

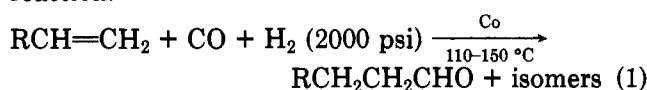
HCo(CO)₄, the Quintessential Catalyst

MILTON ORCHIN

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

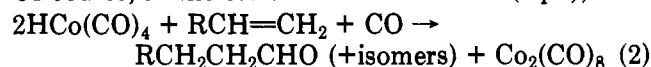
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HCo(CO)₄ secured its place in chemical history because of its role in the commercially important oxo reaction:



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% ThO₂, 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 Co₂(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),



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, Co₄(CO)₁₂, rather than the tetracarbonyl, Co₂(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 C₃ 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 HNO₃ 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 postulated⁹ 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-

(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).

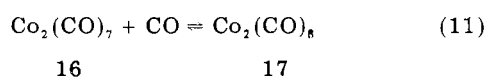
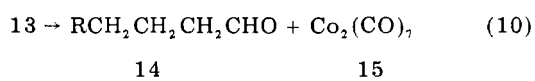
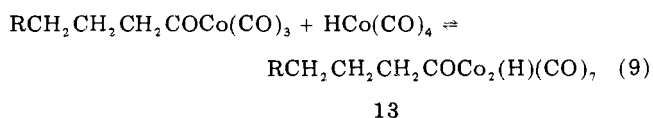
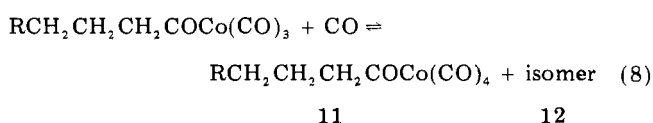
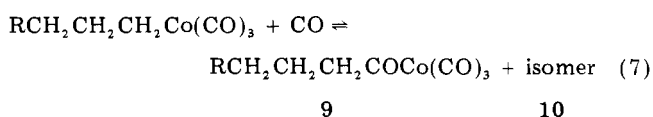
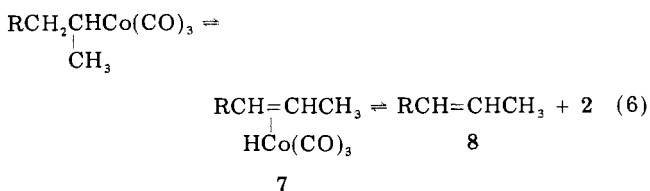
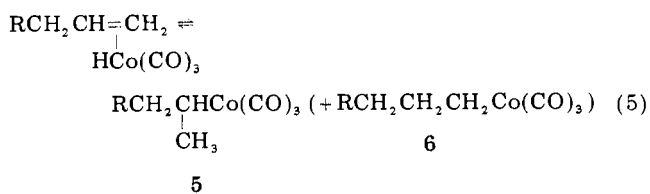
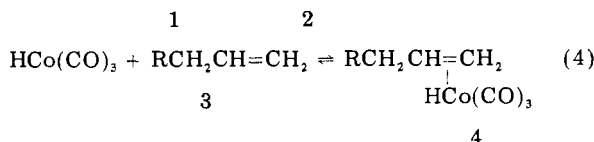
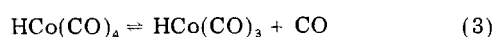
(8) (a) H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 2718 (1953); (b) W. Reppe, *Liebigs Ann. Chem.*, **582**, 116 (1952); (c) F. Ungvary and L. Marko, *J. Organomet. Chem.*, **20**, 205 (1969).

(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).

Milton Orchin received all of his chemical training at The Ohio State University, finishing with a Ph.D. in 1939. After several years in the Food and Drug Administration, he became Head of the Organic Division of the Synthetic Liquid Fuels program in Pittsburgh in 1943. Ten years later he joined the faculty at the University of Cincinnati, where he is presently Director of the Hoke S. Greene Laboratory of Catalysis and Distinguished Service Professor of Chemistry.

Scheme I



(CO)₄ to Co₂(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-hexene¹¹ 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 investigation¹² 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 represented¹⁵ 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 theoretically¹⁶ make such a process allowed. However, when PhCD₂CH=CH₂ is used for the isomerization, it has been shown¹⁷ 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).

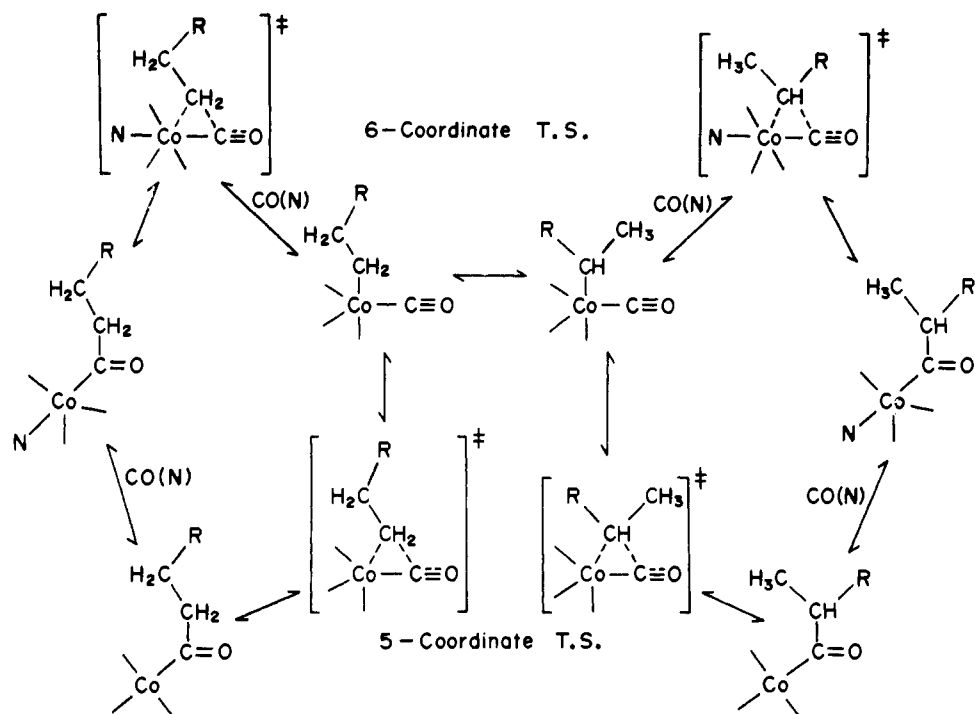
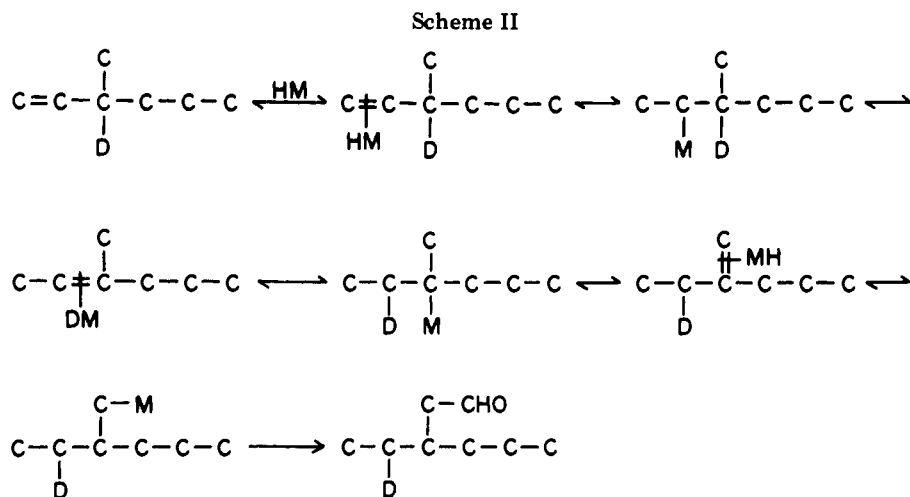
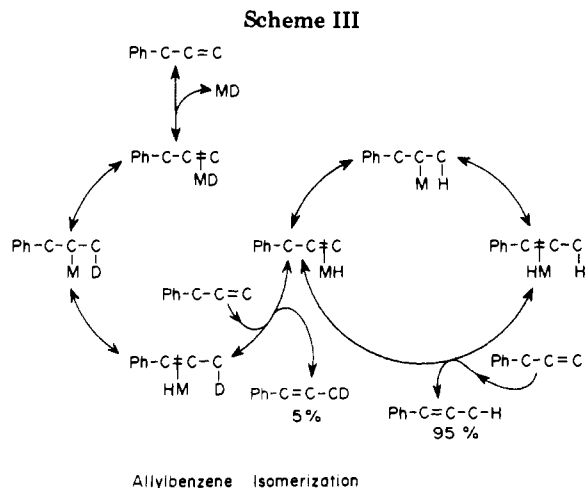


Figure 1. Transition states for migratory insertion.



Migratory Insertion and Product Control in Hydroformylation

Studies on the vapor-phase isomerization of $\text{CD}_2=\text{CDCD}_3$ with $\text{HCo}(\text{CO})_4$ ¹⁸ in the absence of CO show that the addition of the $\text{HCo}(\text{CO})_4$ 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 $\text{HCo}(\text{CO})_4:\text{C}_3\text{H}_6:\text{CO}$ 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



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).

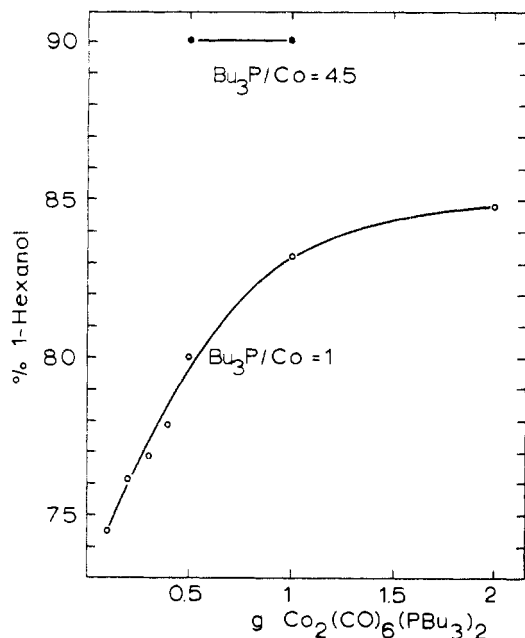
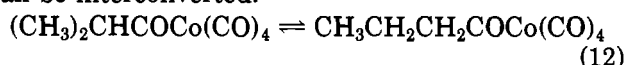


Figure 2. Effect of phosphine concentration on products from 1-pentene (170 °C).

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). Accordingly, 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 nucleophiles coordinate simultaneously with the CO migration, 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 $[\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2]$.²⁰ The effect that phosphine concentration can have on the partitioning between straight- and branched-chain product derived from 1-pentene²¹ is shown in Figure 2. The lower curve shows that at a constant $\text{Bu}_3\text{P}/\text{Co}$ ratio increasing the concentration of catalyst increases selectivity to straight-chain product. The upper curve shows that at low catalyst concentration, addition of excess Bu_3P gives very high selectivity.

Skeletal Rearrangements

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



(20) L. Slauch 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).

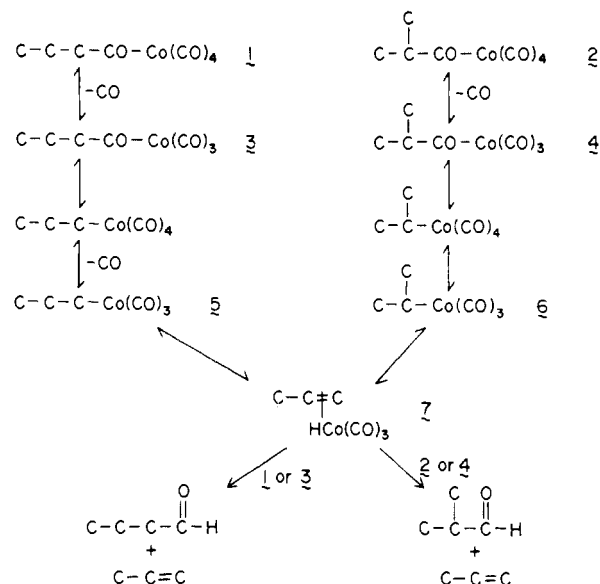


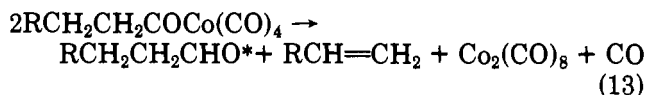
Figure 3. Isomerization and disproportionation of butyrylcobalt tetracarbonyls.

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 $\text{HCo}(\text{CO})_4$, 10 mmol of 1-pentene, 13 mL of pentane. ^b Carbon monoxide atmosphere replaced by nitrogen.

In a study of the mechanism of this reaction it was discovered²³ 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*-butyraldehyde, and isobutyraldehyde are formed. The series of reactions which explains the reaction is shown in Figure 3. The overall reaction thus constitutes a disproportionation of acylcobalt tetracarbonyls:



*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 $\text{HCo}(\text{CO})_4$ disappears. The balance of the potential aldehyde remains as the precursor acylcobalt tetracarbonyl. If the CO is then removed from over the solution and replaced by N_2 , the results²³ shown in Table I are obtained. These results are completely rationalized by the scheme shown in Figure 3, the disproportionation being initiated by the decomposition of the acyltetracarbonyl to the acyltriacarbonyl. Note

(22) Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada, and Y. Okuda, *Bull. Chem. Soc. Jpn.*, **37**, 1190 (1964); Y. Takegami, Y. Watanabe, H. Masada, and T. Mitsudo, *ibid.*, **42**, 206 (1969).

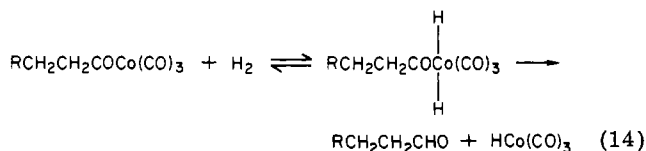
(23) W. Rupilius and M. Orchin, *J. Org. Chem.*, **37**, 936 (1972).

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 tricarbyl (or the tetracarbyl 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 tricarbyl followed by reductive elimination (eq 14).²⁴ This may be competitive with the



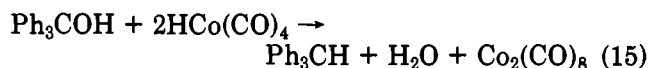
cleavage of acylcobalt carbonyls by HCo(CO)₄, but IR studies under reaction conditions²⁵ seem to indicate that cleavage with HCo(CO)₄ is preferred. It has also been shown that the conversion of Co₂(CO)₈ to HCo(CO)₄ under catalytic conditions is rather rapid.³ A review of all the steps proposed in Scheme 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

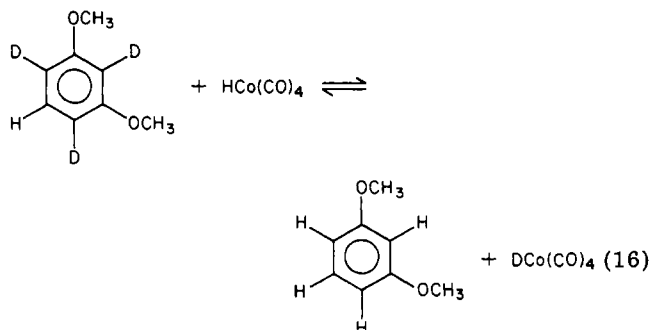
When the conversion of benzyl alcohol to β-phenylethanol was first reported,²⁶ it was suggested that this homologation was an acid-catalyzed [HCo(CO)₄] reaction. Subsequently, it was found that methanol can be converted to ethanol under catalytic conditions.²⁷ This reaction has stimulated a great deal of current interest²⁸ as an alternate nonpetroleum route to C₂ chemicals. A detailed study of the homologation 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 rationalized³⁰ 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 safrole,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}

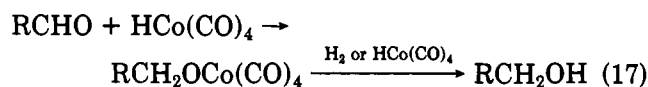


A convincing demonstration³⁵ of the electrophilic character of HCo(CO)₄ is the following reaction, carried out in CH₂Cl₂:



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:



Part of the evidence for such an intermediate is based

(29) I. Wender, H. Greenfield, S. Metlin, and M. Orchin, *J. Am. Chem. Soc.*, **74**, 4074 (1952); *p*-CH₃C₆H₄CH₂OH reacts 10⁶ times as fast as CF₃-C₆H₄CH₂OH.

(30) I. Wender, S. Metlin, and M. Orchin, *J. Am. Chem. Soc.*, **73**, 5704 (1951).

(31) B. I. Fleming and H. I. Bolker, *Can. J. Chem.*, **54**, 685 (1976).

(32) J. Palagyi, Z. Decsy, G. Palyi, and L. Markó, *Hung. J. Ind. Chem. Vespren.*, **1**, 413 (1973).

(33) L. Roos, R. W. Goetz, and M. Orchin, *J. Org. Chem.*, **30**, 3023 (1965).

(34) M. Orchin, *Adv. Catal.*, **5**, 385 (1953), later (unpublished work) by Y. Matsui and M. Orchin.

(35) T. E. Nalesnik and M. Orchin, *J. Organomet. Chem.*, **212**, C16 (1981).

(36) I. Wender, R. Levine and M. Orchin, *J. Am. Chem. Soc.*, **72**, 4375 (1950).

(37) (a) R. W. Goetz and M. Orchin, *J. Org. Chem.*, **27**, 3698 (1962);

(b) L. Markó, *Proc. Chem. Soc.*, **67** (1962).

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

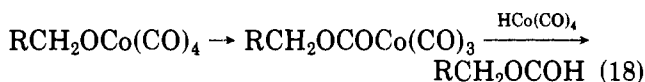
(25) N. H. Alemdarogly, J. L. M. Penninger, and E. Oltay, *Monatsh. Chem.*, **107**, 1153 (1976).

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

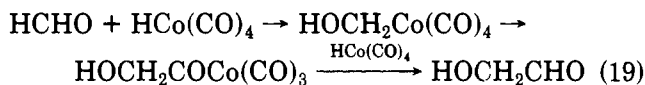
(27) I. Wender, R. A. Friedel, and M. Orchin, *Science (Washington, D.C.)*, **113**, 206 (1951).

(28) W. R. Pretzer and T. P. Kobylinski, *Ann. N.Y. Acad. Sci.*, **333**, 58 (1980).

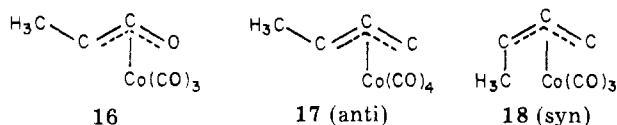
on the fact that formates are frequently found as side products. Their formation can be rationalized on the basis of the intermediate undergoing migratory insertion of CO:



However, the stoichiometric reaction of formaldehyde with $\text{HCo}(\text{CO})_4$ leads to glycolaldehyde,³⁸ and this must involve C-Co bonding:



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 proposed³⁹ that the hydrogenation of α,β -unsaturated ketones and aldehydes proceeds by 1,4-addition to form an intermediate π -



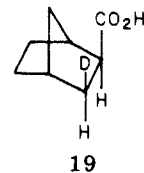
oxapropenyl complex, 16, analogous to the isolable and well-characterized iso- π -electronic complexes 17 and 18 prepared from 1,3-butadiene⁴¹ and $\text{HCo}(\text{CO})_4$.

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 $\text{HCo}(\text{CO})_4$ 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.

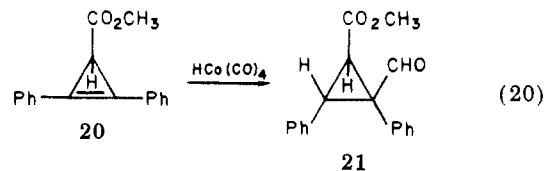
Stereochemistry

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

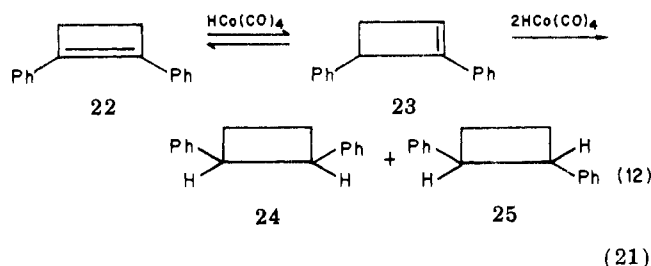
formylation reaction, probably because the required prochiral olefins, if they react at all, mostly undergo hydrogenation rather than hydroformylation. However, treatment of norbornene with $\text{DCo}(\text{CO})_4$ followed by oxidation gave the *exo*-norbornane-2-carboxylic acid (19), indicating *cis*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



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*



addition to the more hindered face of 20.⁴³ Treatment of 1,2-diphenyl-1-cyclobutene (22) with stoichiometric



amounts of $\text{HCo}(\text{CO})_4$ 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 $\text{HCo}(\text{CO})_4$ 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 suggested⁴⁶ in hydrogenation reactions with the isoelectronic $[\text{HCo}(\text{CN})_5]^{3-}$ and with $\text{HMn}(\text{CO})_5$; in the latter case,⁴⁷ a geminate radical pair

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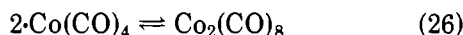
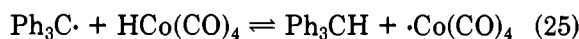
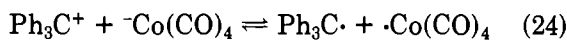
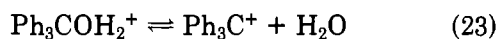
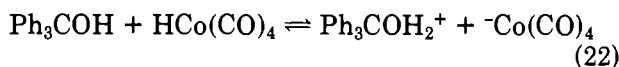
(40) P. Taylor and M. Orchin, *J. Organomet. Chem.*, **26**, 389 (1971).

(41) D. W. Moore, H. B. Jonassen, T. B. Joyner, and J. A. Bertrand, *Chem. Ind. (London)*, 1304 (1960); W. Rupilius and M. Orchin, *J. Org. Chem.*, **36**, 3604 (1971).

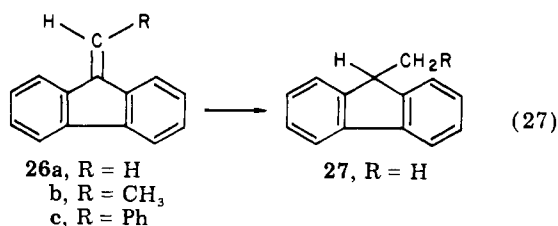
was shown to be present by use of CIDNP measurements during the reduction of α -methylstyrene.

Possible Radical Intermediates

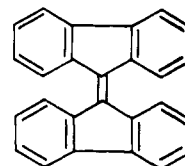
The question of radical involvement in reactions with HCo(CO)₄ is of considerable current interest. As early as 1953, the sequence shown in eq 22–26 was written



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 rapidly⁴⁹ and cleanly with HCo(CO)₄ at essentially the same rate in either CH₂Cl₂, hexane, or methyl methacrylate as solvent. Conventional spin traps such as phenyl-*tert*-butylnitron 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 Ph₂C=CH₂).] The hydrogenation is first order with respect to HCo(CO)₄ and Ph₂C=CH₂. Furthermore, unlike stoichiometric hydroformylation, this stoichiometric hydrogenation is unaffected by 1 atm of CO. ΔH^\ddagger is found to be 17 kcal mol⁻¹ and ΔS^\ddagger -10 cal deg⁻¹ mol⁻¹. Similar to the known reaction between HMn(CO)₅ and α -methylstyrene, the reaction between Ph₂C=CH₂ and DCo(CO)₄ leads to an inverse isotope effect, $k_H/k_D = .58$. In very recent work⁵⁰ it has been shown that 9-methylidene-fluorene (26a) is readily hydrogenated at -67 °C to 9-methylfluorene (27) (eq 27).



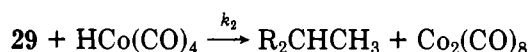
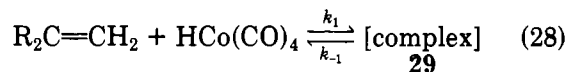
The rate of reaction is 3670 times as fast as the reaction with 1,1-diphenylethylene. The tetrasubstituted ethylene, bifluorenylidene (28), is hydrogenated almost twice as fast as 1,1-diphenylethylene.⁵¹ The results of rate data⁵¹ for the hydrogenation of various olefins with



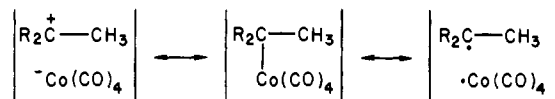
28

HCo(CO)₄ under similar conditions indicate the order (relative rates in parentheses) 26a (3670) > CH₂=C(CN)Ph (80) > 26b (2.5) > 28 (1.66) > CH₂=CPh₂ (1.00) > 26c (0.9) > Ph₂C=CHCH₃ (~10⁻⁵) \cong PhCH=C(CN)Ph > (CH₃)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

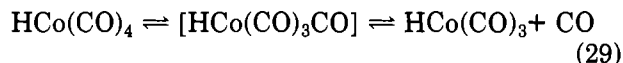


complex 29 may possess a particularly weak C-Co σ bond in substrates where the R groups attached to the C atom enhances effective electron delocalization, and in such cases 29 can be represented by the resonance structures (or equilibria):



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 nucleophiles⁵² 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



occurs into and out of this cage.⁵³

To further complicate the picture, it has been shown recently that HCo(CO)₄ reacts with Co₂(CO)₈ to form a trinuclear species,⁵⁴ HCo₃(CO)₉, which is an effective reducing agent. In both catalytic and stoichiometric reactions, HCo(CO)₄ and Co₂(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

(48) Reference 34, p 413.

(49) J. A. Roth and M. Orchin, *J. Organomet. Chem.*, **182**, 299 (1979).

(50) T. E. Nalesnik and M. Orchin, *J. Organomet. Chem.*, **199**, 265 (1980).

(51) T. E. Nalesnik, J. Freudenberger, and M. Orchin, *J. Organomet. Chem.*, in press.

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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

DEVON W. MEEK* and TERRY J. MAZANEC

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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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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Devon W. Meek is Professor and Chairman of Chemistry at The Ohio State University. He was born in Kentucky and obtained his B.A. Degree at Berea College. He joined the faculty at Ohio State following receipt of the Ph.D. from the University of Illinois, Urbana, in 1961. His principal research interests have been to design and synthesize polydentate ligands for spectral, stereochemical, and catalytic studies on transition-metal complexes with unusual structures and coordination numbers.

Terry J. Mazanec was born in Cleveland, OH. He received his B.S. degree from Cornell University and the Ph.D. from Ohio State in 1978. After a period of postdoctoral work at the University of Illinois with J. R. Shapley, he has recently joined the synfuels group at SOHIO.