

Table I. Specific Activities of ^{14}C and ^3H : ^{14}C Ratios of Yeast Metabolites and Their Transformation Products (See Text)

Compound	Specific activity ^a	^3H : ^{14}C ratio	
		Isotopic	Atomic
MVA ^b	104	10.71	1.00:1
Squalene ^b	491	10.32	5.77:6
2d	7.63	8.72	4.07:5
3a from 2d	1.91	8.65	4.04:5
3b	5.80	8.66	4.04:5
3c	6.00	8.66	4.04:5
3c recovered	6.19	8.63	4.03:5
5	6.04	8.67	4.05:5
4	5.96	6.72	3.14:5

^a Values $\times 10^4$ dpm; dpm per mmol. ^b The MVA and squalene were counted as the benzydrylamide and hexachloride, respectively.

3β -ol acetate (**2d**) (Table I). This confirmed the presence of Δ^7 in the metabolite (**2c**).

We have proven with the use of $(14\alpha,15\alpha)$ - $[^2\text{H}_2]$ and $(8\beta,15\beta)$ - $[^2\text{H}_2]$ - 5α -cholestanol acetates that their photochemical dehydrogenation to 5α -cholest-14-en- 3β -ol acetate in the presence of $\text{C}_6\text{H}_5\text{I}$ Cl_2 involves the overall cis abstraction of the 14α and 15α hydrogen (deuterium) atoms.^{8,9} This procedure was employed for the determination of the presence and the stereochemistry of tritium at C-15 of the (*R*) metabolite (**2c**).

In the absence of an appropriate chemical method for the reduction of **2a** to cholestanol, we opted for a combination of enzymatic and chemical routes.

The (*R*)-**2a** (5×10^5 dpm of ^{14}C) was incubated with a rat liver preparation³ to yield $[^{14}\text{C}_5,^3\text{H}_4]$ cholesterol (**3a**) (2.2×10^5 dpm of ^{14}C) which was acetylated (**3b**) and then hydrogenated to $[^{14}\text{C}_5,^3\text{H}_4]$ cholestanol acetate (**3c**) (Table I). It is apparent that the transformations **2c** \rightarrow **2a** \rightarrow **3a** \rightarrow **3c** proceeded without loss of tritium (Table I). Photochemical dehydrogenation^{8,9} of **3c** in benzene in the presence of $\text{C}_6\text{H}_5\text{I}$ Cl_2 gave cholestanol acetate (**3c**), 5α -cholest-14-en- 3β -ol acetate (**4**), and 5α -cholest-9(11)-en- 3β -ol acetate (**5**) (Table I).

It is clear that the formation of **4** from **3c** proceeded with the loss of a tritium atom. Since we have proven that the introduction of Δ^{14} involves the abstraction of the 14α - and 15α -hydrogen atoms,⁸ it follows that the cholestanol acetate **3c** and hence the (*R*) metabolites **1a** and **2a** have 15α -tritium atoms. Because the (*S*) metabolites **1b** and **2b** do not have a tritium⁴⁻⁶ atom at C-15, it may be inferred that the elimination of the 14α -methyl involves a Δ^{14} intermediate,¹⁰ and that the introduction of this olefinic bond proceeds with the abstraction of a hydrogen originating from 2 pro *S* of MVA. Considering the fact that the (*R*) metabolites have a 15α -tritium atom, it follows that the enzymatic reduction of the Δ^{14} proceeds *via* the trans acquisition of two ionic species of hydrogen at the 14α and 15β positions. In analogy to rat livers¹¹ it seems likely that a hydride ion (from NADPH) and a proton (from the medium) are added at the 14α and 15β positions, respectively. Finally it may be noticed that the retained 15α -tritium atom in **1a** and **2a** underwent an inversion of configuration with respect to its original orientation in protosterols¹² and lanosterol.

Supplementary Material Available. Supplementary text and a table will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 \times 148 mm, 24 \times reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-8107.

Acknowledgment. We are grateful to Professor R. Breslow, Columbia University, for providing the experimental details for the dehydrogenation experiments described here and in the microfilm edition⁸ of the journal prior to their publication.

References and Notes

- (1) This work was supported by Grants AM 12156, CA 13369, and GM 19882 from NIH and by Grant GB 36201 from NSF.
- (2) Extracted in part from the thesis of J.P.M. to be submitted to the University of Orleans, Orleans, France, in partial fulfillment of the requirements for a Doctorat d'Etat.
- (3) P. J. Ramm and E. Caspi, *J. Biol. Chem.*, **244**, 6064 (1969).
- (4) E. Caspi and P. J. Ramm, *Tetrahedron Lett.*, **3**, 181 (1969).
- (5) E. Caspi, J. P. Moreau, and P. J. Ramm, *J. Steroid Biochem.*, in press. J. P. Moreau, D. J. Aberhart, and E. Caspi, *J. Org. Chem.*, **39**, 2018 (1974).
- (6) J. P. Moreau, P. J. Ramm, and E. Caspi, submitted for publication.
- (7) P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch, and G. W. Wood, *J. Chem. Soc.*, 2402 (1951).
- (8) Experimental details will appear following these pages in the microfilm edition of this volume of the journal. See paragraph at end of paper regarding supplementary material.
- (9) R. Breslow, J. A. Dale, P. Kalicky, S. Y. Liu, and W. N. Washburn, *J. Amer. Chem. Soc.*, **94**, 3278 (1972).
- (10) D. H. R. Barton, J. E. T. Corrie, P. J. Marshall, and D. A. Widdowson, *BioOrg. Chem.*, **2**, 363 (1973).
- (11) M. Akhtar, A. D. Rahimtul, J. A. Watkinson, D. C. Wilton, and K. A. Munday, *J. Chem. Soc., Chem. Commun.*, 149 (1969).
- (12) E. Caspi, R. C. Ebersole, L. J. Mulheirn, W. O. Godfredsen, and W. V. Daehne, *J. Steroid Biochem.*, **4**, 433 (1973).
- (13) Postdoctoral Fellow 1967-1969.

E. Caspi,* J. P. Moreau, P. J. Ramm¹³

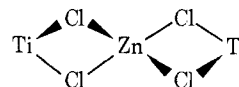
The Worcester Foundation for Experimental Biology, Inc.
Shrewsbury, Massachusetts 01545

Received August 22, 1974

1,3 Magnetic Exchange in Linear Trimetallic Titanium(III) Complexes

Sir:

Trinuclear metal complexes containing two biscyclopentadienyltitanium(III) species coordinated to a tetrahedral bridging group have been known for some time.^{1,2} A representative example is $[\text{Cp}_2\text{Ti}]_2\text{ZnCl}_4 \cdot 2\text{C}_6\text{H}_6$ which is prepared in benzene by reaction of $[\text{Cp}_2\text{TiCl}]_2$ with ZnCl_2 or from Cp_2TiCl_2 and Zn dust. Crystallization occurs in the form of a dibenzene solvate whose structure has been determined by Vonk³ and also independently in our laboratory. Similar results are obtained, and our refinement shows a



linear unit with a Ti-Zn distance of 3.420 (2) Å, a Zn-Cl-Ti angle of 89.9 (1)°, a Cl-Ti-Cl angle of 82.1 (1)°, and a Ti-Zn-Ti angle of 173.4 (1)°. The Ti-Ti distance is 6.828 (4) Å. We have investigated the magnetic properties of this compound and several analogous ones to liquid helium temperature and wish to report the first example of 1,3 magnetic exchange *via* a diamagnetic metal atom in a linear trinuclear complex. Gruber, Harris, and Sinn⁴ have prepared a series of trinuclear compounds having the potential for this interaction, but did not detect a measurable value for the exchange integral between the terminal metals. Studies of the temperature dependence of the susceptibility of $\text{Ni}_3(\text{acac})_6$ have shown that an antiferromagnetic exchange between the terminal nickel atoms *via* the paramagnetic nickel(II) central metal is necessary to fit the experimental data.⁵ In order to study the influence of the nature of the bridging group and cyclopentadienyl rings on the

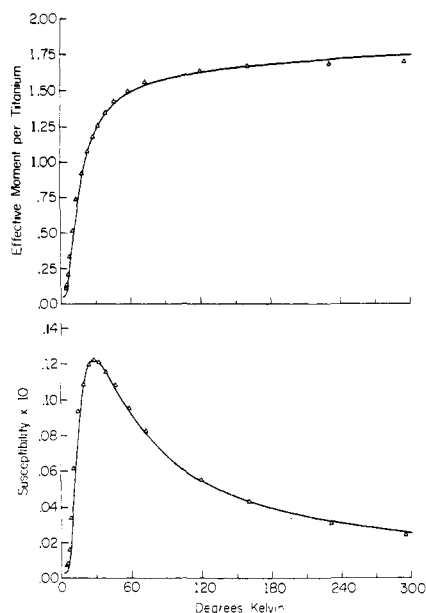


Figure 1. Temperature dependence of the magnetic susceptibility and effective moment per titanium for $[\text{Cp}_2\text{Ti}]_2\text{ZnBr}_4 \cdot 2\text{C}_6\text{H}_6$. A diamagnetic correction of -483×10^{-6} cgs/mol has been applied. Theoretical curves are calculated using the parameters given in Table I.

Table I. Best Fit Parameters for Magnetic Data^a

Compound	J (cm^{-1})	g	θ ($^\circ\text{K}$)
$[\text{Cp}_2\text{Ti}]_2\text{ZnCl}_4 \cdot 2\text{C}_6\text{H}_6$	-8.9	2.01	0.49
$[\text{Cp}_2\text{Ti}]_2\text{ZnBr}_4 \cdot 2\text{C}_6\text{H}_6$	-15.7	1.94	-1.37
$[\text{Cp}_2\text{Ti}]_2\text{BeCl}_4 \cdot 2\text{C}_6\text{H}_6$	-6.9	1.91	1.87
$[(\text{MeCp})_2\text{Ti}]_2\text{ZnCl}_4$	-7.3	1.92	0.69
$[\text{Me}_2\text{Si}(\text{C}_2\text{H}_5)_2\text{Ti}]_2\text{ZnCl}_4$	-6.9	1.90	0.77

^a TIP was taken as 260×10^{-6} per trimer for all compounds.

magnetic exchange, the compounds in Table I have been synthesized and their magnetic susceptibilities determined. Figure 1 shows the experimental data points and theoretical χ_m and μ_{eff} curves for $[\text{Cp}_2\text{Ti}]_2\text{ZnBr}_4 \cdot 2\text{C}_6\text{H}_6$. A well-defined maximum in the susceptibility vs. temperature curve was observed in all cases. Values for J , g , and θ were obtained by a least-squares fit to the Van Vleck equation for the magnetism of two exchange coupled spin $1/2$ centers.

$$\chi_m = \frac{2g^2\beta^2N}{3k(T - \theta)} \left(1 + \frac{1}{3} \exp(-2J/kT) \right)^{-1} + N\alpha$$

This formulation corresponds to a singlet-triplet separation of $-2J$. Since fits of the magnetic data give reasonable g values, we have not attempted to use g values determined by esr in the analysis of the results, although the esr g values are within 0.1 of those derived from magnetic data fits. Examination of the packing in the $[\text{Cp}_2\text{Ti}]_2\text{ZnCl}_4 \cdot 2\text{C}_6\text{H}_6$ crystal does not reveal any interactions between molecules which would implicate intermolecular exchange as the source of the antiferromagnetic behavior. The magnitudes of the exchange integrals are also rather large for intermolecular exchange. Further evidence for the intramolecular nature of the interaction is furnished by the lack of an exchange coupled temperature dependence for the magnetic moment of $[\text{Cp}_2\text{Ti}(\text{DME})]_2[\text{Zn}_2\text{Cl}_6] \cdot \text{C}_6\text{H}_6$ which our crystallographic determination has shown to contain Ti(III) as a monomeric cation.

Coutts, Wailes, and Martin⁶ have investigated the magnetism of the series $[\text{Cp}_2\text{TiX}]_2$, $X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$, and have found the order of interaction is $\text{Br} > \text{Cl} \sim \text{I} > \text{F}$. We note that in the zinc bridged complexes the ratio of ex-

change coupling for the chloride and bromide compounds is nearly the same as in the above dimeric complexes. Availability of d orbitals on the central metal is evidently not a requirement for exchange to occur since the J value for the beryllium compound is only slightly less than that of the zinc-chloride bridged complex. Methyl substitution on the cyclopentadienyl rings also appears to have very little effect on the exchange and is in contrast to the biscyclopentadienyl- and methylcyclopentadienyltitanium monochlorides where we have observed methyl substitution to cause the J value to double. This effect is under further investigation.

Single-crystal epr measurements⁷ on Cp_2VL_2 systems have shown the unpaired electron to reside in a molecular orbital which is primarily d_{z^2} in character and oriented in the VL_2 plane perpendicular to the molecular twofold axis. There is also a small but significant amount of d_{xy} contribution. It is probable that a similar situation exists in the $[\text{Cp}_2\text{Ti}]_2\text{ZnCl}_4$ type complexes. A one-electron scheme for exchange then should consider overlap of the titanium d_{xy} and d_{z^2} orbitals with s and p orbitals of the central metal. This can be envisioned to occur with or without participation of orbitals on the halogen.

Further structural and magnetic studies are now in progress on analogous compounds in this series to elucidate the mechanism of magnetic exchange.

Acknowledgment. This work was supported by National Science Foundation Grant NSF-GH-33634.

References and Notes

- (1) J. J. Salzmann, *Helv. Chim. Acta*, **51**, 526 (1968).
- (2) H. A. Martin and F. Jellinek, *J. Organometal. Chem.*, **8**, 115 (1967).
- (3) C. G. Vonk, *J. Cryst. Mol. Struct.*, **3**, 201 (1973).
- (4) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Chem. Phys.*, **49**, 2183 (1968).
- (5) A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, **7**, 932 (1968).
- (6) R. S. P. Coutts, P. C. Wailes, and R. L. Martin, *J. Organometal. Chem.*, **47**, 375 (1973).
- (7) J. L. Petersen and L. F. Dahl, *J. Amer. Chem. Soc.*, **96**, 2248 (1974).

Rudolph Jungst, Dennis Sekutowski, Galen Stucky*

School of Chemical Sciences and
Materials Research Laboratory
University of Illinois
Urbana, Illinois 61801

Received May 30, 1974

A Hydrocarbon Catalyst for Diazoalkane Decomposition

Sir:

It is well-known that many salts and complexes of Cu^{I} and Cu^{II} cause the decomposition of diazoalkanes.¹ This reaction has found wide synthetic utility in the cyclopropanation of olefins,² but its mechanism is far from being well understood. The catalog of copper-catalyzed carbenoid reactions has been recently extended by the discovery of carbon-hydrogen insertion in organosilanes³ and even in saturated hydrocarbons.⁴ Recently Salomon and Kochi have furthered the understanding of copper-catalyzed cyclopropanation with diazoalkanes by demonstrating that Cu^{I} is the active oxidation state even when Cu^{II} is the nominal catalyst, and that coordination of the olefin by Cu^{I} can be an important step in the cyclopropanation sequence.⁵ The interaction of the metal and the diazo compound has still not been characterized, however, although several hypotheses have been presented.⁶

We have discovered, and here report, a hydrocarbon catalyst for the decomposition of diazoalkanes. This catalyst, tetraphenylethylene, seems to mimic Cu^{I} and Cu^{II} in its