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Thermal Decomposition of Pyridine-Substituted Cobaltic Acetate in Acetic Acid

Charles E. Sumner, Jr.,* James Little, Adam S. Howard, and Weimin C. Liang

Research Laboratories, Eastman Chemical Company, Kingsport, Tennessee 37662

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The thermal decomposition of $[py_3Co_3O(OAc)_5OH][PF_6]$ in acetic acid solution in the absence of oxygen produced carbon dioxide, methane, carbon monoxide, picoline, and formic acid as the major products. The ratio of the products was affected by the water concentration and acidity of the mixture. Increased water concentration caused a decrease in methane and an increase in carbon monoxide. Decreased acidity resulted in an increase in methane and a decrease in carbon monoxide. Isotopic labeling experiments showed that some of the carbon monoxide originated as the carboxyl group of the acetic acid. Labeling experiments also showed that formaldehyde and formic acid could be converted to carbon monoxide under the reaction conditions. Two pathways leading to the formation of carbon monoxide were proposed; one involving the decomposition of glyoxylic acid and another involving the oxidation of the methyl radical by cobalt(III).

Introduction

Cobalt acetate is an integral part of the catalyst system used in the manufacture of terephthalic acid in a continuous autoxidation process that is carried out in aqueous acetic acid solvent. It is believed that the active form of cobalt that ultimately initiates the autoxidation chain reaction in this process is cobaltic acetate. A side reaction that represents a major cost to the process is the oxidation of the acetic acid solvent to CO_2 and methyl acetate along with lesser amounts of CO and methane and is also thought to be initiated by Co(III). In a continuous industrial process, a steady state concentration of Co(III) is present at all times as the cobalt is continuously oxidized and reduced.[1] Thus, the thermal decomposition of Co(III) acetate could have a direct relevance to the oxidation of acetic acid in the process. Partenheimer[2] estimated the half-life of cobaltic acetate to be around 10 min at 100 °C in acetic acid during which time it was reduced to Co(II), and it was postulated that the initial products of the decomposition were CO_2 and methyl radical. Other work has shown that Co(III) carboxylates generally undergo bond homolysis to produce CO_2 and alkyl radicals.[3] Early work on the decomposition of cobaltic acetate found the reaction to be accelerated by the addition of strong acids;[4] however, the products of the decomposition were not reported.

While the exact structure of cobaltic acetate is not known, it is thought to be a mixture of multinuclear complexes that contain an oxygen-centered arrangement of cobalt atoms[5] similar to the pyridine substituted, oxo-centered cobaltic acetate, $[py_3Co_3O(OAc)_5OH]^+$. The pyridine substituted cobaltic acetates represent a well-characterized family of complexes[6] and have been observed to have similar reactivity for the oxidation of methylbenzenes as the unsubtituted cobaltic acetate in stoichiometric and catalytic environments.[7] In a previous paper,[8] we reported the observation of CO_2, methane, and picoline as byproducts formed during the stoichiometric oxidation of methyl toluate by $[py_3Co_3O(OAc)_5OH][PF_6]$ in acetic acid. Herein, we wish to report our results on the thermal decomposition of $[py_3Co_3O(OAc)_5OH][PF_6]$ in aqueous acetic acid carried out in an anaerobic environment, which include the effect of water and acidity on the product distribution and the results of isotopic labeling studies.

Results

Thermal decomposition of $[py_3Co_3O(OAc)_5OH][PF_6]$ in acetic acid solution produced carbon dioxide, methane, carbon monoxide, picoline,[9] and formic acid (eq 1). Small

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*To whom correspondence should be addressed. E-mail: cesumner@eastman.com.

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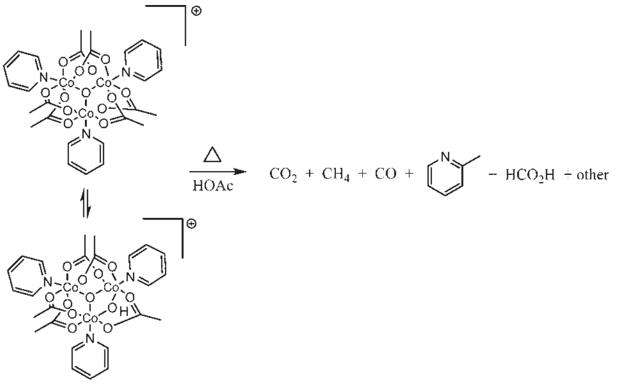
(9) 2-Picoline was the major isomer and was formed in about a six to one ratio to 4-picoline.

Table 1. Influence of Additives on Product Yield for the Thermal Decomposition of $py_3Co_3O(OAc)_5(OH)PF_6$ in 96% HOAc at 155 °C[a]

additive	CO_2	CO	CH_4	picoline	HCO_2H	MeOAc
control	29	4.0	8	2	0.7	0
$Cu(OAc)_2$[b]	29	1.0	trace	0	1.0	4
$Co(OAc)_2$ +pyr[c]	37	0.7	11	4	0.7	0
HOTf[d]	25	5.3	6	3	1.0	0
NaOAc[e]	29	2.7	13	2	1.0	0
$[py_3Co_3O(OAc)_5$-OH][OAc][f]	31	2.0	11	1	1.0	0

[a] Yields are given as mole percent of starting total [Co]. [b] 1 equiv based on total [Co]. [c] 1 equiv Co(II) and pyridine based on total [Co(III)]. [d] 0.3 equiv triflic acid based on total [Co]. [e] 2 equiv based on total [Co]. [f] Used in place of $[py_3Co_3O(OAc)_5OH][PF_6]$.

amounts of acetoxyacetic acid and formaldehyde were also detected, as well as trace amounts of other products such as succinic acid, acetone, and methyl acetate.[10] The reaction was carried out in aqueous acetic acid at 155 °C in a thick walled glass vessel equipped with a means to capture the gaseous products which were analyzed for methane, CO, and CO_2. The CO_2 that remained in solution was assumed to be a constant amount for all of the reactions and was estimated by recovery of known amounts of CO_2 added to the volume of solvent used in the reactions. The liquid product was analyzed by gas chromatography for organic products. The reactions were heated until the color of the mixture turned from dark brown to blue which generally required less than 30 min. The thermolysis reaction typically produced carbon dioxide, carbon monoxide, methane, and picoline in a ratio of 27/4/7/2, respectively (Table 1).



(1)

Addition of 1 equiv of $Cu(OAc)_2$ to the thermolysis resulted in essentially no methane or picoline, but instead methyl acetate was produced in an amount similar to the methane normally produced. Carbon monoxide was still produced as a product (but at lower yield) along with formic acid, acetoxy acetic acid, and glycolic acid (the combined amount of the latter two acids was equivalent to roughly 10% of the total cobalt). This result was consistent with previous observations for cobalt(III) carboxylate complexes that were found to produce CO_2 and alkyl radicals upon thermolysis.[3] The methyl radical produced upon decarboxylation of acetoxy radical was presumably scavenged by cupric ion to give methyl acetate, thus precluding the formation of methane and picoline.[11] Methane was presumably formed by the abstraction of a hydrogen atom from the acetic acid solvent by methyl radical to give the more stable carboxymethyl radical.

Acidity. The ratio of the products was also observed to change depending on the relative acidity of the mixture or the water concentration. Reactions were carried out with added triflic acid and with added sodium acetate to represent an acidic mixture and a basic mixture, respectively. A comparison of the results is shown in Table 1. In the case of the basic mixture, the yield of methane increased by almost a factor of 2 compared to the control reaction. The acidic mixture produced a product mixture similar to the control. A similar comparison can be made of the control reaction with the thermolysis of $[py_3Co_3O(OAc)_5$-OH][OAc], where the acetate salt of the cobalt cluster produced significantly more methane and less carbon monoxide than the control. Addition of 1 equiv cobaltous acetate and pyridine with respect to the total starting amount of Co(III) resulted in a large increase in the amount of methane, carbon dioxide, and picoline but also a large decrease in the carbon monoxide. It was thought that the addition of cobaltous acetate acted to raise the pH of the medium, and the increase in picoline was due to the increase in the amount of pyridine present in the mixture.

Effect of Water Concentration. The concentration of water had a significant effect on the relative amounts of methane and carbon monoxide produced during the reaction. The yield of carbon dioxide and picoline remained essentially unchanged, while the yield of carbon monoxide increased and the yield of methane decreased with increasing water concentration. A series of reactions were carried out where the concentration of water was varied from 0 to 15% (Table 2). When glacial acetic acid was used as solvent, a 6:1 ratio of methane to carbon monoxide was observed. The ratio decreased to about 2:1 when the water concentration was between 4% and 10% and was 1:1 at 15% water. A large amount of acetoxyacetic acid was produced in glacial acetic acid, but decreased by a factor of 4 in the presence of water. The cobalt complex is known to exist in equilibrium in aqueous acetic acid, where a bridging hydroxide ligand is substituted for a bridging acetate ligand depending upon the water concentration.[12] For example, the hexa-acetate complex, $[py_3Co_3O(OAc)_6]^+$, is the major species in glacial acetic acid while $[py_3Co_3O(OAc)_5OH]^+$ is predominant in 90% acetic acid.

Table 2. Effect of Water on Product Yield for the Thermal Decomposition of $py_3Co_3O(OAc)_5(OH)PF_6$ in Aqueous HOAc at 140 °C[a]

% water	CO_2	CO	CH_4	picoline	acetoxyacetic acid
0	29	2	11	2	4
4	26	4	8	2	1
10	27	4	7	2	1
15	27	5	5	2	1

[a] Yields are given as mole percent of starting total [Co].

^{13}C Labeling. The thermolysis reaction was carried out in the presence of ^{13}C labeled formaldehyde (as paraformaldehyde), ^{13}C labeled formic acid, and in acetic acid labeled in the 1- and 2-positions. The gaseous products were analyzed by gas chromatography/mass spectrometry for ^{13}C enrichment. The results are summarized in Table 3. In

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Table 3. Thermolysis of $[Py_3Co_3O(OAc)_5OH][PF_6]$ in the Presence of Labeled Compounds[a]

labeled compound	CO_2	CO	CH_4
$^{13}CH_2O$	19	99	
$H^{13}CO_2H$	58	80	
$^{13}CH_3CO_2H$	5	75	99
$CH_3{}^{13}CO_2H$	83	17	0

[a] Values represent the percent of ^{13}C enrichment. The solvent was acetic acid; 0.8 equiv of formaldehyde and formic acid based on total [Co].

the presence of labeled formaldehyde, 99% of the carbon monoxide was enriched with the ^{13}C label, and 19% of the carbon dioxide, consistent with the conversion of formaldehyde to carbon monoxide as well as carbon dioxide during the thermolysis. Considering the percent enrichment and the total amount of CO and CO_2, we estimate that of the formaldehyde that was oxidized, about 86% was converted to CO. The addition of labeled formic acid resulted in a 58% enrichment of the carbon dioxide and 80% enrichment of the carbon monoxide. Again, considering the percent enrichment and the total amount of CO and CO_2, we estimate that of the formic acid that was oxidized, about 16% was converted to CO. While the formic acid was oxidized to CO_2 by Co(III) as expected, these results show that it was also converted to CO (and presumably water).

When the thermolysis was carried out in $^{13}CH_3CO_2H$, 99% of the methane, 75% of the carbon monoxide, and 5% of the carbon dioxide was enriched with ^{13}C. In these experiments, the cobalt complex was warmed in the labeled acetic acid prior to the thermolysis and a sample was analyzed by electrospray mass spectroscopy to ensure that exchange of the acetate ligands was complete. The observation that only 75% of the carbon monoxide was enriched with ^{13}C suggested that a portion of it originated in the carboxyl group of the acetic acid.[13] To test this, the thermolysis was carried out in $CH_3{}^{13}CO_2H$, which resulted in 17% of the carbon monoxide, 83% of the carbon dioxide, and none of the methane enriched with ^{13}C. The formic acid produced in this reaction was also found to contain 26% ^{13}C enrichment. A control experiment was performed where the thermolysis was done in the presence of ^{13}C labeled carbon monoxide to determine if carbon monoxide was converted to carbon dioxide under reaction conditions, and no ^{13}C enrichment of the carbon dioxide was observed.[14] The results of the two labeling experiments are in agreement with each other in that they show that a portion of the CO originated from the carboxyl group. The presence of the ^{13}C label in the formic acid suggested that a portion of the carboxyl moiety was converted to formic acid which in turn could have been the source of the labeled CO.

Oxidation of Intermediates. The thermolysis reaction was spiked with compounds that were observed (or were predicted) as initial products in order to determine their stability and reaction products. Addition of 0.8 equiv (based on total [Co]) of formaldehyde in the form of paraformaldehyde resulted in carbon monoxide as the major product and a large increase in formic acid along with a decrease in carbon dioxide, methane, and picoline compared to the control reaction where no compound was added (Table 4). The addition of a similar amount of formic acid resulted in an increase in carbon dioxide and carbon monoxide. Treatment of $[py_3Co_3O(OAc)_5OH][PF_6]$ with a large excess of formic acid (50 equiv) resulted in rapid reduction of the Co(III) during heat up. The initial products were mainly CO_2 (81% based on total [Co]) and a small amount of CO (2%) but continued heating of the mixture at 155 °C (for 12 min) resulted in the formation of additional CO (11% based on total [Co]) while the yield of CO_2 remained essentially unchanged. Addition of methanol produced an increase in carbon monoxide and a decrease in carbon dioxide and methane. When the reaction was carried out in the presence of 1 equiv of glycolic acid, carbon dioxide was the only product observed, and the reaction was complete in less than half the normal time required. Similar results were obtained when the reaction was carried out in the presence of oxalic acid, except that the yield of carbon dioxide was about twice that of the control reaction and the reaction was complete by the time the temperature reached 130 °C.

Table 4. Thermal Decomposition of $py_3Co_3O(OAc)_5(OH)PF_6$ in the Presence of Proposed Oxidation Products[a]

additive	CO_2	CO	CH_4	picoline	formic acid	time (min)	*T* (°C)
none	29	4	8	2	1	30	155
paraformaldehyde	18	25	3	1	27	7	155
formic acid	35	6	8	2	51	20	155
methanol	21	6	5	2	2	30	155
glycolic acid	45	0	0	0	1	30	151
glyoxylic acid	46	4	0	0	33	28	155
glyoxylic acid	50	2	0	0	33	3	143
glyoxylic acid	48	2	0	0	15	3	100
oxalic acid	57	0	0	0	0	2	130

[a] Yields are given as mole percent of starting total [Co]. The amount of additive was 0.8 equiv. based on total [Co] except for glyoxylic and glycolic acids which were 1 equiv.

When the reaction was spiked with glyoxylic acid, carbon monoxide was produced along with carbon dioxide. No methane or picoline were observed, and the reaction was complete by the time the temperature of the mixture reached 115 °C. The amount of carbon monoxide appeared to increase with reaction time. For example, if the reaction mixture was heated for 28 min at 155 °C, the ratio of CO_2/CO was about 10:1, but if the reaction time was cut to 3 min (maximum temperature was 148 °C), the ratio was about 20:1. The actual time required for glyoxylic acid to reduce the Co(III) was less than 3 min at a temperature of 100 °C. Thus, it appeared that the reduction products catalyzed the decomposition of glyoxylic acid to give carbon monoxide as one of the products. Control reactions aimed at determining the stability of glyoxylic acid under reaction conditions showed that while it was stable in acetic acid at 155 °C, it was observed to decompose in the presence of pyridine or sodium (or cobaltous) acetate to give CO_2 and CO. The decomposition was faster in the presence of pyridine and the ratio of CO_2 to CO was greater when pyridine was used as the

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[13] In comparison, thermolysis of cobaltic acetate (prepared by oxidation of cobaltous acetate with peracetic acid) in $CH_3{}^{13}CO_2H$ resulted in no ^{13}C enrichment of the carbon monoxide or methane. About 69% of the CO_2 originated as the carboxyl group. The ratio of $CO_2/CO/CH_4$ was 10:2:4.

[14] The reaction was also carried out in the presence of ^{13}C labeled carbon dioxide and stopped after about half of the Co(III) was consumed. Analysis of the recovered $[py_3Co_3O(OAc)_5OH][PF_6]$ by electrospray mass spectroscopy showed no ^{13}C enrichment.

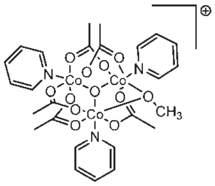
base than when sodium acetate was used. The liquid product contained formic acid.

Discussion

The products observed from the thermolysis of [$py_3Co_3O(OAc)_5OH$][PF_6] are consistent with the initial formation of methyl radical and carbon dioxide, which were presumably produced by the fragmentation of acetoxy radical formed by homolysis of the cobalt–oxygen bond of an acetate ligand. The fragmentation of the acetoxy radical was thought to be irreversible under the reaction conditions, since no labeled carbon was observed to be incorporated into recovered [$py_3Co_3O(OAc)_5OH$][PF_6] when the reaction was carried out in the presence of labeled carbon dioxide. Abstraction of hydrogen atom from the acetic acid solvent by methyl radical would produce methane and the carboxymethyl radical. On the basis of the result with added copper, it is possible that some carboxymethyl radical could be produced directly from the starting cobalt complex similar to the behavior reported for manganic acetate[15] or by reaction of acetoxy radical with acetic acid.[16] Addition of the methyl radical to pyridine would be expected to give picoline after oxidation of the radical formed by the addition. Trace amounts of succinic acid that were observed were probably the result of dimerization of the carboxymethyl radical. Oxidation of the carboxymethyl radical by Co(III) could be expected to produce glycolic, glyoxylic, and acetoxyacetic acids by analogy to the oxidation of benzylic radicals.[8] Reaction conditions that affect the subsequent oxidation of glycolic and glyoxylic acids and carboxymethyl radical probably have a great influence on the product distribution.

Labeling experiments showed that most of the CO produced in the reaction originated as the methyl group of the acetic acid. It is not clear how the remaining CO that originated as the carboxyl carbon was formed, but it is possible that it was formed by the decomposition of glyoxylic acid that was produced via oxidation of the carboxymethyl radical. Control experiments showed that formic acid, CO_2, and CO were products of the decomposition of glyoxylic acid. Thermolysis carried out in $CH_3{}^{13}CO_2H$ showed that some of the formic acid was derived from the carboxyl carbon of acetic acid. Formic acid was oxidized to carbon dioxide by Co(III), but was also decomposed by Co(II) to give carbon monoxide. Thus, the observation of some of the CO originating from the carboxyl group of acetic acid is consistent with the formation of glyoxylic acid during the thermolysis.[17] The amount of CO produced from the thermolysis of [$py_3Co_3O(OAc)_5OH$][PF_6] was much greater, however, than what would be expected if the CO were produced only from the decomposition of glyoxylic acid. For example, the amount of glyoxylic acid produced during the thermolysis should be comparable to the amount of methane that was produced (which was only 8% of the Co(III) that was present at the beginning), and the yield of CO from oxidation of 1 equiv glyoxylic acid was only 4% of the starting Co(III). In addition, the amount of CO was observed to decrease at conditions that produced larger amounts of methane (and consequently carboxymethyl radical). It appears that there are at least two pathways for the production of CO. In addition to the oxidation of glyoxylic acid (or its equivalent), CO might also be formed by the oxidation of methyl radical.

Oxidation of methyl radical by Co(III) could involve the addition of methyl radical to a cobalt–oxygen bond to give a bridging methoxide intermediate. To test this hypothesis, the known complex,[6d] [$py_3Co_3O(OAc)_5OCH_3$][PF_6], was heated in acetonitrile at 135 °C to effect decomposition (eq 2). The major product was CO (17% based on total [Co]), along with CO_2 (16%), formaldehyde (1.7%), and formic acid (1.3%). Trace amounts of methane and picoline were also observed. As a control experiment, [$py_3Co_3O(OAc)_5OH$][PF_6] was treated in a similar manner, and although the reaction was not complete in the same time frame (60 min), the major product was CO_2 which was formed in a 9:1 ratio to CO. The yield of CO was higher when the thermolysis of $py_3Co_3O(OAc)_5OH$]-[PF_6] was carried out in aqueous acetic acid, which is thought to be consistent with formation of a methoxide intermediate due to the higher concentration of bridging hydroxide moieties on the cobalt complex. Conversely, the concentration of bridging hydroxide moieties is thought to be minimal in glacial acetic acid.



$$\longrightarrow \quad CO + CO_2 + CH_2O + HCO_2H \qquad (2)$$

17% 16% 2% 1%

Conclusion

Thermolysis of [$py_3Co_3O(OAc)_5OH$][PF_6] in acetic acid solution produced products that were consistent with the initial formation of methyl radical and CO_2. The ratio of the products was affected by the water concentration and the acidity of the mixture. These factors also influenced the nature of the cobalt complex and thus could have affected the selectivity toward the oxidation of the intermediate radical species by formation of a cobalt methoxide intermediate. Isotopic labeling experiments showed that formaldehyde was converted to CO under reaction conditions, but they could not definitively show that methyl radical was oxidized to CO due to the conversion of glyoxylic acid to CO and CO_2 under reaction conditions. A large fraction of the observed products was derived from the oxidation of the carboxymethyl radical.

Experimental Section

General Procedure. A 50 mL thick walled glass tube (Fischer–Porter bottle) equipped with a spin bar, electronic pressure gage, thermocouple, and gas inlet with a needle valve was charged with [$py_3Co_3O(OAc)_5OH$][PF_6] (887 mg; 1 mmol) and aqueous acetic acid (12 mL). The resulting mixture was purged with argon and sealed under an argon atmosphere. The vessel was heated with stirring in an oil bath set at 160 °C while the temperature of the mixture and pressure were monitored. The t_0 was counted when the temperature of the mixture reached 130 °C. The color of the mixture typically changed from brown to blue within 20 min. The vessel was removed from the bath and

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[17] The mechanism for the formation of formic acid from glyoxylic acid is not known but could involve tautomerization of glyoxylic acid hydrate which would result in scrambling of the ^{13}C label.

allowed to cool to room temperature. The pressure was recorded, and the gas phase was collected by venting the mixture through the needle valve into a 25 mL gastight syringe (internal valve) equipped with a 17-gage needle tipped with a 1/16th inch Swagelok fitting. The gas was analyzed by gas chromatography (Agilent MicroGC) for CO_2, CO, CH_4, C_2H_6, C_2H_4, N_2, O_2, and H_2. The detection limits for methane and ethane were 0.03 and 0.01 volume percent, respectively. Any ethane that was produced in the thermolysis reactions was below the detection limit. The liquid was analyzed by gas chromatography (GC) using a DB1701 column and flame ionization detector (FID). A sample was derivatized by conversion to the trimethylsilyl esters for analysis of glycolic acid, acetoxyacetic acid, oxalic acid, and succinic acid. Formic acid and formaldehyde were determined by GC after conversion of the sample to the trimethylsilyl derivatives. Formaldehyde was difficult to quantify and the limit of detection was near the theoretical concentration produced by the reaction. Yields of products were calculated by dividing the moles of product by the total moles of cobalt present in the starting mixture (for example, 3 mol total of cobalt were present as 1 mol of the starting complex) followed by conversion to percent. Equivalent amounts of additives were based on the total moles of Co(III) in the starting mixture.

Base Catalyzed Decomposition of Glyoxylic Acid. A solution (12 mL) of glyoxylic acid hydrate (1.75 M) and pyridine (0.29 M) in 96% acetic acid was heated in the apparatus described above at 153 °C in an argon atmosphere for 25 min. The color of the mixture was amber. Analysis of the gas found CO_2 (3.8 mmol) and CO (0.1 mmol). The liquid was analyzed for formic acid (0.7 mmol) and formaldehyde (none detected). A similar procedure using sodium acetate in place of pyridine produced CO_2 (0.27 mmol), CO (0.07 mmol), and formic acid (0.08 mmol).

Isotope Labeling. A 3 mL thick walled glass bulb equipped with a microspin bar was charged with $[py_3Co_3O(OAc)_5OH][PF_6]$ (74 mg; 0.08 mmol) and labeled acetic acid (1 g; Cambridge Isotope). The mixture was purged with argon and sealed with a 3/8th inch (graphite ferrule) to 1/16th inch Swagelok fitting connected to a 5 mL gastight syringe (internal valve) equipped with a 1/16th inch male Swagelok. The mixture was warmed at 80 °C for 5 h, and a sample of the cobalt complex was taken for electrospray mass spec analysis that showed around 96% of the acetate ligands contained the ^{13}C label. The vessel was resealed and heated in an oil bath at 160 °C for 30 min. The gas phase was collected after cooling by opening the valve in the syringe. The sample was diluted with argon before analysis by GC/MS.

Preparation of $[py_3Co_3O(OAc)_5OH][OAc]$. $Co(OAc)_2 \cdot 4H_2O$ (5 g; 20 mmol) and pyridine (1.67 g; 21 mmol) were dissolved in acetic acid (34 g) by warming on a steam bath. Peracetic acid (32%; 4.75 g; 20 mmol) was added with stirring over a 5 min period. The color of the mixture changed from blue to brown. The resulting mixture was heated on a steam bath (to about 85 °C) for 15 min. The solvent was evaporated on a rotovap followed by high vacuum to give 5.62 g of residue. The residue (4.55 g) was digested in 50 mL of boiling ethyl acetate to give 3.65 g of product (small plates) after drying. The ^{1}HNMR of the product showed it to be about 90% $[py_3Co_3O(OAc)_5OH]^+$ and 10% $[py_3Co_3O(OAc)_6]^+$.