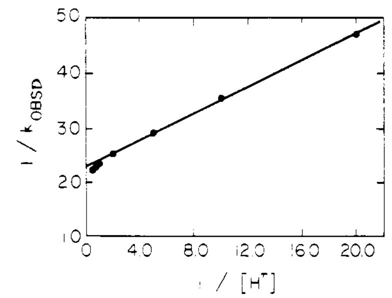


Figure 2. Plot of $1/k_{obsd}$ vs. $1/[H^+]$ for the aquation of $Ru^{II}(NH_3)_5(4\text{-}NH_2py)$ ($T = 25.0$ °C, $I = 2.0$ M (NaCl)).

and SO_4^{2-} cannot be ordered because the concentrations were different in these cases.)

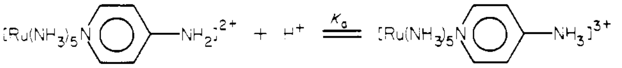
Turning now to the kinetics of aquation of the Ru(II) complex, $1/k_1K_a$ note that a plot of $1/k_{obsd}$ vs. $1/[H^+]$ yields a straight line for most of the proton concentration range covered, as shown in Figure 2. This behavior is consistent with a rate law of the form

$$-\frac{d[RuL]}{dt} = \frac{k_1K_a[H^+][RuL]}{1 + K_a[H^+]}$$

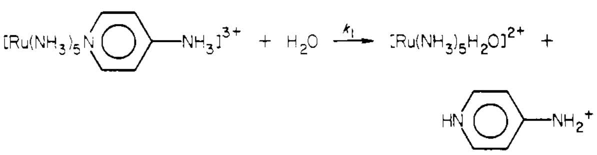
where [RuL] represents the total concentration of (4-aminopyridine)pentaammineruthenium(II) and the observed rate constant is given by

$$k_{obsd} = \frac{k_1K_a[H^+]}{1 + K_a[H^+]}$$

K_a and k_1 are defined by reactions 1 and 2. At high concentrations of H^+, k_{obsd} reduces to k_1, resulting in the observed rate saturation. The deviations from the plot observed at high $[H^+]$ can be ascribed to an additional path involving the reaction of the protonated complex with an additional proton.



(1)



(2)

The plot of $1/k_{obsd}$ vs. $1/[H^+]$ will have a slope of $1/k_1K_a$ and an intercept of $1/k_1$. The value thus determined for k_1 is 4.4×10^{-2} s^{-1} and for K_a, 24. When the intensity of the initial absorbance as determined from the kinetic runs (see below) is plotted against $[H^+]$, the value of K_a obtained, though not precise, is consistent with that recorded above.

In the kinetic runs the initial absorbance at 460 nm was observed to increase in intensity with increasing acid concentration. Since measurement is being made on the long-wavelength side of the band, this shows that the absorption band is shifting to greater wavelengths with decreasing pH. When the amine group is protonated, the 4-aminopyridine becomes a better π acceptor, and since the π^* level lies above the $d\pi$, λ_{max} moves to longer wavelengths, as is observed for other pyridine-derived ligands on Ru(II).

While the proton dependence of the rate shows that an additional proton is contained in the activated complex, its location is not thereby specified. It seems likely that in the transition state the proton shifts from the amine group; note that the increased π-acceptor ability of 4-aminopyridine protonated at the amine nitrogen would result in a slower aquation rate. As has been suggested in other cases, the proton in the activated complex may become coordinated to a pair of $d\pi$ electrons directed at the face of the coordination octahedron. This would withdraw electron density from the metal–pyridine bond and facilitate aquation. If the proton were on a face adjacent to the 4-aminopyridine ligand, it would moreover be available to protonate the pyridine as it is being released.

The work shows that the lone-electron pair of the amine nitrogen of 4-aminopyridine interacts with the pyridine ring and significantly modifies its properties as a ligand. This coupling of the amine nitrogen electron pair with the aromatic rings is also responsible for the increased interaction between the metal centers in the binuclear complex bridged by 4,4′-dipyridylamine[1] as compared to dipyridylmethane as bridging group.

Acknowledgment. Support of this work by National Science Foundation Grant No. CHE79-08633 is gratefully acknowledged.

Registry No. $Ru^{II}(NH_3)_5(4\text{-}NH_2py)$, 78064-39-8; $Ru^{III}(NH_3)_5(4\text{-}NH_2py)$, 78064-35-4; $[Ru(NH_3)_5(4\text{-}NH_2py)](PF_6)_3$, 78656-92-5.

Contribution No. 2863 from the Central Research and
Development Department, E. I. du Pont de Nemours and Co.,
Wilmington, Delaware 19898, and the Department of
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Methane Formation in the Reaction of Carbon Monoxide and Hydrogen in the Presence of Iridium and Osmium Clusters

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and E. L. Muetterties*[1b]

Received March 27, 1981

In a previous publication,[2] homogeneous solutions of $Ir_4(CO)_{12}$ or $Os_3(CO)_{12}$ in toluene were reported to catalyze the formation of methane from carbon monoxide and hydrogen. Also, the rate of methane formation was found to be significantly enhanced by the addition of phosphorus ligands, especially trimethyl phosphite. In this paper, we report the results of a more quantitative investigation. Less than stoichiometric amounts[3] of methane were formed by hydrogenation of carbon monoxide within a 5-day period. Isotopic labeling studies (^{13}C and ^2H) have established that the enhanced formation of methane in the presence of trimethyl phosphite arises from a trimethyl phosphite and hydrogen reaction catalyzed by the iridium and osmium complexes.

Experimental Details

Quantitative Determination of Methane Formation. Reaction tubes were opened at ambient temperature into an evacuated system of

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(1) (a) Central Research and Development Department, Du Pont. (b) University of California.

(2) M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976).

(3) (a) Widely different yields of methane in this reaction have been obtained by several experimenters (ELM research group). The values reported here are believed to be the most accurate ones. (b) On the basis of light scattering, there was no evidence of particles present in the solution phase. However, the wavelength was not varied to very short wavelengths, and it is possible that very small crystallites may have been present.

(4) In related experiments, it was found that a mixture of $[IrCl(C_8H_{14})_2]_2$, trimethyl phosphite, and hydrogen produced methane (CH_4:Ir_2 = 14:1) and that substitution of nitrogen for hydrogen also produced methane but in lower yield (CH_4:Ir_2 = 5:1). Toluene solutions of $Co_4(CO)_{12}$, $Co_2(CO)_8$, and $Fe_3(CO)_{12}$ also effected methane formation from trimethyl phosphite, CO, and H_2, but the reaction systems were not homogeneous.

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known volume (204 mL), and the total pressure was measured (150–250 torr). The moles of gas collected were determined from the ideal gas law. The gas was allowed to expand into an evacuated gas sample bulb (pressure = 75–150 torr) and was analyzed by gas chromatography on a Porapak Q Column to determine the mole fraction of methane in the gas. The GC system was calibrated with the use of standard gas mixtures obtained from the Matheson Gas Co., Inc. The methane response factor was found to be linear with pressure over the range of 50–200 torr. The moles of methane formed in the reaction were then determined from the total moles of gas recovered and the mole fraction of methane determined by the GC analysis.

Reaction of $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ with CO and H_2 in Toluene. Carius tubes of 53-mL internal volume were loaded with $Ir_4(CO)_{12}$ (0.050 g, 4.5×10^{-5} mol) or $Os_3(CO)_{12}$ (0.050 g, 5.5×10^{-5} mol) and 4.0 mL of toluene. The tube was cooled in liquid nitrogen and evacuated, and a 2:1 H_2:CO mixture was admitted to a pressure of 500 torr. The tube was sealed and heated to 170 °C for 90–115 h. The reaction mixtures were homogeneous. The tube was opened into the calibrated volume and the gases were analyzed by gas chromatography. The amount of methane formed did not exceed 10–15% of the molar amount of complex used and consistently exceeded (by a factor of ca. 3:1) the traces observed in runs with no metal complex present. The trace amount of methane observed in the blank runs apparently originated as an impurity in the reactant gas mixture.

Interaction of $Ir_4(CO)_{12}$, Toluene, and D_2. Carius tubes of ~40-mL internal volume were loaded with $Ir_4(CO)_{12}$ (0.05 g, 4.5×10^{-5} mol) and 4 mL toluene. These tubes were cooled in liquid nitrogen, evacuated, pressurized to 500 torr with deuterium or with a 2:1 molar mixture of deuterium and carbon monoxide, and sealed. The tubes were heated to 180 °C for periods ranging from 45 to 125 h. With only deuterium present, the reaction mixtures became heterogeneous with the formation of iridium metal and condensed iridium clusters. In no instance was deuterium incorporated into the toluene. In the presence of both D_2 and CO, the reaction system remained homogeneous. Again, no deuterium was incorporated into the toluene solvent.

Reaction of $Ir_4(CO)_{12}$ with CO and D_2 in Toluene Solutions of Trimethyl Phosphite. Carius tubes of ~40-mL internal volume containing $Ir_4(CO)_{12}$ (0.05 g, 4.5×10^{-5} mol), toluene (4 mL), and trimethyl phosphite (4.5×10^{-5}, 9.0×10^{-5}, and 13.5×10^{-5} mole) were sealed in 3:1 D_2:CO gas mixtures at ~660 torr pressure. These tubes were heated to 180 °C for 60–122 h. Analysis of the gaseous products by high-resolution mass spectrometry showed in addition to H_2, HD, and D_2 the presence of methanes in the approximate molar ratios of 25:5:1:1:4 for CH_3D:CH_4:CD_4:CD_3H:CH_2D_2. The ratio of CH_3D to CH_4 and to other methanes was essentially independent of the $(CH_3O)_3P$ concentration and reaction time, except that the ratios of CH_3D to CD_3H and to CD_4 decreased slightly with reaction time. Analysis of the liquid product by ^1H NMR spectroscopy showed it to contain $CH_3PO(OCH_3)_2$.

Reaction of $Ir_4(CO)_{12}$ with CO and D_2 in Trimethyl Phosphite Solutions. A Carius tube with ~53-mL internal volume was loaded with $Ir_4(CO)_{12}$ (0.050 g, 4.5×10^{-5} mol) and 4.0 mL of trimethyl phosphite. The tube was cooled in liquid nitrogen and evacuated. Carbon monoxide was admitted to a pressure of 165 torr, and deuterium was admitted to a total pressure of 500 torr. The tube was sealed and heated at 180 °C for ca. 110 h, cooled, and opened into the calibrated volume. The reaction mixtures were homogeneous. Gas chromatographic analysis showed that 0.6–1.2 mmol of methane was produced (CH_4:$Ir_4(CO)_{12}$ = 13–26). Mass spectrometric analysis showed the presence of CH_3D and CH_4 in the ratio of 4:1–5:1. Only trace amounts of CH_2D_2, CHD_3, and CD_4 were observed.

Reaction of $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ with ^{13}CO and H_2 in Trimethyl Phosphite. A Carius tube with ~53-mL of internal volume was loaded with $Ir_4(CO)_{12}$ (0.50 g, 4.5×10^{-5} mol) and 4.0 mL (4.21 g, 3.39×10^{-2} mol) of trimethyl phosphite. The tube was cooled in liquid nitrogen and evacuated. Carbon monoxide enriched in ^{13}C (ca. 97% isotopic purity) was admitted to a pressure of 165 torr, and hydrogen was admitted to a total pressure of 500 torr. The sealed tube was heated at 150 °C for 110 h. The tube was opened into a calibrated volume, and samples were taken for gas chromatographic and mass spectroscopic analyses. The gas analyses showed that 0.2–0.6 mmol of CH_4 was produced (CH_4:$Ir_4(CO)_{12}$ = 4.4–12) and that only a small excess of $^{13}CH_4$ over the natural abundance was produced. Similar results were obtained with $Os_3(CO)_{12}$. Both ^{12}CO and ^{13}CO were detected as well as small amounts of dimethyl ether (normal isotopic distribution). Gas chromatographic and ^1H NMR analysis of the liquid product showed it to contain $CH_3PO(OCH_3)_2$.

Reaction of $Ir_4(CO)_{12}$ with ^{13}C-enriched Trimethyl Phosphite, CO, and H_2. ^{13}C-enriched trimethyl phosphite was prepared by refluxing a mixture of 12.8 g (0.103 mol) of distilled trimethyl phosphite, 1.0 g (0.031 mol) of 90% isotopically pure $^{13}CH_3OH$, and 0.1 g of sodium metal for a total of 11 h. The mixture was distilled, and a fraction with a boiling point of 107–109 °C at 760 torr (8.03 g, 65%) was shown by mass spectroscopy and ^1H NMR spectroscopy to contain ca. 11% ^{13}C. The ^{13}C distribution in $(CH_3O)_{3-n}(^{13}CH_3O)_nP$ was as follows: $n = 0$, 72.5%; $n = 1$, 22.6%; $n = 2$, 3.1%; $n = 3$, 1.6%.

Carius tubes were loaded as above with a mixture of $Ir_4(CO)_{12}$ (0.05 g, 4.5×10^{-5} mol) and 2.0 mL (2.1 g, 1.69×10^{-2} mol) of ^{13}C-enriched trimethyl phosphite and were filled to 500 torr pressure with a 1:2 mixture of CO and H_2. Collection and analysis of the gases showed the formation of 4.0 mmol of CH_4(CH_4:$Ir_4(CO)_{12}$ = 88). The ratio of $^{12}CH_4$ to $^{13}CH_4$ was found to be 8.8; the expected ratio based on the ^{13}C content of the enriched trimethyl phosphite was 8.1. Natural abundance CO and ^{13}C-enriched dimethyl ether were also detected.

Reaction of $Ir_4(CO)_{12}$ with $CH_3PO(OCH_3)_2$ and Hydrogen. A Carius tube of ~40-mL internal volume was loaded with $Ir_4(CO)_{12}$ (0.050 g, 4.5×10^{-5} mol) and 4 mL of $CH_3PO(OCH_3)_2$. The tube was cooled in liquid nitrogen and evacuated. Hydrogen was admitted to a pressure of 500 torr while the tube was cooled to −197 °C, and the tube was then sealed. The reaction tube was placed in an oven at 180 °C for 130 h. After the tube was opened into a vacuum line, the gaseous products were collected for mass spectrometric analysis. There was an essentially equimolar mixture of methane and carbon monoxide in addition to hydrogen. The majority of the liquid product was unreacted $CH_3PO(OCH_3)_2$, and the nonvolatile iridium residue contained no detectable Ir–CO groups.

In an analogous reaction with deuterium (45 h), the gaseous products were carbon monoxide, methane, and deuterated methanes. The molar ratios of the methanes were about 50:1:1:1:1 for CH_3D:CH_4:CH_2D_2:CHD_3:CD_4.

Reactions of Other Complexes with Trimethyl Phosphite and Triethyl Phosphite. With use of procedures similar to those described above, greater than stoichiometric amounts of methane were observed with mixtures of $[IrCl(cyclooctene)_2]_2$, trimethyl phosphite, and H_2. Lesser amounts of methane were also formed with mixtures of $[IrCl(cyclooctene)_2]_2$, trimethyl phosphite, and N_2 and $Ir_4(CO)_{12}$, trimethyl phosphite, and CO (no H_2). Greater than stoichiometric amounts of methane were also observed in reactions of trimethyl phosphite, CO, and H_2 in toluene solution with $Co_4(CO)_{12}$, $Co_2(CO)_8$, and $Fe_3(CO)_{12}$ although solids were present at the end of the reaction period. The reaction of $Ir_4(CO)_{12}$, CO, H_2, and triethyl phosphite in toluene gave small amounts of ethane; with substitution of $Os_3(CO)_{12}$ for $Ir_4(CO)_{12}$, the gaseous reaction products were similar.

Results and Discussion

The reaction of hydrogen and carbon monoxide in sealed tubes at 180 °C with toluene solutions of $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ produced methane in quantities equivalent to ca. 10–15% of the metal complex used in a 5-day period. These results differ from those previously reported,[2,3a] presumably because of more accurate quantitative analytical techniques. Since the reaction mixtures appeared[3b] to be homogeneous, the methane is presumed to be formed by a solution-phase hydrogenation of carbon monoxide. The toluene solvent was not involved in the reaction as shown by the lack of deuterium incorporation in the solvent in reactions with use of D_2 in place of H_2. Because of the very low hydrogenation rates, it was not feasible to develop detailed mechanistic features of the CO hydrogenation reaction. Reaction of hydrogen with toluene solutions of $Ir_4(CO)_{12}$ at 160–180 °C produced small, shiny crystals of an iridium carbonyl cluster complex, but none of the crystals was adequate for crystallographic analysis. Attempts to obtain good crystals are continuing.

In the presence of trimethyl phosphite, either $Ir_4(CO)_{12}$ or $Os_3(CO)_{12}$ catalyzed the formation of methane both in toluene solution and in pure trimethyl phosphite with CO and H_2 as coreactants. Isotopic labeling studies showed conclusively that the methane was derived largely from the phosphite methyl groups. When ^{13}CO was used in the reaction, CO exchange occurred between the cluster carbonyl and the ^{13}CO reactant but the methane produced was largely $^{12}CH_4$. On the other hand, the use of ^{13}C-enriched trimethyl phosphite produced a mixture of $^{13}CH_4$ and $^{12}CH_4$ in the relative amounts expected from the isotopic distribution in the labeled phosphite.

The use of D_2 in place of H_2 in either the toluene–trimethyl phosphite or the trimethyl phosphite solutions produced predominantly CH_3D and CH_4 in a ratio of ca. 5:1. Lesser amounts of CH_2D_2, CHD_3, and CD_4 were formed in trimethyl phosphite–toluene solutions, and only trace amounts of these species were detected in the trimethyl phosphite solutions. Both HD and H_2 were observed in the D_2 experiments, indicating that extensive hydrogen–deuterium exchange between D_2 gas and the protons of trimethyl phosphite had occurred.

Although no other hydrocarbon products were observed in the reaction system containing trimethyl phosphite, dimethyl ether was produced. In the ^{13}C-enriched trimethyl phosphite reactions, both mono- and di-^{13}C-labeled dimethyl ether was observed in addition to ether with a normal isotopic distribution. When hydrogen was omitted from these reaction systems, methane was still formed but in lower yield ($CH_4{:}Ir_4(CO)_{12} = 2{:}1$).

Analysis of the liquid products by gas chromatography, gas chromatography/mass spectrometry, and proton nuclear magnetic resonance spectroscopy showed that, during the reaction, trimethyl phosphite was rearranged to dimethyl methylphosphonate, $CH_3PO(OCH_3)_2$. The rearrangement was complete at 180 °C after about 100 h but was incomplete after only 20 h and occurred even in the absence of the iridium complex. No other products were detected. Thermal rearrangement of phosphites has been reported to be complete at 400–410 °C after ca. 6 h; no gaseous products were observed.[5] Methane was also formed when the phosphonate was used in place of the phosphite in the hydrogenation reaction system.

Although the results do not define a mechanism for the catalytic formation of methane from trimethyl phosphite, processes that may have been occurring in the reaction systems include (1) methyl group transfer from the phosphite to iridium, (2) hydrogenolysis of the carbon–iridium bond to give methane, (3) exchange of gaseous and coordinated CO, (4) thermal rearrangement of trimethyl phosphite, and (5) hydrogen–deuterium exchange between D_2 gas and the methyl hydrogen atoms of trimethyl phosphite. The last process may occur by inter- or intramolecular metal–ligand hydrogen transfer[6] involving intermediates containing $HIrCH_2OPIr$ or $H\overline{IrPOC}H_2$ groups.

There is precedence for methyl group migration in reactions of trimethyl phosphite with transition-metal complexes and for cleavage of transition-metal–methyl bonds by hydrogen. Methyl group transfer involving trimethyl phosphite was observed in the reaction of trimethyl phosphite and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ to give $(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3$ and $(\eta^5\text{-}C_5H_5)Mo[P(O)(OCH_3)_2](CO)_2[P(OCH_3)_3]$[7a] and in the reaction of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2[P(OCH_3)_3]]_2$ with trimethyl phosphite to give $(\eta^5\text{-}C_5H_5)Cr(CH_3)(CO)_2[P(OCH_3)_3]$ and $(\eta^5\text{-}C_5H_5)Cr[P(O)(OCH_3)_2](CO)_2[P(OCH_3)_3]$.[7b] The reaction of $(\eta^5\text{-}C_5H_5)_2Co$ with trimethyl phosphite produced $(\eta^5\text{-}C_5H_5)_2Co_3[P(O)(OCH_3)_2]_6$.[8] Methyl group migration from trimethyl phosphite to an arsenido or antiminido group in Mo and W complexes has also been reported.[9] In a related reaction, thermolysis of $Mn(CO)_2[P(OC_2H_5)_3]_3Br$ gave $Mn_6(CO)[P(O)(OC_2H_5)_2]_9$ with gas (not characterized) evolution.[10] Finally, cleavage of methyl groups has been established in reactions of deuterium with methyl complexes of cobalt, nickel, chromium, and rhodium.[11] The predominant product was CH_3D in each case, but some CH_4 was also formed; CH_2D_2, CHD_3, or CD_4 were not detected.

Acknowledgment. This collaborative research was supported by the National Science Foundation (E.L.M.). The iridium and osmium halides used in preparing the carbonyls were obtained on a loan grant from Johnson Matthey, Inc. (E.L.M.). The cooperation of C. B. Matthews and F. G. Kitson in performing the gas chromatographic and mass spectroscopic analyses and the technical assistance of W. M. Gray are gratefully acknowledged (R.A.S.).

Registry No. CO, 630-08-0; H_2, 1333-74-0; $P(OCH_3)_3$, 121-45-9; $Os_3(CO)_{12}$, 15696-40-9; $Ir_4(CO)_{12}$, 18827-81-1; CH_4, 74-82-8; $CH_3PO(OCH_3)_2$, 756-79-6.

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Evidence for a Novel π-Bonded Aquoorganochromium(III) Ion, $(\eta^5\text{-}C_5H_5)Cr(OH_2)_n^{2+}$

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Received May 12, 1981

Early attempts to prepare thermally stable σ bonded alkyl and aryl transition-metal complexes were usually successful only if π-bonding ligands such as carbon monoxide were also present. Accordingly, theories were developed that explained these observations on the basis of electronic effects, and these theories were widely accepted. Now it is acknowledged that the role of L in L_nMR complexes is to be a "good ligand" for M and to firmly occupy coordination positions. Thus aquoorganochromium(III) complexes like $(H_2O)_5CrCHCl_2^{2+}$[1,2] are not now considered extraordinary. Similar statements about the role of L in contributing to the electronic stabilization of π-bonded organo transition metal complexes have been made. Indeed, the great majority of complexes with carbon–metal olefinic bonds do have π-acceptor ligands. There are relatively few such complexes with hard ligands such as water or chloride ion.

We wish to report evidence for the existence in acidic aqueous solution of the ion $(\eta^5\text{-}C_5H_5)Cr(OH_2)_n^{2+}$ with chromium in the formal +3 oxidation state. To our knowledge there is only one other report[3] of a π-bonded organometallic complex with only waters as the coligands. Comparison of the properties of the $(\eta^5\text{-}C_5H_5)Cr(OH_2)_n^{2+}$ ion with results

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