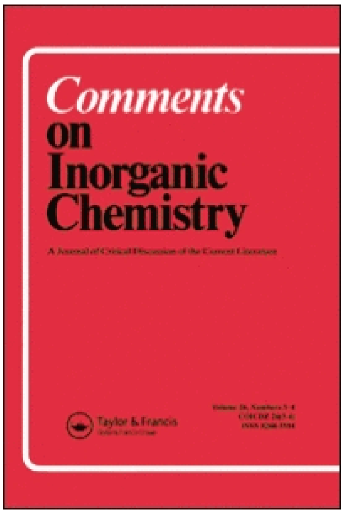

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A Mechanistic Approach to the Study of Homogeneous Catalytic Hydroformylation of Formaldehyde

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A Mechanistic Approach to the Study of Homogeneous Catalytic Hydroformylation of Formaldehyde

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The hydroformylation of formaldehyde is an important reaction in the pursuit of using synthesis gas as a raw material for the production of large volume chemicals. This article describes the development of an efficient catalyst system for the hydroformylation of formaldehyde based on the understanding of a novel, anionic reaction mechanism. The catalytic cycle was elucidated through *in situ* spectroscopic studies and the synthesis and characterization of model intermediates. By using rhodium and iridium complexes as model intermediates, the complete illustration of the reaction mechanism was accomplished.

Key Words: *formaldehyde, hydroformylation, glycolaldehyde, rhodium-catalyzed, rhodium-alkyl, rhodium-acyl, iridium-alkyl, iridium-acyl*

INTRODUCTION

Synthesis gas is potentially the lowest-cost building block for most large-volume chemicals which currently are derived from petroleum.[1] In the 1970's and early 1980's, there was a heightened interest in the study of using syngas as a raw material to make

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commodity chemicals, owing to the escalation of oil price. Today, even though the price of crude oil has been stabilized, the danger of the depletion (or substantial short supply) of petroleum in the foreseeable future is still real.[2] For this reason the study of syngas chemistry still makes good scientific and business sense.

One important consideration in using syngas as a raw material for the production of commodity chemicals is to retain the oxygen moiety of the carbon monoxide in the final product, since the oxygen accounts for more than half of the weight of the syngas. In this regard, the synthesis of ethylene glycol from syngas is a very attractive reaction.

$$2\,CO + 3\,H_2 \xrightarrow{\text{Cat.}} HOCH_2CH_2OH \qquad (1)$$

Not surprisingly, chemical producers such as Union Carbide,[3] Texaco,[4] and a consortium of Japanese companies[5] spent a large effort on the investigation of the direct conversion of syngas to ethylene glycol using rhodium and ruthenium catalysts. However, several mechanistic studies indicate that the rate limiting step in the catalytic cycle of the direct syngas conversion is the conversion of syngas to formaldehyde (or a formyl species) which is thermodynamically unfavorable.[6-8] Therefore, high concentration of the precious metal catalyst and extremely high pressure of syngas are necessary to push the desired reaction forward. The requirement of these severe conditions makes the syngas reaction uneconomical. From a practical standpoint, it is more attractive to convert syngas to methanol and then to formaldehyde, using well established, low cost heterogeneous catalysts. The formaldehyde can then be hydroformylated to glycolaldehyde.

$$H_2C{=}O + CO + H_2 \xrightarrow{\text{Cat.}} HOCH_2CHO \qquad (2)$$

The glycolaldehyde product can be hydrogenated to ethylene glycol[9] or, if desired, be converted to higher value materials such as serine. In this regard, the hydroformylation of formaldehyde is of significant scientific and practical value.

In the early studies of the Rh-catalyzed hydroformylation of formaldehyde, the yields of the glycolaldehyde product were relatively low.[9,10] The product yield was even worse when a cobalt carbonyl catalyst was used.[11] There was very little information on the mechanistic aspect of the reaction. In our opinion, an understanding of the reaction mechanism should offer a better opportunity for the improvement of the reaction.

RESULTS AND DISCUSSIONS

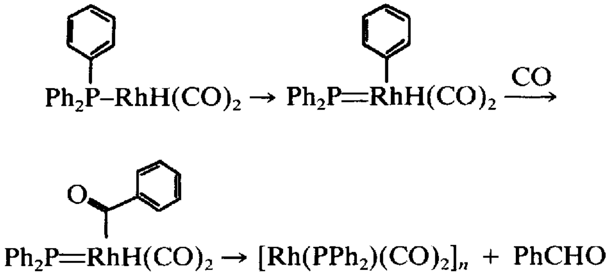
In our initial study of the hydroformylation of formaldehyde, we found that glycolaldehyde undergoes aldol reaction with itself and with other aldehydes such as formaldehyde.[12] The aldol reaction is known to be catalyzed by base and acid. The condensation is more severe when a cobalt catalyst is used, since the active catalyst, $HCo(CO)_4$, is a strong acid which can increase the rate of the condensation. Consequently lower yields of glycolaldehyde are usually obtained in the cobalt-catalyzed system.

$$2\ HOCH_2CHO \rightarrow HOCH_2CH(OH)CH(OH)CHO \qquad (3)$$

$$HOCH_2CHO + HCHO \rightarrow HOCH_2CH(OH)CHO \qquad (4)$$

This finding offers an excellent hint for the improvement of the reaction: the aldol reactions account for a large portion of the glycolaldehyde loss and should be avoided in order to achieve high product yields. By carefully monitoring the composition of the reaction solution and by avoiding "overcooking" the product, we were able to achieve over 90% yield of glycolaldehyde (based on the converted formaldehyde) with a rhodium phosphine catalyst system.[12]

Rhodium is one of the most precious metals in the world. Although it has been extensively used in the chemical industry for the production of commodity chemicals such as acetic acid[13] and butyraldehyde,[14] extreme care has to be taken to insure that the catalyst is long-lasting and readily reusable. In the studies of the rhodium phosphine-catalyzed hydroformylation of olefins, it has been found that the rhodium phosphine catalyst deactivates via an oxidative addition of the P–C bond of the phosphine to the metal.[15]



(5)

This type of oxidative addition usually takes place when the rhodium complex is highly unsaturated. The problem can be alleviated by using excess phosphine ligands to suppress the formation of the highly unsaturated species.[14] Since the catalysts used in the hydroformylation of formaldehyde are similar to those used in the hydroformylation of olefins, it is important to examine the effect of the excess phosphine ligands on the hydroformylation reaction. The profound effect of phosphine ligands on the rate and selectivity of the hydroformylation of formaldehyde is shown in Table I.

It is obvious from Table I that the presence of phosphine ligand is crucial for the higher rate and higher selectivity in the Rh-catalyzed formaldehyde hydroformylation. This is consistent with the expectation that the rhodium phosphine complexes are better catalysts than simple rhodium carbonyl species in this reaction.

TABLE I

The rates and selectivities of formaldehyde hydroformylation versus the level of phosphine ligands used.

Catalyst Precursor	PPh_3/Rh	Conversion of HCHO (%)	Selectivities (%) G.A.	Selectivities (%) CH_3OH
$[Rh(COD)Cl]_2$	0	49	38	41
$[Rh(COD)Cl]_2$	1	90	80	3
$RhCl(CO)(PPh_3)_2$	2	87	80	4
$RhCl(CO)(PPh_3)_2$	3	82	83	4
$RhCl(CO)(PPh_3)_2$	4	68	82	4
$RhCl(CO)(PPh_3)_2$	5	65	82	6
$RhCl(CO)(PPh_3)_2$	30	44	43	11

$[Rh] = 5 \times 10^{-3}$ M; [HCHO] = 2 M; $P_{CO:H_2(1:1)} = 2500$ psig; solvent = N,N-dimethylacetamide; reaction time = 2 hours.

However, as the level of free phosphine ligands increases, both the rate of hydroformylation and the selectivity to glycolaldehyde decrease. The decrease of the rate of hydroformylation can be explained in terms of the formation of the saturated, inactive rhodium species, $HRh(CO)_2(PPh_3)_2$, in the presence of the excess triphenylphosphine ligands. In this respect, the mechanism of the hydroformylation of formaldehyde may be similar to that of the hydroformylation of olefins[16] (Fig. 1).

It is clear from Fig. 1 that the rate-suppression effect of the excess triphenylphosphine ligand is due to its competition with the substrates for the active catalyst, $HRh(CO)_2PPh_3$. In the hydroformylation of propylene, this effect is not too problematic because the olefin is a good coordinating agent and competes well with the excess phosphine. The more severe rate-suppression effect of PPh_3

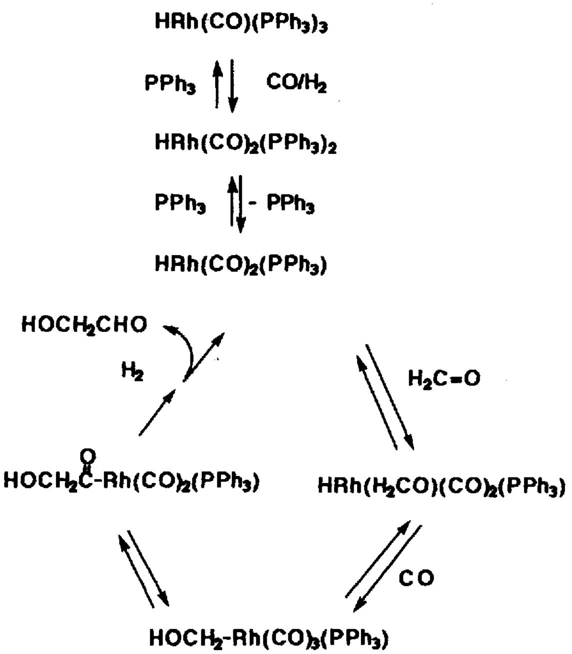


FIGURE 1 A proposed dissociative mechanism for the Rh-catalyzed hydroformylation of formaldehyde.

in the hydroformylation of formaldehyde is likely due to the weaker coordinating ability of formaldehyde.

Since triphenylphosphine is slightly basic, its presence in large excess also causes more severe aldol condensation. Both the slower hydroformylation and more severe aldol condensation lower the yield of glycolaldehyde significantly.

At that stage it appeared that based on the normal dissociative mechanism, the stability of the rhodium species and the catalytic activity of it were mutually exclusive and could not be achieved at the same time. In order to obtain a rhodium phosphine complex that is both stable and highly active, a catalyst system that operates via a different mechanism has to be considered.

An Anionic Catalytic Path

An important difference between formaldehyde (monomer) and an ordinary alkene is that the double bond in formaldehyde is polarized and is more susceptible to nucleophilic attack. Therefore, even though the association of formaldehyde to the neutral rhodium complex is not very strong, its reaction with an anionic nucleophile should be quite facile. To take advantage of this understanding, we designed a catalytic pathway that did not require the dissociation of a phosphine ligand from the coordinatively saturated complex $HRh(CO)_2(PPh_3)_2$. The novel system involved anionic rhodium complexes as active catalysts and a possible mechanism was proposed as in Fig. 2.

The acidity of metal hydrides depends very much on the ligands on the metal complex. For example, $HCo(CO)_4$ is a strong acid and dissociates readily in polar solution to form H^+ and $[Co(CO)_4]^-$. The displacement of the carbonyl ligand with triphenylphosphine ligand decreases the activity of the cobalt hydride significantly. Similarly, while $HRh(CO)_4$ dissociates readily in solution to form H^+ and $[Rh(CO)_4]^-$, the hydride moiety of $HRh(CO)_2(PPh_3)_2$ is not acidic enough to dissociate from the rhodium complex as H^+ under normal conditions. However, under CO atmosphere, we envisioned the abstraction of the hydride as a proton by a Lewis base to give an anionic rhodium complex.

$$HRh(CO)_2(PPh_3)_2 + B\,(\text{base}) \xrightarrow{CO} [Rh(CO)_x(PPh_3)_{4-x}]^- \qquad (6)$$

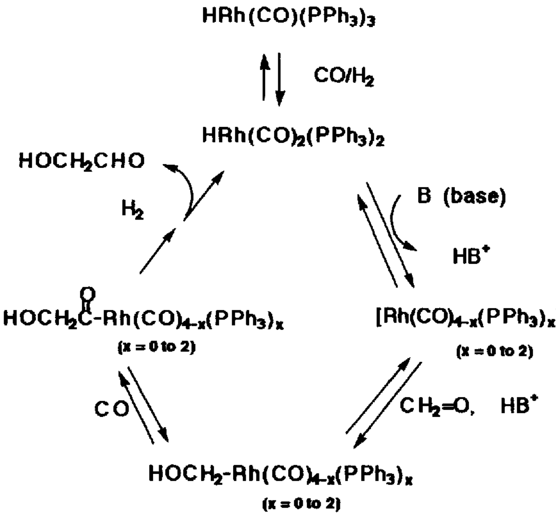


FIGURE 2 A proposed mechanism for the hydroformylation of formaldehyde involving anionic rhodium catalysts.

This concept was experimentally confirmed when we studied the *in situ* infrared spectra of rhodium carbonyl phosphine complexes under CO pressure and in the presence of triethylamine. When a rhodium complex such as $HRh(CO)(PPh_3)_3$ was dissolved in a DMF (N,N-dimethylformamide) solution in the presence of excess triphenylphosphine and under 500 psi synthesis gas ($CO + H_2$), $HRh(CO)_2(PPh_3)_2$ was found to be the dominant species. However, when a small amount of triethylamine was added to this solution, the rhodium complex immediately changed to $[Rh(CO)_4]^-$ and $[Rh(CO)_3PPh_3]^-$.[12]

The concept of stable and highly active anionic rhodium catalyst was supported by our experimental data. Even in the presence of a large excess of triphenylphosphine ligand as stabilizing agent, the electronically saturated rhodium species can still be activated by adding small amounts of an organic base such as triethylamine. Indeed, the anionic rhodium catalyst has been found to be much more active than the corresponding neutral species. Some representative data illustrating this effect are shown in Table II. At that point we had solved a big dilemma and a stable and highly active

TABLE II

The effect of base on the rates and selectivities of the hydroformylation of formaldehyde.[a]

$[NEt_3] \times 10^2$ (M)	Reaction Time (min)	Conversion of HCHO (%)	Product Selectivities[b]	
			GA (%)	MeOH (%)
0.84	30	43	86	9
1.8	30	93	71	27
45	15	95	17	6

[a] Catalyst precursor = $[RhCl(CO)(PPh_3)_2]$ = 5×10^{-3} M; [HCHO] = 2 M; $P_{CO:H_2(1:1)}$ = 2500 psi; solvent = N,N-dimethylacetamide; $[PPh_3]$ = 1.5×10^{-1} M; T = 110°C.

[b] Balance = condensation by-products.

catalyst system was obtained. However, the problem of the selectivity to glycolaldehyde still remained to be solved. As previously discussed, the aldol condensation of glycolaldehyde was catalyzed by base. The addition of a strong base such as triethylamine to the catalyst system also caused a more severe aldol reaction and the loss of glycolaldehyde was quite significant.

Since the concept of an anionic rhodium catalyst in the hydroformylation of formaldehyde was quite novel, from a scientific standpoint it was of interest to elucidate the mechanism in more detail. From a practical standpoint, the understanding of the mechanism also should help us to design better catalysts for the reaction.

Elucidation of the Anionic Mechanism

The first step in our mechanistic study was to synthesize the expected anionic rhodium complexes and then use them as "fingerprints" in the identification of catalytic species in the *in situ* spectroscopic study. The synthesis of anionic rhodium and iridium complexes had been previously published by Collman *et al.*[17] By reacting $RhCl(CO)(PPh_3)_2$ with sodium amalgam in a tetrahydrofuran (THF) solution under an atmospheric pressure of CO, Collman and co-workers suggested that $[Rh(CO)_2(PPh_3)_2]^-$ was the major product. When $IrCl(CO)(PPh_3)_2$ was used as the starting material in the reduction, these researchers suggested that $[Ir(CO)_3(PPh_3)]^-$ was obtained as the dominant species. When we studied these reactions, we found that instead of $[Rh(CO)_2(PPh_3)_2]^-$ and $[Ir(CO)_3(PPh_3)]^-$, the dominant products were $[Rh(CO)_4]^-$ and $[Ir(CO)_4]^-$, respectively. There was no evidence for the formation of $[Rh(CO)_2(PPh_3)_2]^-$ under these reaction conditions.

$$\mathrm{RhCl(CO)(PPh_3)_2} \xrightarrow[\mathrm{CO,\ THF}]{\mathrm{Na{-}Hg}} \underset{(>95\%)}{[\mathrm{Rh(CO)_4}]^-} + \underset{(<5\%)}{[\mathrm{Rh(CO)_3(PPh_3)}]^-} \tag{7}$$

$$\mathrm{IrCl(CO)(PPh_3)_2} \xrightarrow[\mathrm{CO,\ THF}]{\mathrm{Na{-}Hg}} \underset{(>95\%)}{[\mathrm{Ir(CO)_4}]^-} + \underset{(<5\%)}{[\mathrm{Ir(CO)_3(PPh_3)}]^-} \tag{8}$$

The reason for the formation of $[Rh(CO)_4]^-$ and $[Ir(CO)_4]^-$ as dominant anionic species was quite obvious: when the rhodium and the iridium complexes were reduced to the anionic state, they were better stabilized with electron-withdrawing ligands. The strong dative π-bonding ability of the carbonyl ligand served this purpose well. The dative π-bonds in the metal carbonyls helped de-localize the negative charge from the metal center and consequently stabilized the anionic complexes.

When the THF solution of $[Rh(CO)_4]^-$ and the excess of free triphenylphosphine was stirred under an inert atmosphere such as nitrogen gas, the anionic species was slowly converted to $[Rh(CO)_3(PPh_3)]^-$. There was no evidence for the formation of $[Rh(CO)_2(PPh_3)_2]^-$ even in the presence of a large excess of triphenylphosphine in the solution. The reason for the slow ligand substitution was due to the fact that $[Rh(CO)_4]^-$ was a saturated, 18 electron species. The ligand substitution had to go through a dissociative path in which the rate-limiting step was the dissociation of a carbonyl ligand from the anionic complex. However, the dissociation of a carbonyl ligand from the anionic species was unfavorable because these ligands were needed to stabilize the complex by de-localizing the negative charge on the metal. Consequently, a complete conversion of $[Rh(CO)_4]^-$ to $[Rh(CO)_3(PPh_3)]^-$ at ambient temperature required several weeks.

The sodium salt of $[Rh(CO)_3(PPh_3)]^-$ did not crystallize nicely by itself, probably due to the unfavorable packing of the small cation and the large anion. However, when 18-crown-6 ether was added to the solution to trap the sodium cation to form a larger cationic moiety, a crown ether-complexed sodium salt of $[Rh(CO)_3(PPh_3)]^-$ was readily crystallized as nice, yellow crystals. The structure of the complex has been unambiguously characterized by single crystal x-ray diffraction as a distorted tetrahedron.[18] The crown ether-complexed sodium cation is puckered and linked to one of the carbonyl ligands of the anionic rhodium complex (Fig. 3). The identification of the anionic rhodium complexes was the first milestone in the elucidation of the anionic route of the hydroformylation of formaldehyde.

The rate-limiting step in the anionic catalytic cycle appeared to be the reaction of the anionic rhodium complexes with formaldehyde. This was consistent with the fact that only $HRh(CO)_2(PPh_3)_2$, $[Rh(CO)_4]^-$, and $[Rh(CO)_3(PPh_3)]^-$ were observed in the *in situ* high pressure infrared study of the reaction solutions under the conditions of formaldehyde hydroformylation. It was also supported by a kinetic study of the reaction.[19] Since the reactions following the rate-limiting step were much faster, it

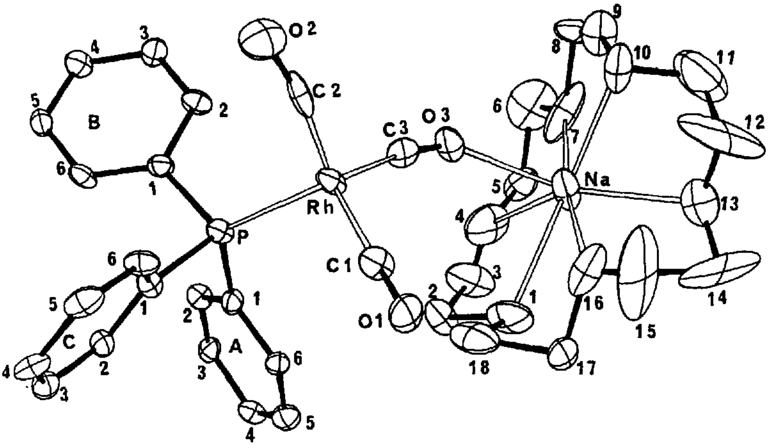


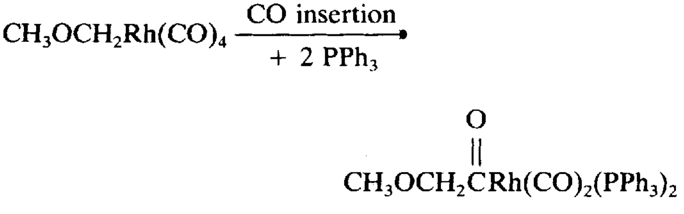
FIGURE 3 A perspective view of the 18-crown-6 ether-complexed sodium salt of $[Rh(CO)_3(PPh_3)]^-$.

was not possible to directly intercept and characterize other key catalytic intermediates such as the metal alkyl and metal acyl species proposed in Fig. 2. For the thorough understanding of the reaction mechanism, it was important to prepare model compounds which could illustrate the chemistry related to the catalytic cycle. Our first attempt was to prepare a rhodium alkyl species with a formula of $CH_3OCH_2Rh(CO)_x(PPh_3)_{4-x}$. The reason to use a CH_3OCH_2 group to replace the expected $HOCH_2$ group was to avoid the decomposition of the complex via β-hydride abstraction:

$$HOCH_2\text{-}Rh(CO)_x(PPh_3)_{4-x} \xrightarrow{-HCHO} HRh(CO)_x(PPh_3)_{4-x} \tag{9}$$

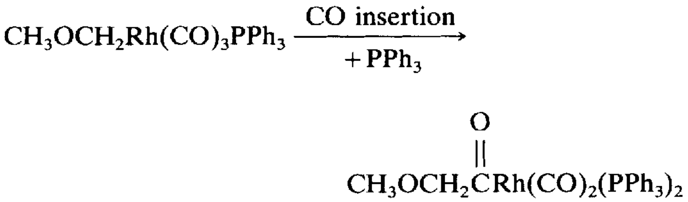
When the anionic rhodium complexes (obtained from the reduction of $RhCl(CO)(PPh_3)_2$ with sodium amalgam under CO atmosphere in THF) were allowed to react with CH_3OCH_2Cl, instead of a rhodium alkyl species such as $CH_3OCH_2Rh(CO)_x(PPh_3)_{4-x}$, $CH_3OCH_2C(O)\text{-}Rh(CO)_2(PPh_3)_2$ was obtained in essentially quantitative yield (ν_{CO} = 1986, 1941, 1663 cm^{-1}). This observation can be explained in terms of rapid carbonyl insertion and ligand exchange after the nucleophilic displacement of the chloride by the anionic rhodium complexes.

$$[Rh(CO)_4]^- + CH_3OCH_2Cl \xrightarrow{-Cl^-} CH_3OCH_2Rh(CO)_4 \tag{10}$$



$$CH_3OCH_2Rh(CO)_4 \xrightarrow[+\ 2\ PPh_3]{CO\ insertion} CH_3OCH_2\overset{\overset{\displaystyle O}{\|}}{C}Rh(CO)_2(PPh_3)_2 \tag{11}$$

$$[Rh(CO)_3(PPh_3)]^- + CH_3OCH_2Cl \xrightarrow{-Cl^-} CH_3OCH_2Rh(CO)_3PPh_3 \tag{12}$$



$$CH_3OCH_2Rh(CO)_3PPh_3 \xrightarrow[+PPh_3]{\text{CO insertion}} CH_3OCH_2\overset{\overset{\displaystyle O}{\|}}{C}Rh(CO)_2(PPh_3)_2 \quad (13)$$

When the solution of $CH_3OCH_2C(O)-Rh(CO)_2(PPh_3)_2$ was pressurized with H_2/CO, CH_3OCH_2CHO was obtained, and $HRh(CO)_2(PPh_3)_2$ was regenerated. This reaction completed our intended model study of the anionic mechanism of the rhodium-catalyzed hydroformylation of formaldehyde. The only missing link in this model study is the rhodium alkyl species. While the isolation of this species is not a necessary condition for the mechanism to be considered to be valid, for the purpose of perfection, it is still highly desirable to synthesize a similar complex to illustrate its chemistry. In this regard, we studied the iridium analog of these complexes. The advantages of using iridium complexes as models for the catalytic intermediates are: (1) the chemistry of iridium complexes is similar to that of their rhodium analogs; (2) the carbonyl insertion step in iridium-alkyl species is slower and the chance of isolating the key intermediate is very high.

When a THF solution of anionic iridium complexes (obtained from the reduction of $IrCl(CO)(PPh_3)_2$ with sodium amalgam under CO atmosphere) was allowed to react with CH_3OCH_2Cl, $CH_3OCH_2-Ir(CO)_2(PPh_3)_2$ was indeed obtained in over 95% yield (ν_{CO} = 1971, 1921 cm^{-1}).

$$\begin{tikzcd} IrCl(CO)(PPh_3)_2 \arrow[r, "Na-Hg", "{CO, THF}"'] & {[Ir(CO)_4]^- + 2\ PPh_3} \arrow[d, "CH_3OCH_2Cl"] \\ & CH_3OCH_2-Ir(CO)_2(PPh_3)_2 \quad (14) \end{tikzcd}$$

White crystals of this complex were isolated upon slow addition of petroleum ether into the THF solution. The structure of this complex was determined by single crystal x-ray diffraction to be a distorted trigonal bipyramidal[20] (Fig. 4). When a THF solution of $CH_3OCH_2{-}Ir(CO)_2(PPh_3)_2$ was pressurized with CO, $CH_3OCH_2C(O){-}Ir(CO)_2(PPh_3)_2$ (ν_{CO} = 1972, 1928, 1654 cm^{-1}) and $CH_3OCH_2C(O){-}Ir(CO)_3(PPh_3)$ (ν_{CO} = 2047, 1983, 1673 cm^{-1}) were obtained. It should be noted that $CH_3OCH_2{-}Ir(CO)_2(PPh_3)_2$, $CH_3OCH_2C(O){-}Ir(CO)_2(PPh_3)_2$, and $CH_3OCH_2C(O){-}Ir(CO)_3$-(PPh_3) are interconvertible, depending on the reaction conditions.

$$CH_3OCH_2{-}Ir(CO)_2(PPh_3)_2 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} CH_3OCH_2C(O){-}Ir(CO)_2(PPh_3)_2 + CH_3OCH_2C(O){-}Ir(CO)_3(PPh_3) \qquad (15)$$

The two iridium acyl complexes, $CH_3OCH_2C(O){-}Ir(CO)_2(PPh_3)_2$ and $CH_3OCH_2C(O){-}Ir(CO)_3(PPh_3)$ were also independently synthesized by reacting the anionic iridium carbonyl species with $CH_3OCH_2C(O)Cl$.

$$IrCl(CO)(PPh_3)_2 \xrightarrow[CO,\ THF]{Na{-}Hg} [Ir(CO)_4]^- + 2\,PPh_3$$

$$\downarrow CH_3OCH_2C(O)Cl$$

$$\underset{(>90\%)}{CH_3OCH_2C(O){-}Ir(CO)_2(PPh_3)_2} + \underset{(<10\%)}{CH_3OCH_2C(O){-}Ir(CO)_3(PPh_3)} \qquad (16)$$

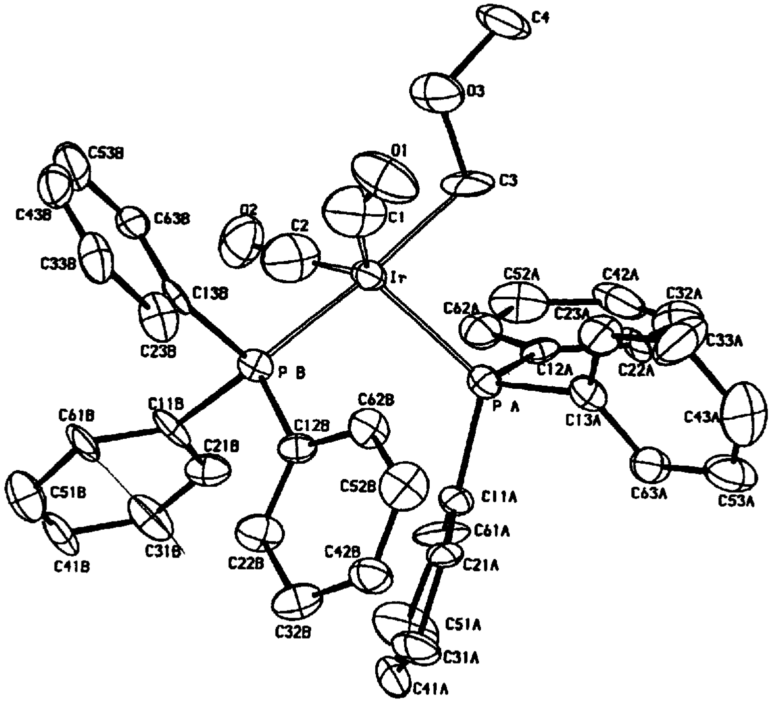


FIGURE 4 A perspective view of $CH_3OCH_2-Ir(CO)_2(PPh_3)_2$.

Single crystals of $CH_3OCH_2C(O)-Ir(CO)_2(PPh_3)_2$ were obtained upon slow addition of petroleum ether into the THF solution of this complex. An x-ray diffraction study revealed a trigonal bipyramidal structure as shown in Fig. 5.[20] These results clearly illustrated the expected structures of the key catalyst intermediates in the homogeneous hydroformylation of formaldehyde and lent credibility to the anionic reaction mechanism.

An Improved Catalyst System

With the understanding of the anionic mechanism, we were able to design a more effective rhodium catalyst system which gave high catalyst stability and high selectivity in the hydroformylation of formaldehyde. The key step in the anionic catalytic cycle is the

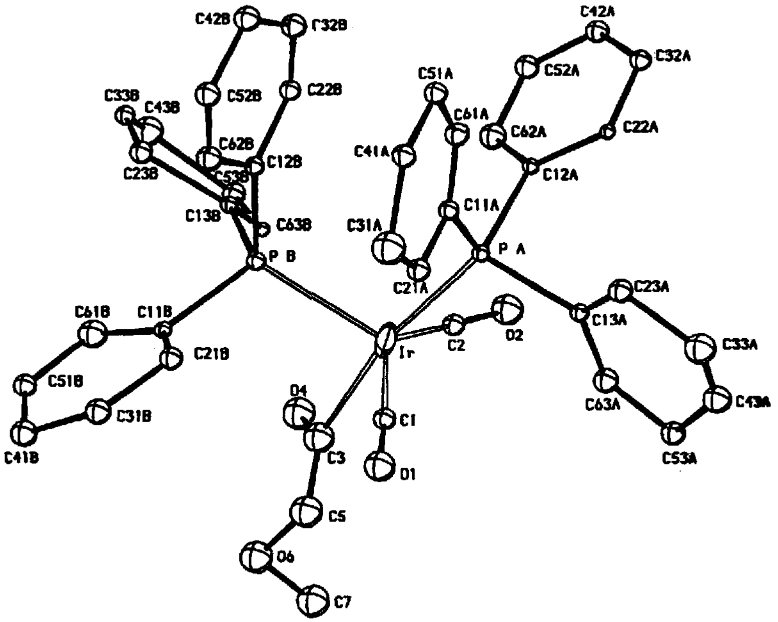


FIGURE 5 A perspective view of $CH_3OCH_2C(O)-Ir(CO)_2(PPh_3)_2$.

generation of the active anionic rhodium catalyst via deprotonation of the saturated rhodium hydride species, $HRh(CO)_2(PPh_3)_2$. An important criterion for an improved catalyst system is the capability of the saturated hydride species to undergo deprotonation without the use of a strong base. The problem of product loss due to aldol condensation can be alleviated if the reaction conditions are less basic. A logical choice is to substitute the triphenylphosphine ligand with more electron-withdrawing phosphine ligands. This change can make the hydride more acidic and consequently the deprotonation can be done more readily without a strong base. To this end we tested tris(*para*-trifluoromethylphenyl)phosphine ligand in the new catalyst system. The results were consistent with our expectation. When the hydroformylation of formaldehyde was carried out in DMF solvent without added bases, very high selectivity to a glycolaldehyde product was obtained even with a high ligand/

TABLE III

The effect of electron-defficient phosphine ligand on the Rh-catalyzed hydroformylation of formaldehyde.[a]

Catalyst Precursor	Conversion of HCHO (%)	Product Selectivity[b] GA (%)	MeOH (%)
$[Rh(CO)_2Cl]_2$ + 10 L	79	91	2
$[Rh(CO)_2Cl]_2$ + 20 L	77	90	2.6
$RhCl(CO)(PPh_3)_2$ + 10 L	75	93	3

[a] $[Rh] = 5 \times 10^{-3}$ M; [HCHO] = 2 M; $P_{CO:H_2}$ = 2500 psi; T = 110°C; solvent = N,N-dimethylacetamide; reaction time = 1.5 hours; L = tris(*p*-trifluoromethylphenyl)phosphine.

[b] Balance = condensation products.

rhodium ratio in the new catalyst system. Typical results of this improved catalyst system are summarized in Table III.

CONCLUSION

Even though our proposed mechanism involving anionic rhodium catalysts is quite novel, it is well supported by our spectroscopic and modeling studies. Furthermore, the rationale of designing catalysts based on a better understanding of the reaction mechanism is sound and our experimental results clearly support this approach. The elucidated mechanism can also be used to explain the observations of other researcher in their studies of formaldehyde hydroformylation.[21,22]

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