the evidence is clearly in favor of specific and intact incorporation of urogen III.

Table I. ^{14}C Feeding Experiments Using Suspended Cells of *P. shermanii* ATCC No. 9614

Expt	Substrate fed	mg fed	Hr	Spec incorp/C
1	PBG	21	70	5.1
2	Urogens I–IV	25	70	0.91
3	Urogen I	7	40	0.000
4	Urogen I[a]	25	70	0.017
5	Urogens III + I	0.1	70	0.0052
6	Urogens III + I	24	70	0.40
7	Uroporphyrins I–IV	34	60	0.000

[a] See ref 10.

On the other hand urogen I (**4**) (prepared by the spinach synthetase procedure[9]) gave either zero or very low[10] incorporation when administered in carefully monitored parallel feeding experiments (Table I; expts 3 and 4).

With proof for the inertness of urogen I in hand, any concern over the use of urogen III–I mixture (70:30 to 50:50) obtained from the wheat germ preparation can be discounted as can the use (expt 2) of the chemically synthesized statistical mixture of the types I–IV isomers which contain 50% of the type III isomer together with 12.5% of type I, the remainder being biologically inert types II and IV isomers. In conformity with heme and chlorophyll biosynthesis,[1] no incorporation of the same statistical mixture of the [^{14}C]uroporphyrins I–IV (from which urogens I–IV were prepared) was observed (expt 7).

In order to confirm these results without recourse to the tedium of carbon-by-carbon degradation of the vitamin, the experiment was repeated using [8-^{13}C]-PBG and the urogen I–IV isomers labeled with ^{13}C (90% enrichment per carbon) as shown above. A preliminary report[2] that PBG was specifically incorporated could be confirmed by using first [8-^{14}C]-PBG (Table I, expt 1; ~5% specific incorporation) and then [8-^{13}C]-PBG. The ^{13}C FT nmr spectrum of [8-^{13}C]-PBG enriched vitamin B_{12} is shown in Figure 1a. The spectrum contains three resonances at 37.75, 33.44, and 31.50 ppm arising from four enriched centers. That four enriched carbons were actually present was demonstrated by conversion of the vitamin to the dicyano form. The sharp signal at 31.50 ppm was cleanly resolved and the ^{13}C spectrum showed four enhanced peaks of equal intensity. When the [^{13}C]-urogen isomers were administered to *P. shermanii* (~12 g of cells/100 ml of medium per flask) and the resultant vitamin B_{12} was subjected to similar ^{13}C nmr analysis, the enriched spectrum showed enhancement[11] (Figure 1b) (~6%) of the *same set of four methylene* carbons as were labeled in the [^{13}C]-PBG experiment.

These results together with the enrichment data for [^{13}C]-ALA[12] not only corroborate positive incorporation with carbon-14 but also provide unequivocal evidence for the location of the label, and strongly support the sequence PBG → urogen III → vitamin B_{12} in *P. shermanii*. Thus, with the important *proviso* that sufficient substrate must be present to permeate the cell wall and to survive *in vitro* oxidative destruction it is our view that vitamin B_{12} is produced by a reductive contraction of urogen III.

A summary of several hypothetical routes from urogen III to the corrinoids is given in Scheme I, paths B and C, both of which imply a hydrolytic ring contraction. Further delineation of these and other alternatives must await the results of cell free experiments which are now in progress.

Acknowledgment. We thank the National Institutes of Health (Grant RR-00356) and the National Science Foundation and Merck & Co. for support of this work.

[9] L. Bogorad, *Methods Enzymol.*, **5**, 855 (1962).

[10] In fact the apparent, small incorporations of the type I isomer (*ca.* 5% of urogen III incorporation) could be traced to minor amounts of the type III isomer present in the spinach enzyme preparation when run for more than 6–8 hr. This effect has been observed during prolonged incubations with this enzyme (Professor L. Bogorad, private communication).

[11] Reference to Table I indicates that the specific incorporation of the [^{14}C]urogen mixture is 0.91%. This experiment utilized *ca.* 25 g of cells/100 ml of medium. In several runs in which the cell weight was reduced to 10–12 g, incorporations of 2–3% were observed. The [^{13}C]-urogen isomers (780 mg; 90% ^{13}C) were therefore administered in high concentration (3.6 l.) to a relatively small cell mass (400 g) and incubated under very strict anerobic conditions in stoppered vessels for 70 hr with pH adjustment (to 7.0) each day.

[12] A. I. Scott, C. A. Townsend, K. Okada, M. Kajiwara, P. J. Whitman, and R. J. Cushley, *J. Amer. Chem. Soc.*, **94**, 8267 (1972).

[13] Carbon-13 Fourier Transform Nuclear Magnetic Resonance. V.

A. Ian Scott,* C. A. Townsend, K. Okada, M. Kajiwara
Sterling Chemistry Laboratory, Yale University
New Haven, Connecticut 06520

R. J. Cushley[13]
Section of Physical Sciences, Yale University School of Medicine
New Haven, Connecticut 06510

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Nucleophilic Reactions of Cationic Transition Metal *Dihapto*allene Complexes

Sir:

There has been considerable current interest in nucleophilic reactions of hydrocarbon ligands which are polyhapto bonded to transition metals.[1] We now have extended investigations on such reactions to the previously unexplored *dihapto*allene complexes.[2] Communicated herein are the remarkable reactivity of $[h^5\text{-}C_5H_5Fe(CO)_2(h^2\text{-}CH_2{=}C{=}CHR)]^+$ toward several nucleophiles and the relevance of these processes to the mechanism of metal-promoted cycloaddition reactions of 2-alkynyl complexes.[3]

The cations **1a** and **1b**[3,4] have been obtained as the crystalline BF_4^- salts by treatment of the corresponding $h^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ with HBF_4 in $(CH_3CO)_2O$.

[1] See, for example, (a) L. Busetto, A. Palazzi, R. Ros, and U. Belluco, *J. Organometal. Chem.*, **25**, 207 (1970); (b) P. J. C. Walker and R. J. Mawby, *Inorg. Chem.*, **10**, 404 (1971); (c) F. Haque, J. Miller, P. L. Pauson, and J. B. Pd. Tripathi, *J. Chem. Soc. C*, 743 (1971); (d) M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, **11**, 1269 (1972).

[2] Although nucleophilic additions to a coordinated *dihapto*allene have not been investigated for isolable metal complexes, such reactions have been reported for some transient intermediates. Accordingly, products of reactions of several palladium(II) complexes (PdX_2) with allene most certainly arise *via* the formation of a metal–h^2-allene intermediate followed by addition of X to the coordinated $CH_2{=}C{=}CH_2$. For a summary of these reactions, see P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. I, Academic Press, New York, N. Y., 1971, pp 188–191, 248–249; Vol. II, pp 41–42.

[3] D. W. Lichtenberg and A. Wojcicki, *J. Organometal Chem.*, **33**, C77 (1971).

[4] J. Benaim, J.-Y. Merour, and J.-L. Roustan, *C. R. Acad. Sci., Ser. C*, **272**, 789 (1971).

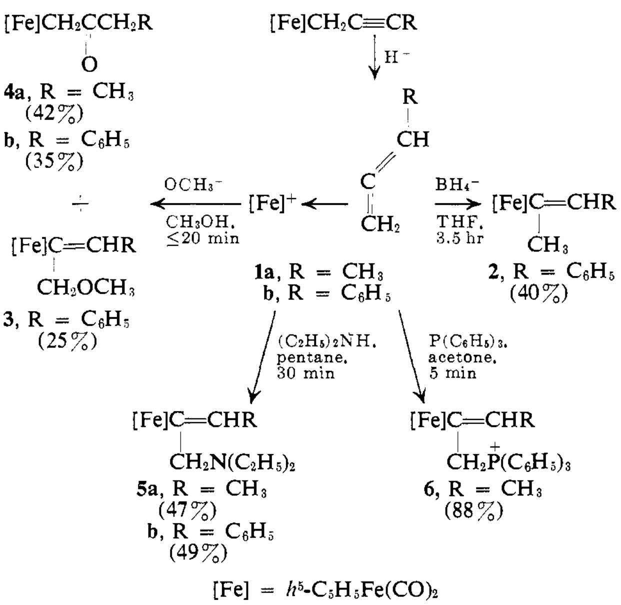
Table I. Some Physical Properties and ^{1}H Nmr and Infrared Absorptions of the Products of Reactions of Allene Complexes with Nucleophiles

Complex	Physical state	^{1}H nmr spectrum[c] C_6H_5, τ	 CH_2X, τ	 $J_{CH_2XC=CH}$, Hz	Infrared spectrum,[d] ν(CO), cm^{-1}
2	Yellow solid	5.15, 5.28 (1:4 ratio)	7.69 d, 7.64 d (1:4 ratio)	1.5, 1.5	2020, 1967
3	Orange oil	5.34	5.91 d	1.45	2018, 1967
4a	Orange oil	5.17	8.23, 7.61 q ($J_{CH_2CH_3}$ = 7.5 Hz)		2020, 1970[e]
4b	Yellow solid, mp 64–66°	5.18	8.18, 6.32		2020, 1970[f]
5a	Orange oil	5.18	6.98 br	Not obsd	2015, 1964
5b	Orange oil	5.21, 5.47 (3:7 ratio)	6.88 d, 6.81 d (3:7 ratio)	1.4, 1.4	2016, 1965
6[a]	Yellow solid, mp 188° dec[b]	4.97	5.52 d, br (J_{CH_2P} = 14 Hz)	Not obsd	2017, 1959[g]

[a] All data for the BF_4^- salt. [b] A 1:1 electrolyte in nitrobenzene. [c] In $CDCl_3$. All singlets except as noted: d, doublet; q, quartet; br, broad. [d] Beckman IR-9 spectrophotometer and pentane solution except as noted. [e] ν(C=O) 1665 w. [f] ν(C=O) 1660 w. [g] $CHCl_3$.

Their reactions with BH_4^-, OCH_3^-, $(C_2H_5)_2NH$, and $P(C_6H_5)_3$ are summarized in Scheme I. In a typical experiment, **1a** or **1b** dissolved or suspended in the specified solvent at 0–25° was treated with a stoichiometric amount or a slight excess of the nucleophile, the solvent was removed, and the residue was chromatographed on alumina. The chemical composition of each product was elucidated by elemental analysis and/or mass spectrometry. Except for **6**, all complexes displayed mass peaks due to their respective molecular ions.

Scheme I



The formulation of **2**, **3**, **5a**, **5b**, and **6** as iron–vinyl complexes is based on the ^{1}H nmr and infrared spectroscopic data (Table I). The positions of the h^5-C_5H_5 and CH_2X resonances, as well as the values of $J_{CH_2XC=CH}$, are those expected for h^5-$C_5H_5Fe(CO)_2Y$ where Y = $C(CH_2X)=CHR$.[3,5–8] The carbonyl stretching frequencies are similar to those reported for several related iron–vinyl derivatives.[3,5–7] The occurrence of two h^5-C_5H_5 and two CH_2X resonances in the spectra of **2** and **5b** is most likely due to the presence of both cis and trans isomers. However, at present we cannot unambiguously assign the geometry about the olefinic bond in the above two compositions and in the other complexes reported herein. The formulation of **4a** and **4b** as iron–2-alkanone derivatives is supported by the cleavage of **4b** with HCl to afford h^5-$C_5H_5Fe(CO)_2Cl$ and $CH_3C(O)CH_2C_6H_5$ (65%).

The foregoing reactions of the cationic h^2-allene complexes with nucleophiles provide still another striking example of the influence that metals exert on the behavior of coordinated organic groups. Since free allenes are virtually inert to attack by nucleophiles,[9] the marked enhancement in their reactivity upon coordination undoubtedly results from σ interaction with the positively charged metal. With most nucleophiles examined, attack occurs at the terminal carbon and is accompanied by migration of the metal onto the center carbon. It is of interest that even $P(C_6H_5)_3$, which readily displaces olefins from metal complexes,[10] yields here a metal–vinyl derivative containing a phosphonium moiety (**6**). However, with OCH_3^- as the nucleophile, attack upon the coordinated allene appears to take place preferentially or exclusively at the center carbon leading to the formation of **4a** or **4b**.[11]

The observed reactivity toward nucleophiles of the terminal carbon atom in these allene complexes adds credence to the proposed mechanism of the currently investigated cycloaddition reactions of transition metal 2-alkynyl derivatives ($MCH_2C≡CR$).[3,12] These reactions, known to occur with SO_2,[6,12] SO_3,[3,13] $CF_3C(O)$-

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(5) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

(6) J. E. Thomasson, P. W. Robinson, D. A. Ross, and A. Wojcicki, *Inorg. Chem.*, 10, 2130 (1971).

(7) Y. Yamamoto and A. Wojcicki, *Proc. Int. Conf. Coord. Chem., 14th*, 692 (1972).

(8) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon, New York, N. Y., 1969, pp 316–326.

(9) (a) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967); (b) S. Danishefsky, S. J. Etheredge, R. Volkmann, J. Egger, and J. Quick, *J. Amer. Chem. Soc.*, **93**, 5575 (1971).

(10) (a) R. J. Angelici and W. Loewen, *Inorg. Chem.*, **6**, 682 (1967); (b) W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441 (1971).

(11) These reactions probably proceed *via* the intermediacy of h^5-$C_5H_5Fe(CO)_2CH_2C(OCH_3)=CHR$ (R = CH_3 or C_6H_5) whose rearrangement to **4a** and **4b** may be somewhat analogous to that reported recently for some reactions of Pt(II)–acetylene complexes. See M. H. Chisholm and H. C. Clark, *J. Amer. Chem. Soc.*, **94**, 1532 (1972).

(12) W. D. Bannister, B. L. Booth, R. N. Haszeldine, and P. L. Loader, *J. Chem. Soc. A*, 930 (1971)

(13) J.-L. Roustan, J.-Y. Merour, J. Benaim, and C. Charrier, *C. R. Acad. Sci., Ser. C*, **274**, 537 (1972).

CF_3,[14] and $ClSO_2NCO$[7] (EN), *inter alia*, lead to the formation of $\mathrm{M\overline{C{=}C(R)ENC}H_2}$. In the light of the results presented in this communication, it seems very probable that they proceed *via* the intermediacy of the allene complex which arises by attack of the electrophilic part (E) of EN upon the acetylenic bond. This then rearranges to the cyclic product through the interaction of the nucleophilic atom (N) of EN with the terminal carbon of the coordinated allene.

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(14) D. W. Lichtenberg and A. Wojcicki, to be submitted for publication.

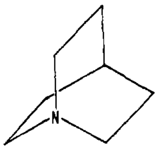
Dale W. Lichtenberg, Andrew Wojcicki*
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received July 20, 1972

Excimer Formation in Saturated Amines

Sir:

To date, virtually all studies of excimers (excited dimers) deal with aromatic hydrocarbons and their derivatives.[1] This communication reports part of the results of an investigation of the photophysical properties of saturated amines. Certain tertiary amines exhibit concentration-dependent fluorescence spectra. This phenomenon is shown in Figure 1 for 1-azabicyclo[2.2.2]octane (ABCO, I) in *n*-hexane at 24°.[2] Each



I

spectrum is arbitrarily normalized, and, therefore, the isoemissive point at 3240 Å is only apparent.[4] It is proposed that the broad, structureless band with λ_{max} at 3760 Å, whose net quantum efficiency increases with increasing concentration, is fluorescence from the ABCO excimer. Further support for this hypothesis is provided by results of kinetic studies. The time dependence of the 3760-Å emission band (isolated with a Corning 0-52 filter) shows a gradual buildup to a maximum and subsequent decay. The time delay between the exciting flash and the maximum in emission intensity increases with decreasing ABCO concentration. The observations provide direct evidence for a dynamic (rather than static) mechanism for the production of the species fluorescing with λ_{max} at 3760 Å. Furthermore, the nature of the absorption spectrum in *n*-hexane solution is invariant from 10^{-4} to 10^{-2} *M*. The band with λ_{max} at 2730 Å is fluorescence from the ABCO monomer. The fluorescence maximum for a tertiary amine with a similar degree of alkylation; *e.g.*, triethylamine, appears at 2825 Å in *n*-hexane solution. The corresponding λ_{max} for triethylamine in the vapor phase is 2780 Å.[7,8] The simple trialkylamines all show maximum fluorescence in this region.[7] There is a very large Stokes shift since the simple amines characteristically have maximum absorption in the vicinity of 2000 Å.[8,9] It has been suggested that, in the vapor phase, the lowest lying excited state of the trialkylamines is largely Rydberg in nature,[3,10] although in a condensed medium, this may not be an accurate description.[11]

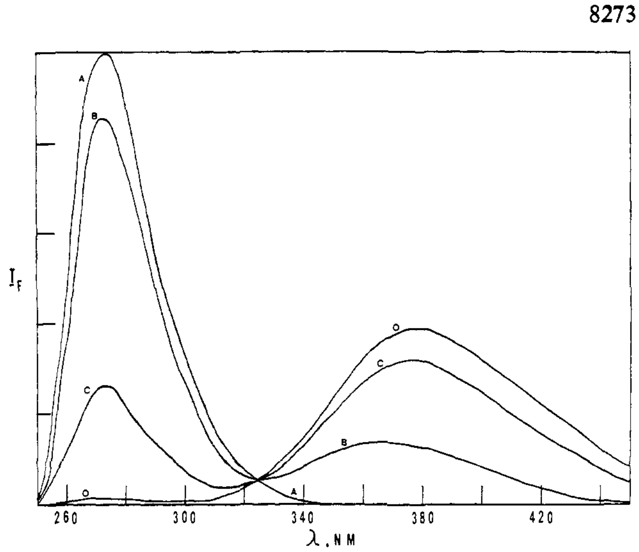


Figure 1. Uncorrected fluorescence spectra of ABCO in *n*-hexane at 24°. Concentrations are: (A) 5.5×10^{-5} *M;* (B) 5.5×10^{-4} *M;* (C) 5.5×10^{-3} *M;* (D) 5.5×10^{-2} *M.*

It is noteworthy that both the spectral and temporal properties mentioned above are also observed for ABCO in the vapor phase at 24°. These results are depicted in Figures 2 and 3. The monomer fluorescence is replaced by a highly structured emission system;[12] however, the structureless excimer fluorescence in the vapor system is not observed unless a few centimeters of an inert gas (such as *n*-hexane or cyclohexane) are added to the amine vapor. Presumably this is necessary in order to achieve complete thermal stabilization of the excimer; apparently internal vibrational degrees of freedom are inadequate in dissipating the energy released by a newly formed ABCO

(1) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley Interscience, London, 1970, Chapter 7.

(2) ABCO was obtained as the hydrochloride from Aldrich Chemical Co. The free base was liberated by combining very concentrated ABCO·HCl and NaOH aqueous solutions. This solid amine was filtered and twice sublimed *in vacuo* through a layer of previously dried sodium hydroxide, mp 159–160° (lit.[3] mp 161.5–162°).

(3) A. M. Halpern, J. L. Roebber, and K. Weiss, *J. Chem. Phys.*, **49** 1348 (1968).

(4) The conditions of the experiment were such that the optical densities of the solutions varied over a wide range. For ABCO in *n*-hexane, λ_{max} is 2090 Å; ϵ_{max} is 1600 M^{-1} cm^{-1}.[5] Therefore, in order to obtain satisfactory signal-to-noise ratios, the exciting wavelength was changed from 237 (for dilute solutions) to 249 nm (for concentrated solutions). Thus, each spectrum would have to be corrected with respect to the optical density and the intensity of the exciting radiation in order to obtain the true isoemissive point. In all cases the emission spectra were otherwise independent of exciting wavelength. Preliminary thermodynamic experiments reveal that there is a well-defined isoemissive point for both the ABCO and 1-AA (*vide infra*) systems.[6]

(5) A. M. Halpern, E. Maratos, and R. B. Walter, unpublished data.

(6) A. M. Halpern and R. J. Sternfels, to be submitted for publication.

(7) C. G. Freeman, M. J. EcEwan, R. F. C. Clairidge, and L. F. Phillips, *Chem. Phys. Lett.*, **8**, 77 (1971).

(8) A. M. Halpern and R. B. Walter, unpublished results.

(9) E. Tannenbaum, E. M. Coffin, and A. J. Harrison, *J. Chem. Phys.*, **21**, 311 (1953).

(10) Y. Muto, Y. Nakato, and H. Tsubomora, *Chem. Phys. Lett.*, **9**, 597 (1071).

(11) See M. B. Robin and N. A. Kuebler, *J. Mol. Spectrosc.*, **33**, 724 (1970), and references cited therein.

(12) A. M. Halpern and E. Maratos, unpublished results. Details will be reported separately.