of $\nu_{as}(CH_3)$ to be represented by the band at 2972.6 cm^{-1}, then we obtain:

$2\nu_{as}(CH_3) + \nu_s(CH_3)$	$\sum_{i=1}^{3}\nu_i^{is}(CHD_2)$
$2 \times 2972.6 + (2906.2 - 23.7)$	$2939.9 + 2935.0 + 2933.4$
$= 8827.7\ cm^{-1}$	$= 8808.3\ cm^{-1}$

The anomaly is removed, however, if we suppose the 2972.6 cm^{-1} band to be in resonance with the lower band at 2950 cm^{-1}, the unperturbed value of $\nu_{as}(CH_3)$ lying at about 2962 cm^{-1}. It has to be emphasized that a genuine splitting of $\nu_{as}(CH_3)$ of about 22 cm^{-1} would lead to a similar splitting of $\nu_{as}(CD_3)$ and of $\nu_{as}(CD_2)$ in the CHD_2 group with components of similar intensity, and of this there is no sign at all. Instead, the resemblance between the Mn and Re spectra from the CD_3 and CHD_2 groups is very strong indeed.

Thus, our conclusion at this stage then is that rotation in the N_2 matrix is restricted and that the predominant species has three, only slightly differing isolated C–H stretching frequencies, which in fact lie close to the centers of the bands observed in the gas phase, at 2955.0 (Mn) and 2934.6 cm^{-1} (Re), respectively.

Registry No. $CH_3Re(CO)_5$, 14524-92-6; $CH_3Mn(CO)_5$, 13601-24-6; *cis*-$CH_3Re(CO)_4(N_2)$, 123307-90-4; *trans*-$CH_3Re(CO)_4(N_2)$, 123408-79-7; *cis*-$CH_3Mn(CO)_4(N_2)$, 123330-23-4; CHD_2CD_2Cl, 258554-33-5; D_2, 7782-39-0; ^{13}C, 14762-74-4; Ar, 7440-37-1; N_2, 7727-37-9.

Rhodium-Catalyzed Reductive Carbonylation of Methanol

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In the presence of diphosphine ligands, CH_3I, and synthesis gas, rhodium catalyzes the reductive carbonylation of methanol. With diphosphine = $Ph_2P(CH_2)_3PPh_2$, acetaldehyde is produced in selectivities approaching 90%; the remaining product is acetic acid. The reaction rates for the rhodium–diphosphine catalysts (up to 6 M h^{-1}) rival those for the best previously reported catalysts. More importantly, these rates are achieved at much lower temperatures (130–150 °C) and pressures (ca. 1000 psi) than normally employed for this chemistry (e.g., 175–220 °C, 4000–8000 psi). If ruthenium is employed as a cocatalyst, acetaldehyde is hydrogenated in situ and ethanol is produced with the same high selectivity and rate. Thus, this catalyst is readily tuned to produce either acetaldehyde or ethanol under relatively mild conditions. The five-coordinate acetyl complexes Rh(diphosphine)$(COCH_3)(I)_2$ [diphosphine = R_2PYPR_2, where R = Ph, *p*-tol, or *p*-ClC_6H_5 and Y = $(CH_2)_2$, $(CH_2)_3$, $CH(CH_3)(CH_2)_2$, or $(CH_2)_2C(CH_2)_2$] are the only rhodium and diphosphine-containing species detected at the end of catalysis experiments. They are isolable in nearly quantitative yield and have been characterized by standard methods. These complexes can, in turn be employed successfully as catalysts (e.g., no loss in rate or selectivity) and again be isolated quantitatively. $Rh[Ph_2P(CH_2)_3PPh_2](COCH_3)(I)_2$ reacts quantitatively with H_2 (100 °C, 100 psi) yielding CH_3CHO and the hydride $Rh[Ph_2P(CH_2)_3PPh_2](H)(I)_2$. $Rh[Ph_2P(CH_2)_3PPh_2](H)(I)_2$ is converted to $Rh[Ph_2P(CH_2)_3PPh_2](COCH_3)(I)_2$ upon treatment with CO in CH_3OH. This reaction likely proceeds via reductive elimination of HI to form Rh(I), followed by oxidative addition of CH_3I (from HI + CH_3OH) and migratory CO insertion. This possibility is verified by the observation that CH_3I adds to Rh(diphosphine)(CO)(I) (diphosphine = $Ph_2P(CH_2)_nPPh_2$, n = 2 or 3) at room temperature, yielding the transient but detectable (^1H, ^{31}P NMR; IR) complexes $Rh[Ph_2P(CH_2)_nPPh_2](CO)(I)_2(CH_3)$ (two isomers). These Rh(III) methyl complexes are converted into $Rh[Ph_2P(CH_2)_nPPh_2](COCH_3)(I)_2$ at a rate competitive with oxidative addition. Alternatively, treating $Rh[Ph_2P(CH_2)_3PPh_2](COCH_3)(I)_2$ with CO in CH_3OH results in the catalytic formation of CH_3CO_2H. Analysis of products from catalytic reactions employing the labeled compounds $CH_3{}^{13}CO_2H$, $^{13}CH_3{}^{13}CHO$, and $^{13}CH_3I$ are consistent with a reaction sequence involving conversion of CH_3OH to CH_3I, followed by irreversible conversion of CH_3I to CH_3CHO or CH_3CO_2H. Kinetic studies on the catalytic reaction indicate a first-order dependence on acetyl concentration and zero-order dependence on CH_3I. These results are discussed in terms of a catalytic cycle wherein the acetyl complexes are involved in a rate and selectivity determining reaction with either H_2 or CO.

Introduction

The reductive carbonylation of methanol (eq 1) represents an entirely synthesis gas based route to two C_2 oxygenates—acetaldehyde (methanol hydroformylation) and ethanol (methanol homologation).[1] These products

$$CH_3OH \xrightarrow[H_2]{CO} CH_3CHO \text{ and/or } CH_3CH_2OH \quad (1)$$

may in turn be used as precursors to other important C_2 (or higher) molecules, such as ethylene from ethanol. The net result is a route to a variety of organic molecules from coal.

This conversion has been studied for nearly 50 years and has been dominated by cobalt catalysts, although other metals have also been studied.[1] During this time, the cobalt-based catalyst has been improved through modification with various promoters/cocatalysts such as iodide, phosphines, and additional transition metals. These traditional catalysts are characterized by operation at high pressures and temperatures, usually on the order of 4000–8000 psi and 175–200 °C. Although the performance of the best catalysts are significant improvements, the high pressures and temperatures required pose significant difficulties. Obviously, a catalyst that operates under more gentle conditions would be of great interest.

(1) See the following and references therein: (a) Roper, M.; Loevenich, H. In *Catalysis in C1 Chemistry*; Keim, W., Ed.; Reidel: Dordrecht, 1983; p 105. (b) Chen, M. J.; Rathke, J. W. *Organometallics* **1987**, *6*, 1833. (c) Wegman, R. W.; Busby, D. C.; Letts, J. B. *ACS Symp. Ser.* **1987**, *No. 328*, 125. (d) Pretzer, W. R.; Kobylinski, T. P. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 58. (e) Keim, W. *ACS Symp. Ser.* **1987**, *No. 328*, 1. (f) Fakley, M. E.; Head, R. A. *Appl. Catal.* **1983**, *5*, 3. (g) Rizkalla, N.; Goliaszewski, A. *ACS Symp. Ser.* **1987**, *No. 328*, 138. (h) Gauthier-Lafaye, J.; Perron, R. *Methanol and Carbonylation*; Editions Technip: Paris, 1987; Chapter 4.

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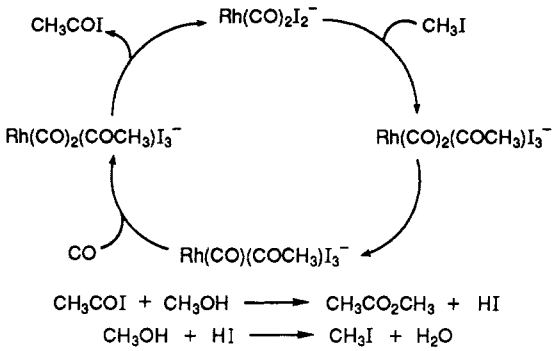
Scheme I



Both rhodium and cobalt catalyze a variety of carbonylation reactions. Particular examples that have found commercial application are the hydroformylation of olefins to aldehydes and the carbonylation of alcohols to acids.[2] The empirical observation is that rhodium catalyzes these carbonylation reactions under much milder conditions than does cobalt. However, in the reductive carbonylation of methanol, simple substitution of rhodium for cobalt does not lead to the formation of acetaldehyde. The reason is quite simple. In the presence of iodide and CO, rhodium is an extremely proficient catalyst for methanol carbonylation. This property forms the basis of the well-known Monsanto acetic acid process.[2a,3] Only when large, impractical synthesis gas ratios (H_2/CO = 40) are used is reductive carbonylation observed with rhodium, and then only to a small degree.[4]

The Monsanto chemistry has been studied extensively,[3] and the generally accepted mechanism is shown in Scheme I. The reaction is first-order in both [Rh] and [I], suggesting that the rate-limiting step is oxidative addition of CH_3I to $Rh(CO)_2(I)_2^-$, producing the methyl complex $Rh(CO)_2(I)_3(CH_3)^-$. Migratory insertion occurs in a rapid reaction to yield $Rh(CO)(COCH_3)(I)_3^-$. Carbonylation of this intermediate gives $Rh(CO)_2(COCH_3)(I)_3^-$, which rapidly reductively eliminates CH_3COI. This latter step has been demonstrated by Forster and is facile at room temperature. The CH_3COI so produced is converted to CH_3CO_2H in the protic reaction medium.

The key, it would seem, to directing the rhodium chemistry toward acetaldehyde is to stabilize the intermediate acetyl with respect to reductive elimination of CH_3COI. If possible, this may allow interception of the acetyl with hydrogen and the formation of CH_3CHO. The best way to achieve this is by judicious choice of the remaining groups ligated to rhodium. Work by Baird[5] and Pignolet[6] suggests just such a ligand environment. They have shown that the five-coordinate, cis-chelate complexes 1 are extremely stable to decarbonylation and reductive elimination.[7] Thus, $Rh[Ph_2P(CH_2)_3PPh_2](COCH_3)Cl_2$ is recovered unchanged when refluxed in chloroform.[5] This example should be compared to $Rh(CO)_2(COCH_3)(I)_3^-$, which reductively eliminates CH_3COI at 25 °C.[3] Complexes 1 are also very stable with respect to migratory deinsertion. For instance, $Rh[Ph_2P(CH_2)_3PPh_2](COPh)Cl_2$ resists decarbonylation upon heating to 190 °C.[6]

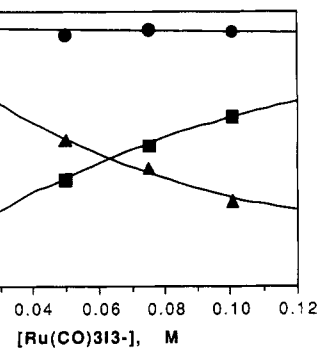
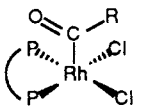


Figure 1. Product distribution as a function of ruthenium concentration: ▲, CH_3CHO; ■, CH_3CH_2OH; ●, CH_3CHO + CH_3CH_2OH. For all experiments: 1a (0.0188 M), $(CH_3)_4NRu(CO)_3(I)_3$ (0–0.10 M), CH_3I (1.0 M), 140 °C, 1000 psi total pressure, 2:1 H_2/CO.



1: R = alkyl, aryl

The robust nature of acetyl complexes 1 prompted us to test the reductive carbonylation of methanol with rhodium in the presence of diphosphine ligands. The results of this study, as well as a mechanistic investigation of the resulting catalyst, are presented here.

Results and Discussion

Catalytic Studies. We find that diphosphine ligands do indeed result in a rhodium-based catalyst for the reductive carbonylation of methanol.[8] More importantly, this catalyst gives rates and selectivities which rival those of the best previously reported catalysts, but at much lower temperatures and pressures. For instance, in the presence of $Ph_2P(CH_2)_3PPh_2$, rhodium, and iodide (charged as $Rh(CO)_2(acac)$ and CH_3I, respectively), methanol is converted to acetaldehyde at rates of 4–6 M h^{-1} and ca. 80% selectivity. Moreover, this performance is achieved at 140 °C and only 1000 psi of synthesis gas (2:1 H_2/CO). Acetic acid (as the free acid and its esters) is the only other byproduct observed in the liquid phase. Small amounts of methane are also invariably produced, generally accounting for ≤5 mol% of the methanol employed.[9]

Adding ruthenium to the rhodium–diphosphine catalyst leads to the in situ hydrogenation of CH_3CHO to CH_3CH_2OH.[10] As shown in Figure 1, the CH_3CHO/CH_3CH_2OH ratio is strongly tied to the amount of ruthenium employed. However, note that the combined CH_3CHO/CH_3CH_2OH selectivity is independent of the ruthenium concentration.

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(3) (a) Forster, D. *J. Am. Chem. Soc.* **1976**, *98*, 846. (b) Forster, D. *Adv. Organomet. Chem.* **1979**, *17*, 255. (c) Adamson, G. W.; Daly, J. J.; Forster, D. *J. Organomet. Chem.* **1974**, *71*, C17. (d) Adams, H.; Bailey, N. A.; Mann, B. E.; Manuel, C. P.; Spencer, C. M.; Kent, A. G. *J. Chem. Soc., Dalton Trans.* **1988**, 489.

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(6) McGuiggan, M. F.; Doughty, D. H.; Pignolet, L. H. *J. Organomet. Chem.* **1980**, *185*, 241.

(7) Complexes of this type have been previously investigated in the carbonylation of methanol to acetic acid: Bartish, C. M. U.S. Patent 4 102 920, 1978.

(8) (a) Wegman, R. W.; Miller, D. S. U.S. Patent 4 594 463, 1986. (b) Wegman, R. W.; Moloy, K. G. U.S. Patent 4 727 200, 1988. (c) Moloy, K. G.; Wegman, R. W. *J. Chem.. Soc., Chem. Commun.* **1988**, 820

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Table I. Rhodium–Diphosphine Catalyzed Reductive Carbonylation of Methanol—Representative Examples

$Rh(CO)_2$ (acac), mmol	$Ph_2P(CH_2)_3PPh_2$, mmol	$RuCl_3$, mmol	CH_3I, mmol	temp, °C	time, h	H_2/CO	total pressure, psi	CH_3CHO/CH_3CH_2OH selectivity, mol %
2	4	6	20	130	4.5	2	1000	80
2	4	6	20	140	2.0	2	1000	70
2	4	6	20	150	1.0	2	1000	53
2	6	6	40	140	3.0	3	1200	89
2	2	6	40	140	3.0	2	1000	82

Table II. Selectivity Dependence on Diphosphine Ligand

cat. (mmol)	CH_3I, mmol	Ru,[b] mmol	time, h	CH_3CHO/CH_3CH_2OH selectivity,[c] mol %
$Rh(CO)_2(acac)$ (2.0) $Ph_2P(CH_2)_3PPh_2$ (2.0)	40	4.0	2.5	82
$Rh(CO)_2(acac)$ (2.0) $(p\text{-tol})_2P(CH_2)_3P(p\text{-tol})_2$ (2.0)	40	4.0	1	54
$Rh(CO)_2(acac)$ (1.0) $(p\text{-}ClC_6H_4)_2P(CH_2)_3P(p\text{-}ClC_6H_4)_2$ (1.0)	40	4.0	2.25	29
$Rh(CO)_2(acac)$ (2.0) $Ph_2P(CH_2)_2PPh_2$ (2.0)	40	4.0	2.5	39
$Rh(CO)_2(acac)$ (2.0) $Ph_2P(CH_2)_2CH(CH_3)PPh_2$ (2.0)	40	4.0	1	65
$Rh(CO)_2(acac)$ (2.0) $Ph_2PCH_2C(CH_3)_2CH_2PPh_2$ (2.0)	40	4.0	2	71
$Rh(CO)_2(acac)$ (2.0) $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$ (4.0)	40	4.0	1	4
$Rh(CO)_2(acac)$ (2.0) $Ph_2P(CH_2)_4PPh_2$ (4.0)	40	4.0	1	7
$Rh(CO)_2(acac)$ (2.0) $(p\text{-tol})_2P(CH_2)_2P(p\text{-tol})_2$ (2.0)	40	4.0	1.4	26
$[Rh[Ph_2P(CH_2)_3PPh_2]Cl]_x$ (2.0)	40	5.0	3.7	80
$Rh[Ph_2P(CH_2)_3PPh_2]_2Cl$ (0.2)	4.0	1.0	2.5	72

[a] All experiments: 140 °C, 1000 psi total pressure, 2:1 H_2/CO, 40 mL of CH_3OH. [b] $RuCl_3(H_2O)_x$ or $R_4NRu(CO)_3I_3$. [c] Remaining product is acetic acid.

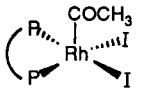
Using ruthenium as a catalyst for the in situ hydrogenation of CH_3CHO allows the use of a 2:1 mixture of H_2/CO while a stoichiometric balance between the gas feed and uptake ratios is maintained. For this reason, as well as our primary interest in the conversion of CH_3OH to homologous alcohols, the bulk or our experiments employed ruthenium as a cocatalyst.

In general, increasing the H_2/CO ratio results in increased selectivity to CH_3CHO/CH_3CH_2OH. Also, high temperatures result in faster reaction rates but sacrifice selectivity. To date we have not quantified these parameters. Representative results are given in Table I.

The reaction selectivity is highly dependent on the diphosphine ligand employed. As shown in Table II, the best results are obtained with $Ph_2P(CH_2)_3PPh_2$. Deviation from this basic ligand structure results in decreased selectivity to CH_3CHO and a commensurate increase in the amount of CH_3CO_2H produced. The only exceptions are where alkyl substitution occurs on the trimethylene bridge; in these instances the selectivity is essentially unchanged. Alternatively, if monodentate phosphines (PPh_3) or no phosphine are employed, the CH_3CHO selectivity is nil and only CH_3CO_2H is observed.

Catalyst Characterization. This catalyst is also quite robust. In fact, at the end of the catalysis experiments the autoclave not only contains the liquid reaction products but also is encrusted with beautiful orange crystals. For diphosphine = $Ph_2P(CH_2)_3PPh_2$, ^{31}P NMR of the crystals shows a doublet at δ 17.9, with a rhodium–phosphorus coupling constant of 132 Hz. This is consistent with a cis-chelate arrangement of the diphosphine ligand to rhodium, with each phosphorus atom equivalent by symmetry. The infrared spectrum shows a strong stretch at 1701 cm^{-1}; the lack of absorptions in the 2100–1750 cm^{-1} region rules out the presence of coordinated carbon monoxide. Rather, the 1701 cm^{-1} absorption is suggestive of an acetyl ($Rh-COCH_3$) group. This conclusion is further supported by the ^1H NMR spectrum which shows, in addition to resonances attributable to the diphosphine, a peak at δ 3.02 which integrates to three protons. Final confirmation of the identity of this species was obtained by elemental analysis, which is in excellent agreement with the formula $Rh[Ph_2P(CH_2)_3PPh_2](COCH_3)I_2$ (**1a**).

On the basis of this evidence, we assign these complexes the square-based pyramid structure shown below. We unequivocally identified a number of these acetyl complexes (**1a–f**), all of which were isolated from catalyst so-



1a: $\left(\begin{smallmatrix}P\\P\end{smallmatrix}\right) = Ph_2P(CH_2)_3PPh_2$

b: $\left(\begin{smallmatrix}P\\P\end{smallmatrix}\right) = Ph_2P(CH_2)_2PPh_2$

c: $\left(\begin{smallmatrix}P\\P\end{smallmatrix}\right) = Ph_2PCH_2C(CH_3)_2CH_2PPh_2$

d: $\left(\begin{smallmatrix}P\\P\end{smallmatrix}\right) = Ph_2P(CH_2)_2CH(CH_3)PPh_2$

e: $\left(\begin{smallmatrix}P\\P\end{smallmatrix}\right) = (p\text{-tol})_2P(CH_2)_3P(p\text{-tol})_2$

f: $\left(\begin{smallmatrix}P\\P\end{smallmatrix}\right) = (p\text{-}ClC_6H_5)_2P(CH_2)_3P(p\text{-}ClC_6H_5)_2$

lutions. The formation and stability of these species therefore appear to be general. As described in the Introduction above, it was the stability of this type of complex that led us to our initial investigations of diphosphine promoters.

The acetyl complexes are virtually insoluble in methanol at room temperature. In fact, ^{31}P NMR and infrared

Table III. Reductive Carbonylation of Methanol with Acetyl Complexes Rh(diphosphine)($COCH_3$)(I)$_2$

cat. (mmol)	CH_3I, mmol	Ru,[b] mmol	time, h	CH_3CHO/CH_3CH_2OH selectivity, mol %
1a (0.75)	40	3.0	1	75
1a (0.75)			2	82
1c (1.0)	4.0	4.0	3	76
1d (2.0)	40	4.0	1	65
1e (0.75)	40		1	47

[a] All experiments: 140 °C, 1000 psi total pressure, 2:1 H_2/CO, 40 mL of CH_3OH. [b] $RuCl_3(H_2O)_x$ or $R_4NRu(CO)_3I_3$. [c] Remaining product is acetic acid.

analyses of the supernatant rarely detect any rhodium or diphosphine species when a 1:1 ratio of diphosphine and rhodium is employed. The acetyl complexes are the only detectable rhodium- or phosphorus-containing products at the end of these reactions. Consistent with this, isolated yields of these acetyl complexes after catalysis experiments are usually better than 85%. To the best of our knowledge, these acetyl complexes account for essentially all of the rhodium and diphosphine charged to the reactor. More importantly, the acetyl complexes can be used as the catalyst charge and are again recoverable in essentially quantitative yield. As shown in Table III the isolated acetyls can be used as catalysts with no change in performance (e.g., rate or selectivity).

If an excess of diphosphine is employed (e.g., diphosphine:Rh > 1), the acetyl complexes are still isolated in quantitative yield. ^{31}P NMR of the supernatant clearly shows that the excess ligand has been quanternized by CH_3I. Likewise, charging ligand and rhodium as the mono- or bis(chelate) complexes [Rh(diphosphine)]$^+$ or [Rh(diphosphine)$_2$]$^+$ [11] again leads quantitatively to complexes **1** (Table II). For [Rh(diphosphine)$_2$]$^+$, one diphosphine ligand is lost through quaternization. Optimum catalyst performance is thus achieved with Rh:diphosphine = 1. Dissociation of diphosphine from rhodium in complexes **1** does not occur, at least over the limited time scale we have investigated (up to 11 h at 140 °C). Reversible dissociation appears unlikely. Once dissociated, quaternization would be very rapid. We independently demonstrated that use of $[Ph_2CH_3P(CH_2)_3PCH_3Ph_2]^{2+}$ in place of $Ph_2P(CH_2)_3PPh_2$ does not give an active reductive carbonylation catalyst. Thus, quaternization appears to be irreversible with respect to the chemistry described here.

When ruthenium is added as a cocatalyst, the known[12] anion $Ru(CO)_3I_3^-$ is detected in the liquid phase. This is readily demonstrated by infrared analysis, which shows bands at 2112 and 2043 cm^{-1}. This complex is produced regardless of the ruthenium source employed and therefore appears to be a thermodynamic sink under these reaction conditions. This species has been detected in other studies employing ruthenium and iodide in homologation catalysis. To date we have not identified the $Ru(CO)_3I_3^-$ counterion. However, Braca et al.[12] have described the formation of the acid $HRu(CO)_3I_3$ under reaction conditions similar to those reported here. It seems likely that this species is present in our catalyst solutions as well.

Labeling Experiments. The stability and isolation of complexes **1** presented us with a unique opportunity to investigate the mechanism of this chemistry. In order to do this we first wanted to roughly outline the key steps involved in the conversion of CH_3OH to CH_3CHO and CH_3CH_2OH. The following labeling studies were performed to accomplish this.

One plausible pathway involves initial formation of CH_3CO_2H or $CH_3CO_2CH_3$, followed by hydrogenation to CH_3CHO. These compounds are observed as products in our reactions. The CH_3CHO/CH_3CH_2OH selectivity may then simply reflect the different ability of various catalysts to hydrogenate the carboxylic acid or ester. To test this possibility, we spiked a typical homologation experiment with labeled acetic acid ($CH_3{}^{13}CO_2H$). After the reaction the products were analyzed by gas chromatography/mass spectrometry. No detectable amount of label is incorporated into CH_3CHO or CH_3CH_2OH (eq 2). This experiment shows that acetic acid/acetate hydrogenation is a negligible pathway to ethanol. This result is not surprising, in that ester/acid hydrogenation is difficult and requires much more forcing conditions than those employed here.[13]

$$CH_3OH + CH_3{}^{13}CO_2H \xrightarrow{H_2/CO} CH_3CH_2OH + CH_3CO_2H + CH_3{}^{13}CO_2H \quad (2)$$

As described above, the rhodium–diphosphine–CH_3I catalysts produce acetaldehyde. When ruthenium is present, the amount of acetaldehyde is greatly diminished and CH_3CH_2OH is the predominant product. These results suggest that ruthenium simply serves to hydrogenate the aldehyde. $Ru(CO)_3I_3^-$, the only ruthenium complex observed at the end of these reactions, is a known[12] hydrogenation catalyst. We have independently verified that it can catalyze the hydrogenation of acetaldehyde at rates consistent with those observed for the homologation. To further test this, a homologation experiment was spiked with a small amount of $^{13}CH_3{}^{13}CHO$. GC/MS analysis shows that the label is incorporated into ethyl groups only, confirming that ruthenium hydrogenates CH_3CHO under reaction conditions used for homologation.

Furthermore, no label is found in acetic acid, its esters, or in the methane produced. These results demonstrate that CH_3CHO is formed irreversibly and is stable under these reaction conditions. CH_3CHO decarbonylation, a reaction commonly catalyzed by rhodium,[14] apparently does not occur to any appreciable extent with the catalyst. These interesting results are further confirmed by spiking a homologation experiment with propionaldehyde. In addition to the usual homologation products, only propanol (and its ethers and acetate esters) is observed; no propionic acid or ethene are detected.

Some reports have excluded CH_3I as an intermediate in the cobalt-catalyzed reactions.[1a] The role of iodide promoters in these cases is suggested to be as a labilizing ligand within the cobalt coordination sphere. Other reports have provided evidence suggesting that CH_3I is itself an important intermediate.[1a] Of course, CH_3I has clearly been established as an important intermediate in the rhodium–iodide catalyzed carbonylation of CH_3OH to CH_3CO_2H.[2a,3] Thus, while iodide is clearly recognized as an important

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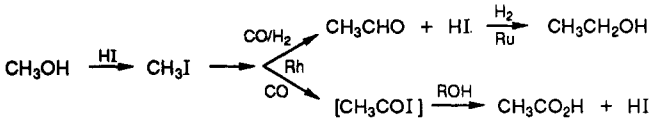
(12) (a) Braca, G.; Raspolli Galletti, A. M.; Sbrana, G. *ACS Symp. Ser.* **1987**, *No. 328*, 220. (b) Raspolli Galletti, A. M.; Braca, G.; Sbrana, G.; Marchetti, F. *J. Mol. Catal.* **1986**, *34*, 183. (c) Braca, G.; Raspolli Galletti, A. M.; Sbrana, G.; Zanni, F. *J. Mol. Catal.* **1986**, *34*, 183.

(13) (a) Grey, R. A.; Pez, G. P.; Wallo, A.; Corsi, J. *J. Chem. Soc., Chem. Commun.* **1980**, 783. (b) Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1980**, *102*, 5948. (c) Wilczynski, R.; Fordyce, W. A.; Halpern, J. *J. Am. Chem. Soc.* **1983**, *105*, 2066. (d) Bianchi, M.; Menchi, G.; Francalanci, F.; Piacenti, F.; Matteoli, U.; Frediani, P.; Botteghi, C. *J. Organomet. Chem.* **1980**, *188*, 109.

(14) (a) Doughty, D. H.; Anderson, M. P.; Casalnuovo, McGuiggan, M. F.; Tso, C. C.; Wang, H. H.; Pignolet, L. H. *Adv. Chem. Ser.* **1982**, *No. 196*, 65–83. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987; p 768 and references therein.

Scheme II



ingredient, its precise role is controversial. This point became important in the work described here when it was found that the reaction rate is zero-order in $[CH_3I]$ (see Kinetics section). This observation indicates either that CH_3I is not an important intermediate in this chemistry or that the chemistry in which it is involved is rapid compared to other steps in the reaction sequence.

For these reasons, we examined the fate of labeled CH_3I during CH_3OH reductive carbonylation. A typical homologation experiment was carried out by using $^{13}CH_3I$ (99%) as the promoter, and the products were analyzed by GC/MS. Diluted amounts of the label were detected in both CH_3CHO/CH_3CH_2OH and CH_3CO_2H. The CH_3I in the product was found to be almost entirely ^{12}C. Thus, CH_3I is converted to CH_3CHO/CH_3CO_2H and regenerated under the reaction conditions. This result is consistent with CH_3I being an intermediate in the reductive carbonylation of CH_3OH.

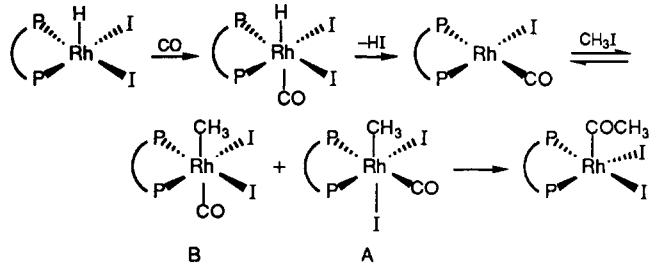
These labeling studies allow us to map out a rough reaction scheme for the conversion of methanol to CH_3CHO/CH_3CH_2OH and CH_3CO_2H. This reaction sequence is shown in Scheme II. First, methanol is probably converted to methyl iodide in the presence of iodide and acid (e.g., "HI"). This is a well-known reaction and is an important step in the Monsanto acetic acid process.[2a,3] The reaction then branches at this or a subsequent step to produce CH_3CHO or CH_3CO_2H. The rhodium-based Monsanto catalyst is known to carbonylate CH_3I and generate CH_3COI. In our reaction medium CH_3COI would be converted instantly to CH_3CO_2H and HI. We propose the same general sequence of steps for this branch of the reaction as that previously described for the Monsanto process. Alternatively, CH_3I carbonylation (to a rhodium acetyl) followed by hydrogenation might yield CH_3CHO and HI. The diphosphine ligands presumably control the degree to which the reaction branches to CH_3CHO. When ruthenium is present, CH_3CHO is hydrogenated to CH_3CH_2OH.

Reaction Studies. As described above, the crystalline acetyl complexes isolated at the end of these reactions account for essentially all of the rhodium and diphosphine charged to the reactor. Furthermore, these complexes can be used as a catalyst charge and again be recovered in nearly quantitative yield. These observations suggest that the acetyls may be active catalytic components for methanol reductive carbonylation. In fact, it is possible that these acetyls serve as the branch point in the reaction scheme above and therefore determine the reaction selectivity. The acetyls appear to be uniquely suited to produce either CH_3CHO or CH_3CO_2H. Thus, they are stable enough that conversion of the acetyl ligand into CH_3CHO may be possible. Alternatively, the cis arrangement of acetyl and iodide ligands may allow the reductive elimination of CH_3COI, which would then be rapidly converted to CH_3CO_2H.

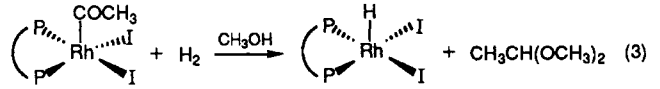
The reaction chemistry of **1a** was investigated to test the feasibility of these proposals. The first series of experiments was designed to determine if this complex could generate acetaldehyde and, if so, under what conditions.

A possible route to CH_3CHO is direct hydrogenolysis of the acetyl with H_2. The reaction of **1a** with H_2 was examined and does indeed yield CH_3CHO. Thus, treating

Scheme III



this complex with H_2 (120 psi, 120 °C, CH_3OH) results in quantitative formation of CH_3CHO (as dimethyl acetal). Workup of the resulting reaction solution yields the hydride complex $Rh[Ph_2P(CH_2)_3PPh_2](H)I_2$ in high yield. The hydrogenolysis may therefore be written as shown in eq 3. $^{31}P\{^1H\}$ NMR of this hydride shows a doublet at δ 26.3 with J_{Rh-P} = 125 Hz. These data suggest a cis-chelate arrangement of the diphosphine ligand, with each phosphorus atom equivalent by symmetry. The hydride resonance is observed at δ −10.83 as a pseudoquartet. $^2J_{P-H}$ is ca. 6 Hz, consistent with a cis arrangement of hydride and phosphorus atoms. The hydride structure is therefore deduced to be that shown in eq 3.



If this hydrogenolysis is operating during catalytic reactions, then conversion of the hydride to the acetyl **1a** is a requisite step in the overall catalytic scheme. Consistent with this, treating $Rh[Ph_2P(CH_2)_3PPh_2](H)I_2$ with CO in methanol (100 psi, 100 °C, 45 min) leads to clean, quantitative formation of **1a**. A scheme to account for this reaction is given in Scheme III. This sequence involves reductive elimination of HI from the hydride, probably via a carbonylation induced reductive elimination. This induced elimination is likely because the hydride is otherwise stable at these temperatures. The elimination is followed by oxidative addition of CH_3I (formed from the reaction of CH_3OH with HI) and migratory insertion to produce **1a**.

The latter steps in this scheme were tested by investigating the reaction of $Rh[(Ph_2P(CH_2)_nPPh_2](CO)I$ (n = 2, 3; prepared independently[15]) with CH_3I. Oxidative addition of CH_3I to these Rh(I) complex occurs under mild conditions (25 °C, hours).[16] For n = 2, the reaction can be monitored by both NMR and IR spectroscopies. These data show that the initially formed Rh(III)–CH_3 complexes are detectable intermediates. Although the IR shows a single band for these intermediates at 2065 cm^{-1} (CH_2Cl_2), two isomers are clearly distinguishable in the ^1H and ^{31}P NMR spectra. Isomer A shows inequivalent phosphorus nuclei at δ 62 and 37. The ^1H spectrum of isomer A shows

(15) For $Rh[(Ph_2P(CH_2)_nPPh_2](CO)Cl$, monomeric and dimeric isomers have been reported,[15a,b] with the nuclearity depending on the value of n. For n = 2, a monomer is reported, whereas for n = 3, a dimer with bridging diphosphine ligands is obtained. We find that for the iodo derivatives both monomers and dimers can be obtained, depending on the reaction conditions and starting materials employed for their synthesis. To date we do not know which isomers are favored thermodynamically or kinetically. (a) Sanger, A. R. *J. Chem. Soc., Chem. Commun.* **1975**, 893. (b) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 120.

(16) For similar results with monodentate phosphines see: (a) Douek, I. C.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 2604. (b) Franks, S.; Hartley, F. R.; Chipperfield, J. R. *Adv. Chem. Ser.* **1982**, *No. 196*, 273. (c) Franks, S.; Hartley, F. R.; Chipperfield, J. R. *Inorg. Chem.* **1981**, *20*, 3238. (d) Doyle, M. J.; Mayanza, A.; Bonnet, J.-J.; Kalck, P.; Poilblanc, R. *J. Organomet. Chem.* **1978**, *146*, 293.

a Rh–CH_3 resonance at δ 0.63 coupled to rhodium and two distinct phosphorus nuclei. Both ^1H–^{31}P coupling constants are small (4.2 and 2.4 Hz) and consistent with the methyl cis to each phosphorus. This isomer is therefore assigned the structure shown in Scheme III. The second isomer is more symmetrical, showing equivalent phosphorus nuclei in the ^{31}P spectrum (δ 56.7). The methyl resonance (δ 1.07) shows a cis coupling constant of 5.4 Hz. We assign structure B to this isomer. Migratory insertion occurs at a rate comparable to oxidative addition to quantitatively yield the acetyl complexes. Note that only isomer A has the cis arrangement of CH_3 and CO ligands required for migratory insertion. This oxidative addition must therefore be reversible, at least with respect to isomer B.

Other pathways for the liberation of CH_3CHO from these complexes were also investigated. Many acyl complexes are known to produce aldehydes upon protonation.[17] Given the acidic reaction medium in which this catalysis is carried out, this reaction appears quite plausible.

This possibility was tested by treating **1a** with the strong acids HI and HO_3SCF_3. This does not lead to formation of CH_3CHO, or derivatives thereof. In fact, infrared analysis of a solution (CH_2Cl_2) of **1a** in the presence of HO_3SCF_3 shows no shift in the acetyl carbonyl vibration at 1701 cm^{-1}. This shows that protonation of the acetyl oxygen atom, a likely first step in the conversion these ligands to aldehydes upon protolysis,[17] does not occur to any appreciable extent, even with a powerful acid.

Reaction of the acetyl with hydride, e.g., Rh–H, is also a potential route to CH_3CHO.[18] However, treating **1a** with a variety of hydridic reagents (R_3SnH, R_3BHLi) does not result in liberation of CH_3CHO. Bimolecular reaction of **1a** with a rhodium hydride is also inconsistent with kinetic studies (vide infra) which show that the reaction is first-order in rhodium.

Although stabilized relative to other complexes with *cis*-Rh($COCH_3$)I geometries, the acetyls may also be responsible for the formation of CH_3CO_2H. Reductive elimination of acetyl iodide and rapid reaction of this intermediate with solvent would produce CH_3CO_2H and HI. To test this possibility, **1a** was heated to 140 °C in CH_3OH under a nitrogen atmosphere. After 45 min, GC analysis showed only traces of CH_3CO_2H and **1a** was recovered intact. This rate is much too slow to account for the formation of CH_3CO_2H during the catalytic reaction. However, conducting this experiment under 90 psi of CO results in a greater than 10-fold enhancement in the rate of CH_3CO_2H formation. Possibly, the much higher CO partial pressures (300 psi) used for catalytic reactions would result in a rate equal to that observed during catalysis. This result suggests that CO coordination is required prior to reductive elimination of CH_3COI. Evidence for CO-induced reductive elimination was presented above and is also believed to be involved in the Monsanto chemistry.[3a,19]

Interestingly, treating **1a** with CO in this manner resulted in the catalytic carbonylation of CH_3OH to CH_3CO_2H, even though no additional CH_3I was added. In addition, **1a** was isolated intact after the experiment. $(CH_3)_2O$ and traces of CH_3I were observed, implying that HI is formed in this reaction. That the catalytic reaction proceeds in the presence of only small steady state amounts of CH_3I suggests that the rate is zero-order in CH_3I (vide infra).

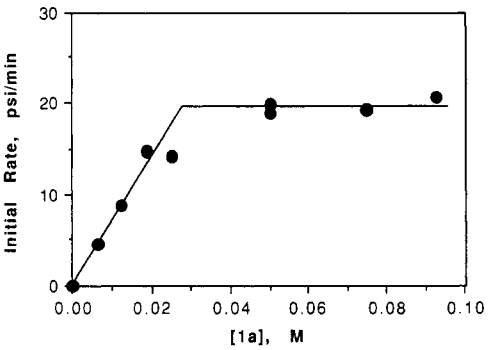
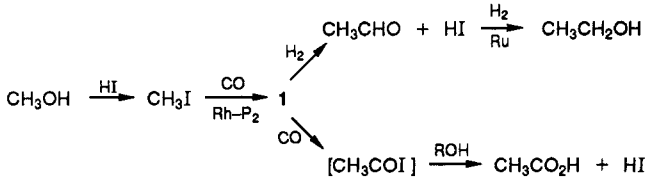


Figure 2. Initial gas uptake rate as a function of rhodium concentration. Conditions: **1a** (0–0.094 M), $(CH_3)_4NRu(CO)_3(I)_3$ (0.10 M), CH_3I (1.0 M), 140 °C, 1000 psi total pressure, 2:1 H_2/CO.

Scheme IV



Kinetics. Combination of these reaction and labeling studies allows us to postulate the overall reaction (Scheme IV). This scheme proposes that the acetyl complexes **1** are pivotal intermediates in the observed chemistry, accounting for both the reaction rate and selectivity. If this scheme is correct, then a first-order dependence on rhodium (or, more precisely, on **1**) is expected. Further, if complexes **1** are indeed thermodynamic sinks, then no other chemistry involved will appear in the overall rate law. The reaction should therefore be zero-order with respect to iodide. In order to test these hypotheses, a kinetic analysis of the catalytic reaction was undertaken.

The kinetic analysis were performed by monitoring the initial rate of gas uptake as a function of time. Gas uptake is typically linear for the first 40–50 min; at times much longer than this significant curvature occurs. This time period corresponds to a ca. 5% CH_3OH conversion, well within the guidelines established for this method of determining reaction orders.[20] Rate dependencies as a function of concentration were determined by measuring the initial gas uptake rate vs time at different concentrations of catalyst component. Concentrations of the component in question were varied by at least 1 order of magnitude for these experiments.

The rate dependence on **1a** was first investigated. A plot of the initial rate of gas uptake as a function of [**1a**] is shown in Figure 2. These data show that the reaction is first-order in **1a** over the concentration range 0–1 mmol/40 mL of CH_3OH. This result is consistent with the reaction scheme postulated above.

(17) Reference 14b, p 107.
(18) (a) Wegman, R. W. *Organometallics* **1986**, *5*, 707. (b) Ungvary, M.; Marko, L. *Organometallics* **1983**, *2*, 1608.
(19) Rh[$Ph_2P(CH_2)_3PPh_2$](CO)($COCH_3$)(Cl)(I) has been reported as an isolable complex.[15b] We have not detected or isolated the analogous diiodide, e.g., Rh[($Ph_2P(CH_2)_3PPh_2$](CO)($COCH_3$)$(I)_2$. Note that we isolate the 16e acetyl complexes **1a–f** from CO-rich atmospheres. It seems likely that the reported carbonyl adduct (ν_{CO} = 2001, 1707 cm^{-1}) is actually a mixture of monomeric Rh[($Ph_2P(CH_2)_3PPh_2$](CO)(I) (2010 cm^{-1}; Table IV) and the acetyl complex Rh[($Ph_2P(CH_2)_3PPh_2$]($COCH_3$)(CI)(I).
(20) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; p 65.

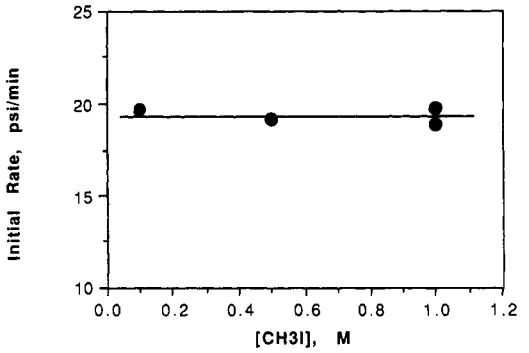


Figure 3. Initial gas uptake rate as a function of methyl iodide concentration. Conditions: **1a** (0.0188 M), $(CH_3)_4NRu(CO)_3(I)_3$ (0.10 M), CH_3I (0.1–1.0 M), 140 °C, 1000 psi total pressure, 2:1 H_2/CO.

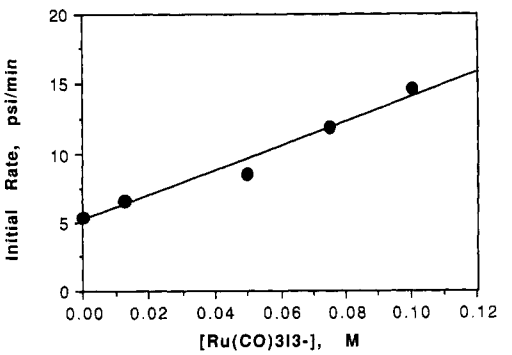


Figure 4. Initial gas uptake rate as a function of ruthenium concentration. Conditions: same as Figure 1.

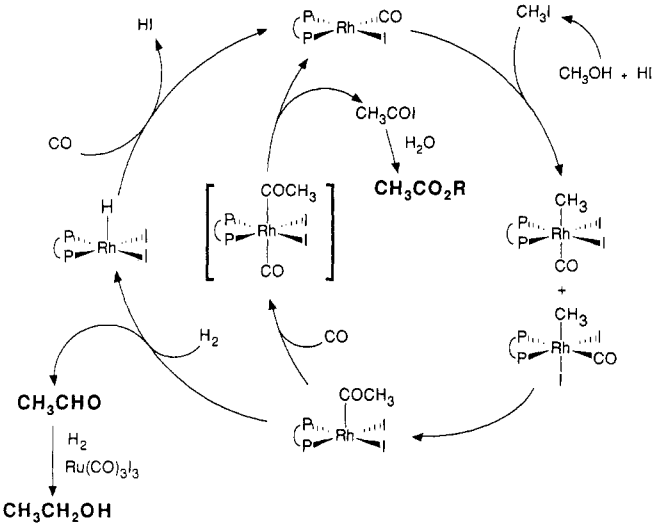


Figure 5. Postulated mechanism for the rhodium–diphosphine–methyl iodide catalyzed reductive carbonylation of methanol.

Interesting, however, is the abrupt change to zero-order dependence at concentrations above ca. 1 mmol of **1a**. The explanation for this perplexing result became obvious during our studies of the reaction chemistry of **1a**. We find, as noted previously, that **1a** is sparingly soluble in CH_3OH at room temperature. If the solubility limit of **1a** is reached during the kinetics experiments, then precisely the type of behavior depicted in Figure 2 would be expected. At concentrations below the solubility limit, the rate would be a function of **1a**, in this case first-order. Experiments above the solubility limit would display a zero-order dependence because the concentration of **1a** would remain constant at its saturation value. In order to test this explanation the solubility of **1a** in CH_3OH was determined as outlined in the Experimental Section. The solubility product of **1a** at 140 °C coincides exactly with the point where the abrupt change in rate law occurs.

This solubility/rate behavior is very significant. While **1a** was used as the catalyst charge for the kinetics experiments, the experiments in reality measure the rate as a function of rhodium concentration. In other words, the kinetics do not distinguish among the many possible rhodium species responsible for the catalytic rate. The observation that the rate behavior depends on a distinct physical property of **1a** is consistent with a model where this species is involved in the rate-determining step. However, we cannot rule out the possibility that another rhodium species with very similar solubility properties is actually responsible for the catalysis kinetics.

The next set of experiments was designed to measure the reaction order in CH_3I. Recall that previous observations suggested that the catalytic reaction is zero-order in this reagent. Indeed, varying the CH_3I concentration over a wide range (0–40 mmol/40 mL of CH_3OH, 0–1 M) results in zero-order behavior (Figure 3). Note that in these experiments rhodium and ruthenium are charged as the iodo complexes **1a** and $[(CH_3)_4N][RuCO)_3I_3]$, respectively. Thus, while the amount of CH_3I charged for a particular experiment may be small (or zero), there is a reservoir of iodide available. GC analysis shows that experiments with little or no CH_3I initially charged have only trace amounts of CH_3I present at the end of the reaction; the iodo complexes **1a** and $Ru(CO)_3I_3^-$ are recovered intact. This is further confirmation that very little free CH_3I is required for catalysis.

The gas uptake rate dependence on ruthenium concentration was also determined. As shown in Figure 4, the rate is clearly first-order in ruthenium. Note that these data correspond to the rate of gas uptake; the CH_3OH conversion rate should be zero-order in ruthenium according to our proposed mechanism. We have not quantified this prediction (the total CH_3OH conversion is only ca. 5% during these experiments), but qualitative observations suggest that this is indeed the case. The nonzero intercept corresponds to the rhodium-catalyzed reductive carbonylation of CH_3OH to CH_3CHO. Upon addition of ruthenium, gas uptake increases due to hydrogenation of CH_3CHO to CH_3CH_2OH. Although this rate dependence is linear over the concentration range investigated, the rate should eventually level off to a zero-order dependence as the system becomes starved of CH_3CHO. Figure 1 shows that at the highest ruthenium concentration investigated (0.10 M) CH_3CHO accounts for approximately 30% of the CH_3CHO/CH_3CH_2OH mixture. Experiments at significantly higher ruthenium concentrations were thwarted by the insolubility of $(CH_3)_4NRu(CO)_3(I)_3$ at these higher concentrations. That ruthenium simply hydrogenates CH_3CHO is further demonstrated in Figure 1, which shows the relative amounts of CH_3CHO and CH_3CH_2OH as a function of ruthenium concentration. As the amount of ruthenium is increased, the CH_3CHO decreases and is accompanied by a commensurate increase in CH_3CH_2OH. Also note from Figure 1 that the total selectivity (defined as $CH_3CH_2OH + CH_3CHO$) remains constant at ca. 78%. This result is consistent with the labeling studies discussed above, which showed that CH_3CHO is formed irreversibly and is stable under the reaction conditions. For instance, if decarbonylation of CH_3CHO occurred during catalysis, one would expect that interception of this species by ruthenium-catalyzed hydrogenation would result in an increase in selectivity. This is clearly not the case.

Table IV. Spectroscopic Data for New Complexes

complex	^1H,[a] δ	^{31}P, δ; J_{Rh-P}, Hz[a]	ν_{CO}, cm^{-1}
$Rh(COCH_3)I_2L$, L =			
$Ph_2P(CH_2)_3PPh_2$ (1a)	7.8–7.1 (20 H, m), 3.4–1.3 (6 H, m), 3.02 (3 H, s)	17.9; 132	1701[b]
$Ph_2P(CH_2)_2PPh_2$ (1b)	8.1–7.2 (20 H, m), 3.5–1.9 (4 H, m), 2.73 (3 H, s)	70.1; 139	1712[b]
$Ph_2P(CH_2)_2C(CH_3)_2PPh_2$ (1c)	7.8–7.3 (20 H, m), 3.01 (2 H, m), 2.76 (3 H, s), 2.26 (2 H, m), 1.21 (3 H, t, J_{P-H} = 3.8), –0.12 (3 H, s)	20.7; 133	1700[c]
$Ph_2P(CH_2)_2CH(CH_3)PPh_2$ (1d)	8.3–7.0 (20 H, m), 3.4–1.6 (5 H, m), 2.78 (3 H, s), 1.00 (3 H, m)	289.3 (P_A), 26.6 (P_B); 130 (Rh–P_A), 118 (Rh–P_B), 20 (P_A–P_B)	1698[c]
$(p\text{-tol})_2P(CH_2)_3P(p\text{-tol})_2$ (1e)	7.6–7.0 (16 H, m), 3.2–1.4 (6 H, m), 2.96 (3 H, s)	17.6; 132	1693[c]
$(p\text{-}ClC_6H_4)_2P(CH_2)_3P(p\text{-}ClC_6H_4)_2$ (1f)	8.0–6.7 (16 H, m), 3.02 (3 H, s), 3.3–0.9 (6 H, m)	17.7; 132	1692[c]
$RhI(CO)[Ph_2P(CH_2)_3PPh_2]$			2010,[b] 1994[d]
$RhI(CO)[Ph_2P(CH_2)_2PPh_2]$[g]	7.8–7.35 (20 H, m), 2.5–2.1 (6 H, m)	71.2 (dd, P_A), 53.6 (dd, P_B); 161 (Rh–P_A), 122 (Rh–P_B), 32 (P_A–P_B)	2005[b]
$Rh[Ph_2P(CH_2)_3PPh_2](I)I_2$	7.8–7.0 (20 H, m), 3.9–1.5 (6 H, m), –10.83 (1 H, q, $J_{H-Rh} \approx J_{H-P} \approx 6$ Hz)		2135,[e] 2082[f]
$Rh[Ph_2P(CH_2)_3PPh_2](CO)(CH_3)I_2$ (isomer A)	0.63 (ddd, CH_3), J_{H-Rh} = 2.1, J_{H-P_A} = 4.5, J_{H-P_B} = 2.4 Hz	62 (dd, P_A), 37 (dd, P_B); 116 (Rh–P_A), 103 (Rh–P_B), 14 (P_A–P_B)	2065[b]
$Rh[Ph_2P(CH_2)_3PPh_2](CO)(CH_3)I_2$ (isomer B)	1.07 (td, CH_3), J_{H-Rh} = 1.5, J_{H-P} = 5.4 Hz	56.7; 120	2065[b]

[a] All NMR data were recorded in CD_2Cl_2. J values in Hz. [b] CH_2Cl_2. [c] Nujol. [d] KBr. [e] ν_{Rh-H}, CH_2Cl_2. [f] ν_{Rh-H}, KBr. [g] NMR spectra show fluxional behavior at room temperature; data recorded at –30 °C.

Conclusion

Figure 5 depicts a catalytic scheme consistent with the available kinetic, mechanistic, and labeling results. Much of this chemistry parallels that proposed for the Monsanto acetic acid catalyst. Thus, oxidative addition of CH_3I to Rh(I), possibly Rh(diphosphine)(CO)(I), yields a Rh(III) methyl complex. With Rh(diphosphine)(CO)(I), two isomeric methyl complexes are produced, as shown and discussed above. With these particular complexes, migratory insertion occurs at a rate competitive to oxidative addition to yield the five-coordinate acetyl complexes 1. Starting with Rh(diphosphine)(CO)(I), this series of oxidative addition/migratory insertion reactions occurs quantitatively over the course of a few hours at 25 °C. At the 130–150 °C temperatures employed for catalytic reactions this sequence of steps is expected to be very rapid.

The next step in the reaction is the most critical. Interception of 1 with H_2 occurs in what appears to be the rate- and selectivity-determining step, generating CH_3CHO and the five-coordinate hydride Rh(diphosphine)(H)$(I)_2$. Alternatively, coordination of CO to 1 induces reductive elimination of CH_3COI from the 18e carbonyl Rh(diphosphine)(CO)$(COCH_3)(I)_2$. The key to the successful application of diphosphine ligands to this chemistry lies in the stability of acetyls 1 with respect to CH_3COI elimination, while at the same time allowing reaction with hydrogen and formation of CH_3CHO. A plausible explanation for this behavior is that reductive elmination of CH_3COI directly from 1 is unfavorable because these complexes are unsaturated with 16e. This is consistent with the evidence indicating that carbonylation of 1 to give 18e Rh(diphosphine)(CO)$(COCH_3)(I)_2$ is followed by reductive elimination. Reductive elimination from this complex to yield a 16e intermediate (formally Rh(diphosphine)(CO)(I)) should be more favorable than a 16e → 14e transformation as required by direct elimination from 1.

Returning to the catalytic reaction depicted in Figure 5, the cycle is closed by the observation that Rh(diphosphine)(H)$(I)_2$ is quantitatively converted to 1 upon reaction with CO. Because Rh(diphosphine)(H)$(I)_2$ is otherwise stable at elevated temperatures (it is prepared at 100 °C), it is likely that CO coordination must occur prior to reductive elimination of HI. CH_3I formation and oxidative addition to Rh(I), followed by migratory insertion to yield 1 are rapid, as discussed above.

The most important step in this cycle, hydrogenolysis of 1 to CH_3CHO and Rh(diphosphine)(H)$(I)_2$, is also the least understood. Hydrogenolysis of Rh(I)–carbon bonds is well-known, but the corresponding reaction with Rh(III) is perplexing. Several possible mechanisms can be envisioned for this transformation, but few can be conclusively judged with the limited data available thus far. the elucidation of this crucial step will be the focus of future studies.

In conclusion, we have demonstrated that with the proper choice of ligands, rhodium can be employed as a catalyst for the reductive carbonylation of methanol. This catalyst is advantageous in that good rates and selectivities are attainable at much lower extremes of temperature and pressure than previously realized. The zero-order dependence on CH_3I concentration is also significant. The ability to operate with low levels of volatile iodides reduces the problem of their separation from the reaction product as well as minimizes corrosion. The in situ hydrogenation with a ruthenium cocatalyst demonstrates the versatility of this catalyst, allowing the production of either acetaldehyde or ethanol. A more detailed study of the effect of reaction variables (e.g., temperature, pressure, etc.) on catalyst performance will be discussed elsewhere.[21]

Experimental Section

General Data. ^1H NMR spectra were recorded on a Nicolet/GE NT-200 or GE QN-300NB spectrometer and are reported relative to TMS. ^{31}P NMR spectra were recorded on a Varian FT-80A or GE QN-300NB spectrometer and are reported relative to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 281B spectrometer. Spectroscopic data for all new complexes are given in Table IV. Liquid products were analyzed on a 30-m Durabond 1701 capillary column using a Hewlett-Packard 5890 GC with flame ionization detector. The column was held at 35 °C for 2 min and then heated to 200 °C at 20 °C/min. Gases (H_2, CO, CO_2, CH_4) were analyzed at 225 °C on a 10 ft × $^1/_8$ in. Carbosieve SII column using a Varian 3700 GC with thermal conductivity detector and argon carrier gas. The gas samples were cooled to –78 °C before sampling to condense heavy components before the analysis. Gas chromatography

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analyses are reported as mole percent and were calculated using experimentally determined response factors.

Correction factors for the flame ionization detector used in this study were measured by the usual procedure using acetonitrile as a standard. Individual component selectivities were calculated in the usual way. Due to the acidic nature of these catalytic reactions, ether, ester, and acetal producing equilibria are prevalent. These equilibria are taken into account when calculating the reaction selectivity, following the literature convention for this chemistry.[1] Methane was not quantified; selectivities are based on liquid products only.

Diphosphine ligands were obtained commercially or prepared by standard methods. As a general precaution all operations were carried out under a nitrogen or argon atmosphere.

Reductive Carbonylation of Methanol—Representative Example. In a glovebox $Rh(CO)_2(acac)$ (0.26 g, 1 mmol) and $Ph_2P(CH_2)_3PPh_2$ (0.41 g, 1 mmol) were charged to a 100-mL Parr autoclave containing 40 mL of CH_3OH. When gas evolution ceased (displacement of CO by diphosphine), $RuCl_3(H_2O)_3$ (0.82 g, 4 mmol) was added. After removal from the box, the reactor was connected to a gas manifold, magnetic drive stirrer, and heating mantle. The entire apparatus was flushed with synthesis gas (66.6% H_2/33.3% CO) by pressuring to 30 psig and venting to atmospheric pressure three times. CH_3I (2.5 mL, 40 mmol) was syringed into the reactor through a rubber septum, and the reactor was then sealed. The reactor was pressurized to 400 psig and heated to 140 °C. Upon reaching 140 °C the operating pressure was increased to 975 psig. The reaction was monitored by gas uptake, and after each 50-psig drop, the reactor was repressurized to 975 psig. After 2.5 h, the reactor was cooled to 18 °C and the gas was vented through a dry ice cooled trap. Analysis of the liquid products by gas chromatography showed the formation of CH_3CHO and CH_3CH_2OH in 80% selectivity. The rate to these products was 3 M h^{-1}. Analysis of the gaseous products showed small amounts of CH_4 (ca. 3 mol % based on CH_3OH) and trace amounts of CO_2. The autoclave contained an orange, crystalline material. Analysis of this material and the supernatant by ^{31}P NMR and IR showed only **1a** and $Ru(CO)_3I_3^-$.

$Rh(COCH_3)$(diphosphine)I_2 (1a–f). The following is a typical procedure for the preparation of these complexes. $Rh(CO)_2(acac)$ (4 g, 0.0154 mol), $Ph_2PCH_2CH_2CH_2PPh_2$ (6.3 g, 0.0154 mol), and methanol (50 mL) were combined in a 100-mL Parr stirred minireactor, under a nitrogen atmosphere. After gas evolution was complete, the reactor was attached to a gas manifold and the entire system was flushed with three pressure/vent cycles of 33.33% CO in H_2. CH_3I (5 mL, 0.80 mol) was syringed into the reactor. The reactor was pressured to 400 psig with the CO/H_2 mixture. After being heated to 140 °C, the reactor was pressured to 750 psig and stirred vigorously for 1.5 h. After the reactor was cooled to 15 °C, the pressure was vented and the reactor contents were removed. Red-orange crystalline **1a** was collected by filtration and dried under vacuum. This product is slightly air-sensitive (particularly in solution) and was stored under nitrogen. Yield: 11 g, 88%. Spectroscopic data for these complexes is tabulated in Table IV. Anal. Calcd for $C_{29}H_{29}I_2OP_2Rh$ (**1a**): C, 42.89; H, 3.60; I, 31.25; P, 7.63; Rh, 12.67. Found: C, 42.96; H, 3.59; I, 30.81; P, 7.73, Rh, 12.77. Anal. Calcd for $C_{28}H_{27}I_2OP_2Rh$ (**1b**): C, 42.13; H, 3.41; I, 31.80; P, 7.76. Found: C, 42.16; H, 3.38; I, 31.49; P, 7.56. The identity/purity of the remaining acetyl complexes **1c–f** was confirmed by spectroscopic methods.

Experiment with Labeled Acetic Acid. This experiment was carried out in the manner described above for catalytic reactions using $Rh(CO)_2(acac)$ (0.52 g, 2 mmol), $Ph_2P(CH_2)_3PPh_2$ (0.82 g, 2 mmol), $RuCl_3(H_2O)$ (0.82g, 4 mmol), and CH_3I (2.5 mL, 40 mmol) in 40 mL of methanol. The solution was also spiked with $CH_3{}^{13}CO_2H$ (0.95 mL, 16 mmol). After 2.5 h at 975 psig and 140 °C the reactor was then cooled and vented. Analysis by GC/MS detected the label only in acetic acid and its esters; none was found in the ethanol or acetaldehyde produced.

Experiment with Labeled Acetaldehyde. In a glovebox **1a** (0.52 g, 0.64 mmol), $[(CH_3)_4N][Ru(CO)_3I_3]$ (1.03 g, 1.6 mmol), and methanol (10 mL) were placed in a 50-mL stainless-steel reactor fitted with a pressure gauge, pressure relief valve, magnetic stir bar, vent, and gas inlet. After removal from the glovebox, methyl iodide (0.65 mL, 10 mmol) and $^{13}CH_3{}^{13}CHO$ (0.5 g, 11 mmol) were added by syringe and the reactor was sealed. The reactor was pressurized and heated to 940 psig and 140 °C in the manner described above. After 30 min the reactor was cooled to 10 °C and the gas vented and collected. Both liquid and gas were analyzed by GC/MS. The label was detected only in ethanol and acetaldehyde.

A similar experiment was conducted with added propionaldehyde. Analysis of the products showed conversion to propanol only. No propionic acid or ethane were detected.

Experiment with Labeled Methyl Iodide. **1a** (0.81 g, 1 mmol), $[(CH_3)_4N][Ru(CO)_3I_3]$ (2.56 g, 4 mmol), and methanol (30 mL) were charged to a 100-mL Parr minireactor. After removal from the glovebox $^{13}CH_3I$ (5 g, 35 mmol) was added and the reactor was sealed, pressurized, and heated to 975 psig and 140 °C as described above. After 45 min the reactor was cooled to 18 °C and the products were collected. GC/MS analysis showed that no label remained in the CH_3I. Traces of label were found in all of the products formed (e.g., acetic acid, acetaldehyde, and ethanol).

Hydrogenolysis of 1a—Preparation of $Rh[Ph_2P(CH_2)_3PPh_2](H)I_2$. A 3-oz Fischer-Porter glass reaction vessel was charged with 0.984 g (1.21 mmol) of **1a** and a stir bar. The vessel was then attached to a high-pressure manifold. Methanol (20 mL) was added via syringe. The vessel was pressurized to 100 psig with H_2 and vented to atmospheric pressure three times. The vessel was then pressurized with 125 psig of H_2 and lowered into a 120 °C oil bath. After 5 h the oil bath was removed and the solution cooled. The volatiles were removed under vacuum and collected in a liquid-nitrogen-cooled trap. Gas chromatographic analysis showed dimethyl acetal, in addition to solvent. Acetonitrile (62 μL, 1.19 mmol) was added as an internal standard, and the dimethyl acetal yield was found to be 92% by using a previously determined calibration curve. The remaining yellow-brown crystals were slurried into 20 mL of methanol, isolated by filtration, and dried under vacuum. Yield: 0.79 g, 85%. Anal. Cald for $C_{27}H_{27}I_2P_2Rh$: C, 42.11; H, 3.53; I, 32.95; P, 8.04. Found: C, 42.10; H, 3.53; I, 30.53; P, 8.04.

Conversion of $Rh[Ph_2P(CH_2)_3PPh_2](H)I_2$ to 1a. A 3-oz Fischer-Porter bottle was charged with 0.831 g of $Rh[Ph_2P(CH_2)_3PPh_2](H)I_2$ (1.08 mmol) and a stir bar. The vessel was attached to a high-pressure manifold, and 20 mL of methanol was added. The resulting suspension was pressurized/vented three times with 125 psig of CO. The vessel was then pressurized with 100 psig of CO and lowered into a 100 °C oil bath. After 45 min the oil bath was removed and the reaction allowed to cool. The resulting red-orange crystals were collected by filtration, washed with methanol, and dried under vacuum. ^{31}P analysis showed that this material was pure **1a**. Yield: 0.69 g, 79%.

$\{Rh[Ph_2P(CH_2)_3PPh_2](CO)I\}_n$. To 0.499 g (2.57 mmol) of $[Rh(CO)_2Cl]_2$ dissolved in 25 mL of acetone was added a solution of 0.414 g (2.76 mmol) of NaI in 15 mL of acetone. After 30 min infrared analysis showed complete loss of $[Rh(CO)_2Cl]_2$ (2083, 2032, 2009 cm^{-1}) and the presence of $Rh(CO)_2(Cl)(I)^-$ at 2053 and 1985 cm^{-1}. Next, a solution of 1.06 g (2.57 mmol) of $Ph_2P(CH_2)_3PPh_2$ in 15 mL of acetone was added in a fast trickle. Gas evolution was immediate and accompanied by a color change to bright yellow and the formation of a bright yellow precipitate. After 1 h the solvent was removed in vacuo. The product was found to be sparingly soluble in all solvents tested, precluding recrystallization or NMR analysis. The product was slurried into methanol, filtered, washed with methanol, and dried under vacuum. Yield: 1.62 g, 94%. Analysis of the crude material thus obtained: Calcd for $C_{28}H_{26}IOP_2Rh$: C, 50.18; H, 3.91; I, 18.93; P, 9.24. Found: C, 51.47; H, 4.22; I, 18.03; P, 9.22. $\{Rh[Ph_2P(CH_2)_2PPh_2](CO)I\}_n$ was prepared similarly from $Rh(CO)_2(acac)$ in methanol. Yield: 88%.

Reaction of Rh(diphosphine)(CO)I with CH_3I. (a) Diphosphine = $Ph_2P(CH_2)PPh_2$. $Rh[Ph_2P(CH_2)_2PPh_2](CO)I$ (2.0 g, 3.1 mmol) was partially dissolved in 20 mL of CH_2Cl_2. To this was added 0.4 mL (6.4 mmol) of CH_3I. Within 10 min the bright yellow suspension turned orange and all of the solid dissolved. After 15 min infrared analysis showed bands at 2065, 2005, and 1710 cm^{-1}, attributable to the complexes $Rh[Ph_2P(CH_2)_2PPh_2](CO)(CH_3)I_2$, $Rh[Ph_2P(CH_2)_2PPh_2](CO)I$, and **1b**, respectively. $Rh[Ph_2P(CH_2)_2PPh_2](CO)I$ gradually disappeared during the reaction. $Rh[Ph_2P(CH_2)_2PPh_2](CO)(CH_3)I$ increased in intensity for the first 2 h and then diminished. The acetyl

complex was the only species remaining after ca. 9 h. This reaction could also be monitored by NMR; these data are given in Table IV. After 2–3 h reaction time, a precipitate formed. The reaction was allowed to proceed overnight, and the product was isolated by filtration. After being washed with CH_2Cl_2, it was dried under vacuum. Analysis (^1H, ^{31}P, NMR; IR) showed it to be pure **1b**. Yield: 1.80 g, 74%.

(b) Diphosphine = $Ph_2P(CH_2)_3PPh_2$. A similar reaction was carried out by using 0.87 g (1.3 mmol) of $Rh[Ph_2P(CH_2)_3PPh_2](CO)I$, 15 mL of CH_2Cl_2, and 0.25 mL (4 mmol) of CH_3I. The reaction was allowed to proceed for 3 days due to the sparing solubility of $Rh[Ph_2P(CH_2)_3PPh_2](CO)I$. After this time infrared analysis of the solution showed complete loss of the carbonyl band at 1992 cm^{-1} and formation of **1a** at 1701 cm^{-1}. The product was isolated by filtration, washed with CH_2Cl_2, and dried under vacuum. Yield: 0.96 g, 91%.

Kinetic Measurements—General Procedure. For these experiments, the catalyst charge consisted of the appropriate amounts of **1a**, $[Me_4N][Ru(CO)_3I_3]$, and CH_3I. The rhodium and ruthenium complexes were combined in 40 mL of methanol in a 100-mL stirred Parr minireactor. The reactor was purged of air by pressure/venting several times with 2:1 H_2/CO. The CH_3I was then added via syringe, and the reactor was sealed. A hydrogen/carbon monoxide (2:1 ratio) gas mixture was used to pressure the reactor to 400 psi; if no leaks were noted, the reactor was heated to an internal temperature of 140 °C. H_2/CO was again added to bring the pressure to 970 psi. Gas uptake was monitored by the pressure drop in the reactor with an ElectroSyn 8600 digital pressure meter. When the pressure dropped to 920 psi, it was manually repressured to 970 psi. These measurements were generally halted after 1-h reaction time, and the products were analyzed in the usual manner. Plots of total gas uptake vs time were generally linear for at least the first 45 min; significant deviation from linearity occurred at reaction times much longer than 60 min.

Solubility Measurements. In a glovebox a 0.038 M solution of **1a** in methanol (0.61 g, 0.75 mmol, in 20 mL) was charged to a 3-oz Fisher Porter glass reaction vessel. A magnetic stir bar was used for thorough mixing. A thermocouple was inserted through the top of the reactor and immersed in the solution. The vessel was attached to a high-pressure gas manifold, and 40 psig of carbon monoxide was added. The tube was immersed in a hot oil bath such that the oil and liquid levels were coincident. Upon reaching 139 °C not all of complex dissolved. The reactor was cooled, and an additional 20 mL of methanol was added to give a 0.019 M solution. Upon heating to 139 °C most of the complex dissolved, and only a few small crystals remained at the gas/liquid interface. This procedure was repeated once more, using 10 mL of methanol to give a 0.015 M solution. This resulted in complete solution of **1a** at 139 °C.

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Registry No. **1a**, 122924-33-8; **1b**, 67913-10-4; **1c**, 122924-34-9; **1d**, 122924-35-0; **1e**, 122924-36-1; **1f**, 122924-37-2; $Ph_2P(CH_2)_3PPh_2$, 6737-42-4; $Ph_2P(CH_2)_2PPh_2$, 1663-45-2; $Ph_2PCH_2C(CH_3)_2CH_2PPh_2$, 80326-98-3; $Ph_2P(CH_2)_2CH(CH_3)PPh_2$, 94631-05-7; $(p\text{-tol})_2P(CH_2)_3P(p\text{-tol})_2$, 115583-11-4; $(p\text{-}ClC_6H_4)_2P(CH_2)_3P(p\text{-}ClC_6H_4)_2$, 114076-81-2; $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$, 23743-26-2; $Ph_2P(CH_2)_4PPh_2$, 7688-25-7; $(p\text{-tol})_2P(CH_2)_2P(p\text{-tol})_2$, 70320-30-8; $Rh[Ph_2P(CH_2)_3PPh_2]_2Cl$, 71264-67-0; CH_3CHO, 75-07-0; CH_3CH_2OH, 64-17-5; $Rh(CO)_2(acac)$, 83642-66-4; $CH_3{}^{13}CO_2H$, 1563-79-7; $^{13}CH_3{}^{13}CHO$, 1632-98-0; $^{13}CH_3I$, 4227-95-6; $Rh[Ph_2P(CH_2)_3PPh_2](H)I_2$, 122924-38-3; $[(CH_3)_4N][Ru(CO_3)I_3]$, 122924-39-4; $[Rh(CO)_2Cl]_2$, 14523-22-9; $Rh(CO)_2(Cl)(I)^-$, 122924-40-7; $Rh[Ph_2P(CH_2)_3PPh_2](CO)I$, 122924-41-8; $Rh[Ph_2P(CH_2)_2PPh_2](CO)(CH_3)I_2$ (isomer A), 122924-42-9; $Rh[Ph_2P(CH_2)_2PPh_2](CO)I$, 122924-43-0; $Rh[Ph_2P(CH_2)_2PPh_2](CO)(CH_3)I_2$ (isomer B), 123000-57-7.

Synthesis and Chemistry of Cationic Alkyl, Alkenyl, and Allyl Complexes Derived from the Soluble, Cationic Hydride $(C_5H_4Me)_2Zr(H)(THF)^+$

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Reaction of $Cp'_2Zr(CH_2Ph)_2$ ($Cp' = C_5H_4Me$) with $[Cp'_2Fe][BPh_4]$ in THF produces the cationic benzyl complex $[Cp'_2Zr(CH_2Ph)(THF)][BPh_4]$ (**4**) which contains a normal η^1-benzyl ligand. Hydrogenolysis of **4** in THF solution (1 atm of H_2, 23 °C) produces the soluble cationic hydride complex $[Cp'_2Zr(H)(THF)][BPh_4]$ (**5**). Hydride **5** reacts with olefins $H_2C{=}CH_2R$ to yield cationic alkyl complexes $[Cp'_2Zr(CH_2CH_2R)(THF)][BPh_4]$ (**8a**, R = H; **8b**, R = Me; **8c**, R = Et), with 2-butyne to give the cationic 2-butenyl complex $[Cp'_2Zr\{(E)\text{-}C(Me){=}C(H)(Me)\}(THF)][BPh_4]$ (**9**), and with allene to give the allyl complex $[Cp'_2Zr(\eta^3\text{-}C_3H_5)(THF)][BPh_4]$ (**13**). Solutions of **4**, **5**, or **13** in CH_2Cl_2 catalyze the polymerization of ethylene to polyethylene. Solutions of **5** and of **8a**,**c** in THF catalyze the oligomerization of ethylene to butene, hexene, and octene. Alkyl complexes **8a–c** also insert 2-butyne to give cationic alkenyl complexes $[Cp'_2Zr\{(Z)\text{-}C(Me){=}C(Me)(R)\}(THF)][BPh_4]$ (**10a**, R = Et; **10b**, R = ^{n}Pr; **10c**, R = ^{n}Bu). No evidence for multiple 2-butyne insertion or for competing β-H elimination reactions is observed. The structure of the cationic alkenyl complex $[Cp'_2Zr\{(Z)\text{-}C(Me){=}C(Me)(^n Pr)\}(THF)][BPh_4]$ (**10b**) has been determined by X-ray diffraction. Complex **10b** crystallizes in space group $P2_1/n$ with a = 12.084 (4) Å, b = 20.469 (9) Å, c = 16.436 (2) Å, β = 100.26 (2)°, V = 4000 (2) Å^3, and Z = 4. The alkenyl ligand lies in the plane between the two Cp′ ligands in the exo conformation, and the THF ligand is rotated 50° from the optimum conformation for Zr–O π bonding.

Cationic, d^0 metal–alkyl complexes $Cp_2M(R)^+$ (M = Ti, Zr; Cp = η^5-C_5H_5) have been implicated as active species in classical soluble Cp_2MX_2/AlR_nX_{3-n} Ziegler–Natta olefin polymerization catalyst systems as well as in the recently

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