded as an ion pair passing through a σ-bonded compound which then dissociates into a radical pair. If radicals are formed in reactions with $HCo(CO)_4$ they do not appear to have a substantial lifetime or they exist as caged radical pairs. Reactions involving readily polymerizable olefins never lead to any polymers, nor have any dimeric products resulting from coupled organic radicals ever been isolated. 1,1-Diphenylethylene reacts very rapidly[49] and cleanly with $HCo(CO)_4$ at essentially the same rate in either CH_2Cl_2, hexane, or methyl methacrylate as solvent. Conventional spin traps such as phenyl-*tert*-butylnitrone and 2-nitroso-2-methylpropane have no effect. These facts do not necessarily preclude a radical mechanism, but direct evidence is still lacking. [Added in proof: We have now (T. E. Nalesnik) observed the first CIDNP effect with $HCo(CO)_4$ (low-temperature reduction of $Ph_2C=CH_2$).] The hydrogenation is first order with respect to $HCo(CO)_4$ and $Ph_2C=CH_2$. Furthermore, unlike stoichiometric hydroformylation, this stoichiometric hydrogenation is unaffected by 1 atm of CO. ΔH^* is found to be 17 kcal mol^{-1} and ΔS^* -10 cal deg^{-1} mol^{-1}. Similar to the known reaction between $HMn(CO)_5$ and α-methylstyrene, the reaction between $Ph_2C=CH_2$ and $DCo(CO)_4$ leads to an inverse isotope effect, $k_H/k_D = .58$. In very recent work[50] it has been shown that 9-methylidenefluorene (26a) is readily hydrogenated at -67 °C to 9-methylfluorene (27) (eq 27).

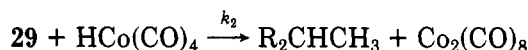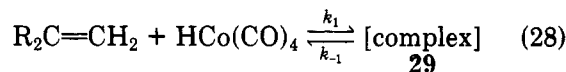

(27)

26a, R = H
  b, R = CH_3
  c, R = Ph

27, R = H
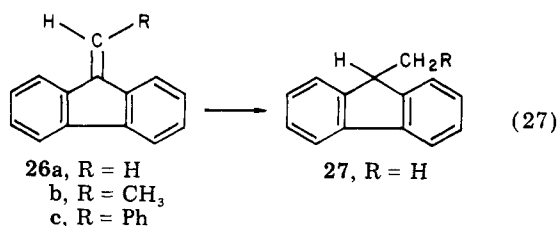
The rate of reaction is 3670 times as fast as the reaction with 1,1-diphenylethylene. The tetrasubstituted ethylene, bifluorenylidene (28), is hydrogenated almost twice as fast as 1,1-diphenylethylene.[51] The results of rate data[51] for the hydrogenation of various olefins with
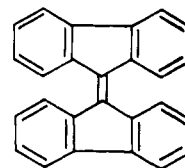

28

$HCo(CO)_4$ under similar conditions indicate the order (relative rates in parentheses) 26a (3670) > $CH_2=C(CN)Ph$ (80) > 26b (2.5) > 28 (1.66) > $CH_2=CPh_2$ (1.00) > 26c (0.9) > $Ph_2C=CHCH_3$ ($\sim10^{-5}$) $\cong$ $PhCH=C(CN)Ph > (CH_3)_2C=C(CN)Ph$.

The formation of a highly stabilized radical or carbocation or of a transition state having the character of these intermediates is very likely involved, with steric factors playing a somewhat lesser role. The mechanism of the reaction can be expressed by eq 28. The caged

$$R_2C=CH_2 + HCo(CO)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{[complex]} \quad (28)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad 29$$

$$29 + HCo(CO)_4 \xrightarrow{k_2} R_2CHCH_3 + Co_2(CO)_8$$

complex 29 may possess a particularly weak C–Co σ bond in substrates where the R groups attached to the C atom enhances effective electron delocalization, and in such cases 29 can be represented by the resonance structures (or equilibria):
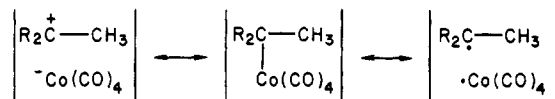
Studies with $DCo(CO)_4$ and incorporation of D into the starting material indicate that in eq 28, $k_{-1} > k_2 > k_1$.[49] There is actually no evidence as yet that either carbocations or radicals have discrete existence in $HCo(CO)_4$ systems; if present, such species must be locked into solvent cages into which the $HCo(CO)_4$ must diffuse so as to complete the reaction, or the geminate radical pair must diffuse out of the cage to be trapped by $HCo(CO)_4$. (See earlier note added in proof.)

In order to explain the effect of nucleophiles[52] in the course of the stoichiometric hydroformylation, even $HCo(CO)_4$ has been treated as though its dissociation, eq 29, involves a solvent cage and subsequent diffusion

$$HCo(CO)_4 \rightleftharpoons [HCo(CO)_3CO] \rightleftharpoons HCo(CO)_3 + CO \quad (29)$$
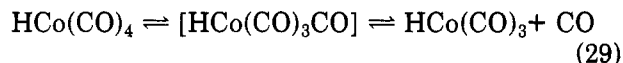
occurs into and out of this cage.[53]

To further complicate the picture, it has been shown recently that $HCo(CO)_4$ reacts with $Co_2(CO)_8$ to form a trinuclear species,[54] $HCo_3(CO)_9$, which is an effective reducing agent. In both catalytic and stoichiometric reactions, $HCo(CO)_4$ and $Co_2(CO)_8$ are simultaneously present, and possible equilibrium reactions between trinuclear, dinuclear, and mononuclear species need to be considered.

Concluding Remarks

Despite the more than 30 years of work on the mechanism of the hydroformylation, much remains to be investigated. $HCo(CO)_4$ has unquestionably turned

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(49) J. A. Roth and M. Orchin, *J. Organomet. Chem.*, 182, 299 (1979).
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(54) G. Fachinetti, private communication; see *Angew. Chem.*, 18, 619 (1979).

out to be a most unusual compound. It is considered a metal hydride that functions as an acid catalyst; its reactions are influenced by the coordination state of the cobalt; it forms π (η^2), π-allyl (η^3), and σ (η^1) complexes; the σ complexes undergo migratory insertion, oxidative addition, and reductive elimination reactions as well as skeletal rearrangements; it is a potent isomerization catalyst, and its reactions with olefins can lead to aldehydes, alcohols, and/or hydrocarbons. The partitioning among these products can be influenced by temperature, pressure, and ligand structure. It can show both normal and inverse isotope effects and can be a remarkably effective hydrogenation agent. Its reactions encompass the whole gamut of the known reactions of organometal catalysts entitling it to be called the quintessential catalyst.

Fortunately, I have been blessed with many talented collaborators during the more than 30 years that I have worked with the chemistry of HCo(CO)₄ and the hydroformylation reaction. Many of my co-workers are mentioned in the references, and to all of them I give my deepest thanks, for it is their effort which has given form to much of the work presented in this article.

Determination of Structural and Dynamic Aspects of Organometallic and Coordination Chemistry by Phosphorus-31 NMR Spectroscopy

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In recent years, transition-metal complexes of tertiary phosphine ligands have been used in many important and diverse chemical reactions such as (i) homogeneous hydroformylation,[1] oxidation,[2] hydrogenation,[3] and hydrosilylation of olefins;[4] (ii) oxidative addition to the metal center;[5] (iii) stabilization of small elemental fragments (e.g., S_2,[6] Se_2,[7] P_3,[8,9] and As_3[9]); and (iv) asymmetric synthesis via optically active metal phosphine catalysts.[10] It is expected that the use of polyphosphine ligands will become increasingly important in such future studies, since the special properties of phosphine ligands can be accentuated by a chelating polyphosphine;[11] also, the steric and electronic properties of the ligands can be altered relatively easily by changing the organic substituents on phosphorus.

Research efforts in our laboratories have been concentrated on the synthesis of chelating polydentate ligands and on the electronic, catalytic, and structural properties of the resulting complexes of transition metals.[11] Compared to a monodentate phosphine, a polyphosphine ligand can provide simultaneously (i) more control on the coordination number, stoichiometry, and stereochemistry of the resulting complex; (ii) an increased basicity (or nucleophilicity) at the metal; (iii) slower intra- and intermolecular exchange processes; and (iv) detailed structural and bonding information in the form of metal–phosphorus and phosphorus–phosphorus coupling constants. For example, polydentate ligands may be used to change the mag-

netic states and coordination geometries of complexes by judiciously selecting parameters such as (i) sets of donor atoms, (ii) "chelate bite angle", and (iii) sterically demanding substituent groups.[12] Flexible polyphosphine ligands (e.g., 1–5), which contain either ethylene or trimethylene linkages, have been used to form complexes with different coordination numbers (four, five, and six) and different structures (distorted tetrahedral, planar, square pyramidal, trigonal bipyramidal, and octahedral).[13–15] A properly designed polyphosphine ligand can define the relative positions

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(5) Collman, J. P. *Acc. Chem. Res.* 1968, 1, 136.
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