tive; only small amounts of methane were detected in both types of reaction systems. We conclude that small metal particles probably were not responsible for the catalysis in this iridium system.[22,23]

A selective Fischer-Tropsch synthesis, of great technological significance, has never been demonstrated. Our new catalytic hydrogenation system based on $Ir_4(CO)_{12}$ clearly presents the possibility of such a selective synthesis. In addition, the preliminary results raise many intriguing scientific questions. For example, iridium *metal* is a relatively poor CO hydrogenation catalyst and iron and ruthenium *metal* are particularly active,[24] whereas in our reaction system $Ir_4(CO)_{12}$ is more active than $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ is inactive. What is the reaction mechanism here? Is there any formal mechanistic relationship between our reaction and the metal or metal oxide[8]-based syntheses? We offer no speculation on reaction mechanism,[25] but are investigating this complex issue through kinetic, spectroscopic, and isolation studies. Alternative catalyst precursors and alternative acidic or acceptor solvents are being examined. With respect to the latter, two observations are particularly noteworthy. The reaction medium appears to require "acidic" character since we find molten $NaAlCl_4$ to be relatively ineffective under our reaction conditions. Composition of the hydrocarbon product mixture is almost qualitatively altered in going from a chloride to a bromide-based melt in that propane became a major product with a $NaBr-2AlBr_3$ reaction medium. Hence, the character of the reaction medium may be varied to further control the distribution of hydrocarbon products.

Note Added in Proof. Further experiments have demonstrated the following effects upon rate and hydrocarbon product distribution. Higher reaction temperatures (200 °C) lowered both the apparent rate (conversion) and the C_2/C_1 product ratio; increased hydrogen chloride concentration had a similar effect. Short contact times shifted the product distribution to favor C_3H_8 and i-C_4H_{10}. Substitution of BBr_3 for the $NaCl \cdot 2AlCl_3$ reaction medium gave an active reaction system that produced CH_4, C_2H_6, C_3H_8, i-C_4H_{10}, and n-C_4H_{10} with the last two the major and minor constituents, respectively.

Acknowledgment. This research was supported by the National Science Foundation.

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

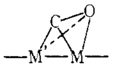
(3) Methanation is a reaction that is very effectively catalyzed by nickel surfaces.

(4) Active were $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$.

(5) Very small amounts of ethane were also detected when $Os_3(CO)_{12}$ was used.

(6) (a) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); (b) *ibid.*, **85**, 451 (1976).

(7) An interaction of the form



is unknown in molecular cluster chemistry, but is common for acetylenes in clusters and is known for nitrogen in two very complex nickel clusters.[6b] Such a $\mu-\pi$ interaction for carbon monoxide rarely may be realized in an intermediate, but perhaps more commonly in transition states, for example, in the dissociative chemisorption of carbon monoxide on certain metal surfaces.

(8) (a) H. Storch, N. Golumbic, and R. Anderson, "The Fischer-Tropsch and Related Syntheses", Wiley, New York, N.Y., 1951; (b) Y. T. Eidus, *Russ. Chem. Rev.*, **36**, 338 (1967); (c) H. Pichler and H. Schultz, *Chem.-Ing.-Tech.*, **42,** 1162 (1970). M. A. Vannice, *Catal. Rev. Sci. Eng.*, **14**, 153 (1976).

(9) There is extensive evidence that aluminum(III) halides can interact with the oxygen atom of a carbonyl ligand in metal carbonyls; cf. J. F. Kristoff and D. F. Shriver, *Inorg. Chem.*, **13**, 499 (1974), and N. E. Kim, N. J. Nelson, and D. F. Shriver, *Inorg. Chim. Acta*, **7**, 393 (1973).

(10) Syntheses gas mixtures of D_2 and CO were also used to produce the perdeuterioalkanes for a further analytical confirmation of product identities through high resolution mass spectrometry.

(11) Chromatographic analyses employed a molecular sieve 5A (6 ft) column for CH_4–CO–air separations and a Poropak Q (12 ft) column for alkane separations.

(12) The iridium metal was thermally generated in vacuo from the cluster in the reaction vessel before the melt mixture was added. This metal was largely present as a shiny mirror on the glass walls.

(13) Trace quantities of methane were produced in these cases after a 3-day reaction period. All systems were visually homogeneous.

(14) (a) The hydrocarbon product was different than with the iridium catalyst. Typically, propane was the major product; a sample analysis was C_3H_8, C_2H_6, and CH_4 in 1.9:1.3:1 molar proportions, respectively. (b) With the more soluble $Rh_4(CO)_{12}$ cluster, the catalytic reaction was visually homogeneous, but only in the early stages of reaction.

(15) This was demonstrated for *n*-hexane at 160 °C with the formation of lower and higher alkanes.

(16) An accurate characterization requires a labeling study since $Ir_4(CO)_{12}$ reacts with hydrogen to produce hydrocarbons.[17] Other factors that undoubtedly influence the nature of the hydrocarbon products are the partial pressures[17] of hydrogen, carbon monoxide, and hydrogen chloride.

(17) Reaction of $Ir_4(CO)_{12}$ with a 3:1 H_2:argon mixture in a $NaCl \cdot 2AlCl_3$ reaction medium at 180 °C was homogeneous in the early reaction stages, but small shiny particles of iridium metal appeared later as hydrogenation became extensive. The hydrocarbon product was largely methane, ethane, and propane in about 3:4:1 molar proportions, respectively. The high propane content here is notable.

(18) Unless hydrogen was present in large excess, and the reaction time was extended beyond a 1- or 2-day period.[17]

(19) M. A. Vannice, *J. Catal.*, **37**, 462 (1975).

(20) The iridium metal was supported on alumina.[19]

(21) The metal was preheated in hydrogen at elevated temperatures. The sample of this metal was kindly supplied by Matthey Bishop, Inc.

(22) Also significant is our observation that $Ir_4(CO)_{12}$ is not especially active in a $NaAlCl_4$ melt at 180 °C. Rates were less than one-quarter those for $NaCl \cdot 2AlCl_3$ reactions.

(23) In progress are experiments to establish the "homogenety" and the active catalytic species for the rhodium and ruthenium carbonyl systems.

(24) For the metal catalyzed hydrogenation of CO (largely to CH_4) at atmospheric pressure, the rates decrease in the order Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir.[19]

(25) Nor can we say at this stage whether the active catalyst is a mono- or polynuclear iridium species.

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An Extension of the Role of O(2) of Cytosine Residues in the Binding of Metal Ions. Synthesis and Structure of an Unusual Polymeric Silver(I) Complex of 1-Methylcytosine

Sir:

Extensive investigations into the interaction of metal ions with nucleic acids and nucleic acid constituents have identified the ring nitrogen atoms as the major binding sites on the heterocyclic purine and pyrimidine bases.[1,2] In comparison, fewer studies have definitively shown involvement in metal binding of the exocyclic groups of these heterocycles.[1,2] The interaction of Ag^+ ion with nucleic acids has been well studied and occurs primarily at guanosine-cytidine (G-C) regions of DNA.[1-4] Although this preferential binding has been exploited to separate nucleic acids of different G-C content,[4] there have been no structural studies on Ag(I) complexes of either G or C derivatives.

We report here on a study of the product formed between $AgNO_3$ and 1-methylcytosine. In the solid, the exocyclic oxygen at C(2) of the base unexpectedly exhibits strong binding to one Ag(I) and weaker, but still appreciable interaction, with a *second* Ag(I). Such bridging by an exocyclic group of a common nucleic acid base has not been previously observed.[1,2] The Ag(I) geometry has unusual features, and we are not aware of an analogous Ag(I) to carbonyl oxygen interaction. Furthermore, the columnar stacking of the 1-methylcytosine moieties affords a better comparison to the situation which might prevail in the biopolymer complex than is typically found in studies of monomer complexes.

The complex was prepared by the reaction of equal molar quantities of $AgNO_3$ and protonated 1-methylcytosine per-

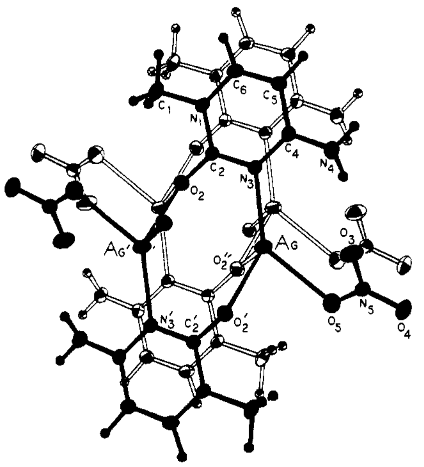

Figure 1. The structure of the complex [(1-methylcytosine)silver(I)] nitrate. Two dimers in the columnar stack along the c axis are displayed. O(2′) is related to O(2) by the transformation $-x, -y, -z$; O(2″) is related to O(2) by $-x, -y, -1-z$.

chlorate in dilute nitric acid (pH 3). After about 3 days, clear colorless crystals of the complex were harvested. The complex is slightly photosensitive, turning to a light-gray color after several weeks. Crystal data are as follows: a = 10.474 (3) Å, b = 11.141 (3) Å, c = 3.642 (1) Å, α = 97.33 (2)°, β = 95.82 (2)°, γ = 76.76 (2)°, V = 409.2 Å^3, Z = 2, space group $P\bar{1}$. Intensity data for 1838 symmetry-averaged reflections were collected on a Syntex P-1 automated diffractometer, employing Mo radiation and the θ-2θ scan technique. The structure was solved by Patterson methods and has been refined by the least-squares technique (anisotropic refinement of the nonhydrogen atoms and isotropic refinement of the hydrogen atoms) to a final R value of 0.033.

Some aspects of the structure of the [(1-methylcytosine) silver(I)] nitrate complex are illustrated in Figure 1. The most pronounced structural feature is the formation of centrosymmetric dimers in which the 1-methylcytosine ligands bridge two Ag ions, see Figure 1. Within these dimers, there are two strong metal-to-ligand bonds: Ag-N(3) = 2.225 (2) Å and Ag-O(2′) = 2.367 (2) Å. The N(3)-Ag-O(2′) bond angle at 136.2 (2)° is very nonlinear even in comparison to other dimeric systems involving Ag(I) (e.g., the Ag(I) complexes of glycine and the glycinate anion, ref 5, where the Ag-O distances are about 2.2 Å and the O-Ag-O angles are about 160°). The Ag···Ag distance across the crystallographic inversion center is 3.370 (1) Å, and can be compared to the value of 2.9 Å found in the glycine dimers.[5]

The dimers are formed into columnar stacks along the c axis, Figure 1, and connected by Ag-O(2″) bonds (Ag-O(2″) = 2.564 (3) Å). The Ag···Ag (or O(2′)···O(2″)) repeat length in this polymeric bridging system is 3.642 Å, the length of the c axis. The O(2′)-Ag-O(2″) bond angle is 95.1 (2)°. Within these columnar arrays, there is significant base-base overlap (mean distance = 3.34 Å). The coordination sphere about the silver is completed by a Ag-O(5)[nitrate] bond at 2.469 (3) Å. While the coordination sphere about the Ag(I) does not rigorously correspond to any common coordination polyhedra, it most closely approximates a trigonal pyramid.

The formation of the Ag-N(3) bond was anticipated, but the role that O(2) of the 1-methylcytosine base plays, both within the dimers and in the propagation of the columns along the c axis, suggests a wider scope than has previously been appreciated for this ligating atom. We have recently suggested that the binding of copper(II) to cytosine derivatives[6] may well be enhanced by the formation of an intramolecular chelate system involving Cu-N(3) and Cu-O(2) bonds. Furthermore, in a study of an octahedral complex of Mn(II) and cytosine 5′-monophosphate,[7] the Mn(II) forms a strong bond, 2.08 (3) Å, to O(2) of the 5′-CMP ring. It is interesting that Mn(II), which normally prefers hard donors, and Ag(I), which normally prefers soft donors, both form strong bonds to O(2) of a cytosine derivative. This previously unrecognized versatility in the binding of metal ions by the carbonyl group O(2)=C(2) of cytosine contrasts with the lack of evidence that the 6-oxo group of guanine derivatives plays anywhere near such a significant role in direct metal binding. The 6-oxo group can form a weak bond to a metal center in concert with a strong metal-N(7) bond.[8]

The binding mode observed in the dimeric units provides a partial model for the cross-linking of two strands of a DNA helix. The Ag···Ag repeat length (3.642 Å) in the polymeric, columnar stacks is reminiscent of the base-base stacking distance of about 3.5 Å in duplex DNA.[9] These nearly commensurate spacings suggest that cooperative propagation of base-Ag-base polymers parallel to the helix axis could be induced. In light of the versatility of O(2) of cytosine, both of these features could be readily accommodated in regions of high G-C content.

Acknowledgments. Support of this research by the National Institutes of Health, Public Health Service Grant No. GM 20544, is gratefully acknowledged.

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A Novel Substituent Effect in the Intramolecular Cycloaddition Reactions of Nitrile Ylides[1]

Sir:

Nitrile ylides are members of a class of 1,3-dipoles which contain a central nitrogen atom and a π-bond orthogonal to the 4π-allyl system.[2] 1,3-Dipolar cycloaddition of this dipole has been widely investigated[3,4] and in many cases had led to the synthesis of a variety of interesting heterocyclic compounds,[5] some of which would be tedious to synthesize by other routes. Recent ab initio LCAO-MO-SCF calculations by Houk and Caramella[6] have suggested that the nonplanar bent nitrile ylide geometry is favored over the linear form. The system still resembles the normal three-orbital, four-electron system present in other 1,3-dipoles so that concerted 1,3-dipolar cycloadditions can still occur. The bent geometry of the ylide[7] nicely rationalizes the intramolecular 1,1-cycloadditions observed with this 1,3-dipole.[8] Houk's calculations also indicate that electron-releasing substituents on the 3-carbon of the ylide should increase the preference for the bent geometry while electron-withdrawing groups at C-3 should favor linearization of the dipole. We now wish to report evidence which corrobo-