in $Ni_4(CNR)_7$ complexes, μ_4-acetylene bonding situations are established for metal clusters,[12] and we describe[13] in another paper a simple $\mu_3(\eta^2)$-acetylene bonding mode at three edge sites in $Ni_4(CNR)_4(RC{\equiv}CR)_3$ which is isostructural with $Ni_4(CO)_4(CF_3C{\equiv}CCF_3)_3$.[14] We suggest that a $\mu_x(\eta^2)$-ligand bonding will prove to be an important phenomenon in metal clusters and will extend to other molecules with triple bonds, such as CO and N_2, at least in reaction intermediates in catalysis.

We find that $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ catalyze the hydrogen reduction of carbon monoxide to give methane. Reaction conditions were quite mild: 140° and ~2 atm of pressure. These catalytic reactions were effected[15] in sealed glass tubes so that homogeneity of the reaction system could be monitored under reaction conditions; there was *no* evidence for the presence of solids at reaction temperatures. Selectivity was a distinctive feature of the osmium and iridium cluster catalyzed reactions in that only methane was detected. Analysis of reaction products was based on high resolution mass spectrometric analysis; with D_2 and CO as reactants, only D_2O and CD_4 were detected. Reaction rates under these mild conditions were explicably low (~1% conversion in 3-5 days with 3-5 catalyst turnovers), but we consider such reaction condition constraints essential to mechanistic studies of this important reduction reaction and to a constant definitive survey of reaction homogeneity. An elevation of reaction rates by a factor of at least 100 is necessary for mechanistic features to be effectively probed. Substitution of carbonyl groups in $Ir_4(CO)_{12}$ by triphenylphosphine[16] did increase the methane production rate but selectivity was lost because ethane and propane were formed in addition to the methane. Most significant was the result with trimethyl phosphite[17,18] as a substituent ligand where rates were at least threefold higher than in the triphenylphosphine-$Ir_4(CO)_{12}$ system and where selectivity to methane was maintained. Similar results were observed with the osmium cluster. Reduction of CO pressure seemed to lead to a rate increase in methane formation which would be consistent with a mechanism in which the key intermediate is a highly unsaturated carbonyl cluster (wherein there could be an η^2-CO ligand). Hydrogenation of $Ir_4(CO)_{12}$ or $Os_3(CO)_{12}$ in a nitrogen atmosphere gave no ammonia; methane production was relatively fast but this system was not homogeneous since either an insoluble cluster or metal was formed as the reduction proceeded.

A careful search was made for alcohols and alkenes in these reaction mixtures using both H_2-CO and D_2-CO reactant combinations. In none of these catalytic reactions was methanol or an alkene detected as a product. A set[19] of patents has described the catalytic conversion of CO and H_2 to methanol, ethylene glycol, and propylene glycol, at 220° and 30 atm with rhodium catalysts; $Rh_6(CO)_{16}$ was specifically cited as a catalyst. These patents claim that *no* hydrocarbons are formed in the rhodium catalyzed reactions. Hence, either rather striking selectivity may be found in clusters or large changes in reaction conditions may effect correspondingly large changes in reaction modes for this reduction reaction.

It should be noted that we have examined a large number of classic mononuclear coordination catalysts in the H_2-CO reaction with a wide range of solvents and have found none to be active, but of course, our examination of this class has not been exhaustive. One apparent exception was η^3-$C_3H_5Mn(CO)_4$ which has given evidence of CH_4 formation although results have ***not been consistent***. In this reaction, there was a rather fast cleavage of the allyl group; cluster formation may follow the cleavage reaction but the manganese product isolated at the end of the reaction was $HMn(CO)_5$.

We are now seeking a higher rate in this homogeneous catalytic hydrogen reduction of carbon monoxide, through substitution of the metal carbonyl clusters with phosphines and phosphites, to facilitate a mechanistic study of this important reaction under homogenous conditions.

Acknowledgment. We acknowledge support of this research by the Advanced Research Projects Agency, Cornell Materials Science Center, and by the National Science Foundation.

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(8) For example, the skeletal sequence of HM $\rightarrow$ HMolefin $\rightarrow$ RM $\rightarrow$ RC(O)M $\rightarrow$ RCHO + HM is discussed in more mechanistic detail by J. Halpern, *Adv. Chem. Ser.*, **No. 70**, 1 (1968), and by M. Orchin and W. Rupilius, *Catal. Rev.* **6**, 85 (1972).

(9) Formaldehyde is not a thermodynamically favorable product in this CO + H_2 reaction but possibly could serve, *bound to a metal center*, as an intermediate to an alcohol or an alkane.

(10) Neither CH_2O as a product nor HC(O)M complexes have been prepared directly from H_2, CO, and a metal complex. The only well-authenticated formylmetal complex $HC(O)Fe(CO)_4^-$ was prepared from $Fe(CO)_4^{2-}$ and $HCOOCOCH_3$. (J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95**, 4089 (1973).) This complex slowly reverted to $HFe(CO)_4^-$ although hydrolysis of the complex did yield CH_2O.

(11) Such a precedent may well be near at hand. We only wish to note that the mechanistic precedent does not appear to exist now.

(12) Acetylene binding in metal clusters is of variable form; common modes are μ_3 and μ_4. Four electron donation has been proposed in $Mo(CO)(C_2H_2)[S_2PR_2]_2$ (J. W. McDonald, J. L. Corbin, and W. E. Newton, *J. Am. Chem. Soc.*, **97**, 1970 (1975).)

(13) V. W. Day, M. G. Thomas, and E. L. Muetterties, submitted for publication.

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(15) The reaction vessels were not agitated. A 2-ml toluene solution with ~50 mg of metal cluster was used in all the catalytic reactions.

(16) A 1:1 molar ratio of $(C_6H_5)_3P$ to $Ir_4(CO)_{12}$ was used.

(17) A 1:1 molar ratio of $(CH_3O)_3P$ to $Ir_4(CO)_{12}$ was used.[18]

(18) The series of phosphite derivatives of $Ir_4(CO)_{12}$ will be reported separately, B. F. Beier, and E. L. Muetterties. An analogous study is being made by Professor J. R. Shapley (private communication).

(19) Belgium Patent 815-841 (1974); U.S. Patents 3 878 214, 3 878 290, and 3 878 292 (1975), and 3 833 634 (1974).

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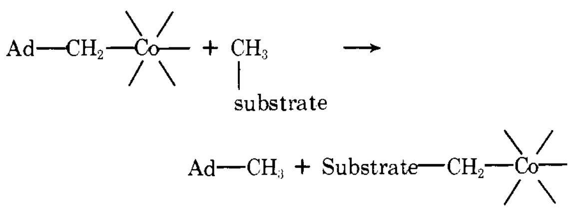
An Intramolecular Model for the Enzymatic Insertion of Coenzyme B_{12} into Unactivated Carbon-Hydrogen Bonds

Sir:

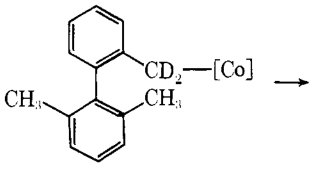
Extensive work[1] on the biochemical reactions catalyzed by coenzyme B_{12}, such as the isomerization of methylmalonyl CoA to succinyl CoA, has led to a unified picture of the mechanisms involved. First, coenzyme B_{12} inserts into an unactivated C-H bond of the substrate methyl group. The result is that the adenyl group of the coenzyme now carries a hydrogen atom of the substrate (and is thus 5′-desoxyadenosine), while the substrate methylene group becomes bonded to the cobalt of B_{12} (replacing the original adenyl-B_{12} carbon-cobalt bond). Second, a rearrangement or other reaction occurs within the B_{12}-substrate molecule to produce a product-B_{12} molecule. Finally, this undergoes the equivalent of a reverse of reaction 1 in which the adenyl-cobalt bond of coenzyme B_{12} is again formed, and the reaction product is released carrying one of the hydrogen atoms of the 5′-desoxyadenosine methyl group.



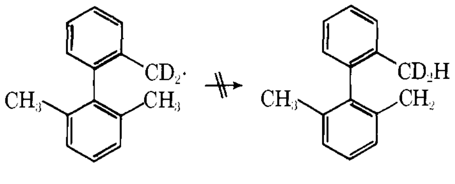
$$\mathrm{Ad{-}CH_2{-}Co} + \underset{\text{substrate}}{\mathrm{CH_3}} \longrightarrow \mathrm{Ad{-}CH_3} + \mathrm{Substrate{-}CH_2{-}Co} \qquad (1)$$

Detailed model reactions are needed for the various versions of step 2, depending on the nature of the substrate.[2] However, step 1 and step 3 are general in character but without good chemical precedent. We thus have examined various potential model systems for reactions such as eq 1, and have succeeded in finding simple chemical reactions which furnish good precedent for the steps of such an insertion into unactivated carbon.

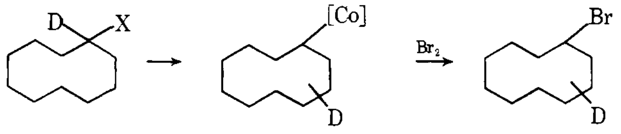
It has seemed to us[3] most likely that a process such as eq 1 occurs in steps: (a) homolytic cleavage of the carbon-cobalt bond, forming adenyl radical and B_{12r} (Co^{II}), (b) hydrogen atom transfer from the substrate to the adenyl radical, then (c) coupling of the resulting substrate radical with B_{12r}. Our first approach to a model system involved compounds I and II. Irradiation of I and simpler analogues[4] (cobaloxime is a model[5] for B_{12}), or simple storage of II (cobalamine is B_{12} itself), led to carbon-cobalt homolysis to generate the expected benzylic radical. However, this dimerized cleanly without hydrogen transfer from the nearby CH_3's. Thus we turned to a system in which intramolecular hydrogen transfer to a carbon free radical has already been demonstrated.



I, [Co] = cobaloxime
II, [Co] = cobalamine



Only a few such systems are known,[6] and the best for our purposes was the cyclodecyl radical. This species rearranges by transannular hydrogen transfer[7] in a process analogous to that for the better known cyclodecyl cation.[8] We used deuterium as a marker, and prepared cyclodecyl-*1-d* tosylate (III). With NaI in acetone this afforded cyclodecyl-*1-d* iodide (IV), without rearrangement. The tosylate III did not react with B_{12s}^- on prolonged standing (15 h), but the iodide IV reacts rapidly (15 min) with a solution[9] of B_{12s}^- to form cyclodecyl-B_{12} (V).

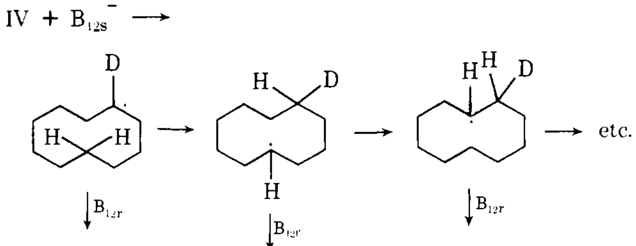


III, X = OTs
IV, X = I
V, [Co] = cobalamin
VI

Bromination of V affords cyclodecyl bromide (VI) with the deuterium marker distributed over several ring carbons. Thus proton NMR shows that VI has ca. 32% *d* on C_1, whereas deuterium NMR shows the deuterium distributed 25% on C_1, 13% on the two C_2's, and 62% on the other carbons. Proton decoupled ^{13}C NMR shows deuterium satellites on the C_2 signal, on the signal for the unique C_6 (C_1 and C_6 are the only carbons which do not occur as pairs, with double the NMR intensity), and on at least one other carbon (C_3, C_4, or C_5).

Transannular hydrogen transfer has thus occurred in the overall sequence. It seems unlikely in the bromination step, since such brominations apparently proceed by a direct S_E2 mechanism.[10] The iodide IV does not rearrange on standing, and V decomposes slowly over 7-10 days without change in its (nonstatistical) deuterium distribution.[11] Thus the most likely step for rearrangement is in the alkylation to form V.

The reaction of IV with B_{12s}^- is certainly not a simple displacement at carbon, or the tosylate III should have comparable or greater reactivity. Instead the most likely path is electron transfer[12] from B_{12s}^- to IV, generating cyclodecyl radical and B_{12r}. These then couple to afford V. We conclude that transannular hydrogen transfer has occurred in the cyclodecyl radical at a rate comparable with its capture by B_{12r}.



V-*1-d*
V-*5-d*
V-*2-d*

Homolytic fragmentation of alkyl-B_{12} bonds is well precedented. We see in our model system that the resulting radical can abstract a suitable hydrogen atom from a nearby unactivated carbon, and that the resulting radical can then be captured by B_{12r} to generate a new carbon-B_{12} bond. In the enzymatic reaction this nearby carbon would be that of a closely bound substrate. Thus the insertion reactions common to all coenzyme B_{12} catalyses now have good chemical precedent.

Acknowledgment: We thank Mr. I. Miura for careful NMR studies, and the National Institutes of Health for support of this work.

References and Notes

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(2) An important model for one such process has been reported by Dowd (ref 1).
(3) See R. H. Abeles, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **15**, 113, (1972), who kindly acknowledged our suggestion of this mechanism. See also our elaboration, *ibid.*, 119-120 (1972).
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(9) The reactions were performed in 50% aqueous methanol by reduction of hydroxocobalamin with $NaBH_4$, addition of the corresponding alkyl tosylate or iodide, then precipitation of the B_{12} product with acetone. It was washed with acetone, and then cleaved by Br_2 in CH_2Cl_2. Cyclodecyl bromide was isolated in ca. 7% overall yield, and identified by VPC, mass spectrum (d_1), and NMR spectra.
(10) M. Tada and H. Ogawa, *Tetrahedron Lett.*, 2639 (1973); F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Am. Chem. Soc.*, **92**, 1414 (1970).
(11) The decomposition is probably homolytic, but the resulting radical–B_{12r} pair recouples to only a small extent, consistent with the low yield in the original alkylation. Thus further cyclodecyl radical rearrangement is not detectable.
(12) B_{12s}^- is a powerful reducing agent.[5] While iodide and tosylate are comparable leaving groups in simple displacements, the C–I bond is much more easily reduced.

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Book Reviews

A Dictionary of Spectroscopy. By RONALD C. DENNEY (Thames Polytechnic). Halsted Press, John Wiley & Sons, Inc., New York, N.Y. 1973. xv + 161 pp. $8.95.

A dictionary of spectroscopic terminology could be quite useful. The diverse techniques and concepts of spectroscopy are anything but deficient in jargon and nomenclature of dubious descriptive value. I would be grateful to Dr. R. C. Denney for his dictionary if it were not flawed by unnecessarily trivial and specialized entries, important omissions, and physically unsound discussions. This dictionary is clearly directed at individuals who are not interested in understanding spectroscopy.

Analytical atomic, infrared, and mass spectroscopy are particularly well represented, but Delves cup, gallium cut-offs, and McLafferty rearrangements, for example, seem out of place. Chromatography, except in its connection to mass spectroscopy (Watson–Biemann separation), appears to have been excluded. Other omissions include Hund's rules and coupling cases, Faraday, Kerr, and Stark effects, a distinction between Rydberg and valence states, and a discussion of resonance-enhanced Raman spectroscopy.

Following are excerpts from several of the more misleading definitions:

> *Bonding Orbitals.* "If the two electrons have opposite spins the electron cloud of the molecular orbital is mainly between the two nuclei .... This constitutes a bonding orbital. If, however, the two electrons have identical spins, the molecular orbital is formed with a nodal plane between the two nuclei and the charge is localized at each end of the bond." Spin is confused with phase of the atomic orbital.
>
> *Brewster Angle.* "The Brewster angle is the angle at which the incident light is totally reflected if in one polarization and totally refracted if in the opposite polarization." Although total transmission does occur for one polarization, *total* reflection at Brewster incidence does not occur for the other polarization.
>
> *Ground State.* "When electrons in an atom or molecule occupy the vibrational levels [?] in the lowest possible energy levels, the condition is referred to as the ground state."
>
> *Population Inversion.* "This is the name given to a situation in which the number of active species occupying a particular energy state is greater than that predicted by the Boltzmann ratio. This is of special consideration in lasers in which excited states of extended lifetimes are produced and population inversions deliberately created." An inversion is more than a departure from equilibrium; an upper level must have a larger population than a lower energy level. Upper laser levels do not necessarily have extended lifetimes.
>
> *Raman Effect.* ".... after being raised to an excited state, some of the excited molecules returned to a higher or lower vibrational level in the ground electronic state. The lifetime of the Raman excited state is about 10^{-12} s and only about 1 in 10^6 molecules exhibit the effect at any particular moment." The excited state in the Raman effect is not a *real* but a *virtual* level. The Raman effect might be approximately 10^6 times weaker than fluorescence excited from a *real* upper level.
>
> *Schrödiger Wave Equation.* "Solutions of the equation are only possible for finite, non-zero, unique values of E; such solutions are termed eigenvalues and correspond to the energy states developed from the Bohr Theory of the atom." No comment.
>
> *Triplet State.* "The triplet state can only arise from the promotion of one of the two π electrons, forming part of an unsaturated system, to an upper unoccupied orbital." There are many other ways of forming triplet states.

Perhaps a physical chemist specializing in diatomic molecular spectroscopy is too much of a purist to properly review this dictionary of spectroscopy.

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Structure and Bonding. Volume 20. Edited by J. D. DUNITZ (Zurich), P. HEMMERICH (Kontanz), R. H. HOLM (Cambridge, Mass.), J. A. IBERS (Evanston), E. G. JØRGENSEN (Geneva), J. B. NEILANDS (Berkeley), D. REINEN (Marburg), and R. J. P. WILLIAMS (Oxford). Springer-Verlag, New York, N.Y. 1974. 167 pp. $27.10.

This is the latest in a series of volumes "issued at irregular intervals, according to the material received". This volume was given the secondary title "Biochemistry". All four of the review articles in this volume deal for the most part, at least, with the physical and chemical properties of certain metal ions in proteins and smaller polypeptides. Moreover, the last three articles all cover aspects of naturally occurring, iron-containing compounds.

The first article entitled "The Role of Divalent Cations in the Mechanism of Enzyme Catalyzed Phosphoryl and Nucleotidyl Transfer Reactions", by A. S. Mildvan and C. M. Grisham, both summarizes and critically examines experimental findings on the enzymes staphylococcal nuclease, DNA polymerases, pyruvate kinase, phosphoenolpyruvate carboxylase, fructose diphosphatase, creatine kinase, phosphoglucomutase, alkaline phosphatase, and (Na^+ and K^+) adenosine 5′-triphosphatase. In each case the authors speculate on possible roles of divalent metal ions in coordinating with either the atom or group which attacks (or leaves from) the transferred phosphoryl moiety, or in coordinating with the transferred phosphoryl moiety itself.

The second article, "The Enzymatic Reduction of Ribonucleotides", by H. P. C. Hogenkamp and G. N. Sando, is a thorough summary of the chemistry and biochemistry of the currently dynamic area of research which is examining how nature provides the deoxyribonucleotide precursors needed in DNA synthesis. The authors correlate information gathered in a variety of different systems and show where some common themes have emerged. In