

Figure 1. Temperature dependence of the magnetic susceptibility and effective moment per titanium for [Cp2Ti]2ZnBr4 · 2C6H6. 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

Compound	$J(cm^{-1})$	g	θ (°K)
$[Cp_2Ti]_2ZnCl_4 \cdot 2C_6H_6$	-8.9	2.01	0.49
$[Cp_2Ti]_2ZnBr_4 \cdot 2C_6H_6$	-15.7	1.94	-1.37
$[Cp_2Ti]_2BeCl_4 \cdot 2C_6H_6$	-6.9	1.91	1.87
[(MeCp) ₂ Ti] ₂ ZnCl ₄	-7.3	1.92	0.69
$[Me_2Si(C_5H_4)_2Ti]_2ZnCl_4$	-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 $[Cp_2Ti]_2ZnBr_4 \cdot 2C_6H_6$. 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 $\frac{1}{2}$ centers.

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

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 gvalues are within 0.1 of those derived from magnetic data fits. Examination of the packing in the [Cp₂Ti]₂ZnCl₄. $2C_6H_6$ 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 $[Cp_2Ti(DME)]_2[Zn_2Cl_6] \cdot C_6H_6$ 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 $[Cp_2TiX]_2$, X = F, Cl, Br, and I, and have found the order of interaction is $Br > Cl \sim I > F$. We note that in the zinc bridged complexes the ratio of exchange 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 biscyclopentadienvl- and methylcyclopentadienyltitanium monochlorides where we have observed methyl substitution to cause the Jvalue to double. This effect is under further investigation.

Single-crystal epr measurements⁷ on Cp₂VL₂ 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_{xv} contribution. It is probable that a similar situation exists in the $[Cp_2Ti]_2ZnCl_4$ type complexes. A one-electron scheme for exchange then should consider overlap of the titanium d_{xv} 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.

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A Hydrocarbon Catalyst for Diazoalkane Decomposition

Sir:

It is well-known that many salts and complexes of Cu¹ and Cu¹¹ cause the decomposition of diazoalkanes.¹ This reaction has found wide synthetic utility in the cylopropanation 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 Cu¹ is the active oxidation state even when Cu¹¹ is the nominal catalyst, and that coordination of the olefin by Cu¹ 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 Cu¹ and Cu¹¹ in its



Figure 1. Esr signal from tetraphenylethylene-induced decomposition of degassed solution of diphenyldiazomethane in tetrahydrofuran.

ability to effect cyclopropanations with diazoalkanes and to mimic Cu¹¹ in oxidizing the diazo compound. We hope, by studying the mechanism of this reaction, to shed light on the interaction of diazoalkanes with catalysts capable of causing their decomposition.

While preparing reaction mixtures for the photochemical generation of diphenylmethylene in the presence of tetraphenylethylene, it was observed that when solutions of diphenyldiazomethane containing tetraphenylethylene (0.1 mmol each, in 6 ml of solvent) were degassed by repeated freeze-pump-thaw cycles on a vacuum line, gas evolution occurred. After sealed deoxygenated mixtures were stored for several hours in a dark refrigerator, the dark red color of the diazo compound was replaced by a dark green.⁷ The green solutions are paramagnetic and give rise to the esr spectrum shown in Figure 1. The radical signal persists undiminished for weeks in the absence of air but disappears immediately along with the green color upon exposure of the reaction mixtures to the atmosphere.

The radical whose spectrum is shown was identified as the radical cation of benzophenone azine $Ph_2C=NNC$ - Ph_2 ⁺⁺ by comparison of the esr spectrum with that of the electrochemical oxidation product of the azine.⁸ The decomposition of diphenyldiazomethane by tetraphenylethylene in *degassed* solutions is remarkable since, *under air*, solutions of diphenyldiazomethane containing tetraphenylethylene are stable for many days.⁹ Reaction of diphenyldiazomethane with Cu¹, Cu¹¹, and Zn¹¹ in the absence of air also gives rise to the azine radical cation.¹⁰

Until further facts become available, one can only speculate upon the mechanism of tetraphenylethylene-catalyzed decomposition of diphenyldiazomethane. Preliminary experiments have indicated quite complex reaction kinetics. An induction period has been observed, suggesting the possibility of a chain reaction, which is also indicated by the inhibition due to air. The major product, formed in greater than 75% yield, is benzophenone azine. This product and the buildup of the radical cation of the azine can be rationalized by the following sequence:¹¹

chain
$$Ph_2CN_2 + Ph_2C = CPh_2 \rightarrow$$

initiating $Ph_2CN_2 + Ph_2C = CPh_2$ $Ph_2CN_2 \cdots Ph_2C = CPh_2$
 $Ph_2CN_2 \cdots Ph_2C = CPh_2$ $Ph_2CN_2 \rightarrow$
 $Ph_2CN_2CPh_2^{\cdot *} + Ph_2C = CPh_2^{\cdot *} + N_2$
chain $Ph_2CN_2CPh_2^{\cdot *} + Ph_2CN_2 \rightarrow$
 $Ph_2CN_2CPh_2^{\cdot *} + Ph_2CN_2 \rightarrow$
 $Ph_2CN_2CPh_2^{\cdot *} + Ph_2CN_2 \rightarrow$
 $Ph_2CN_2CPh_2^{\cdot *} + Ph_2CN_2 + Ph_2CN_2^{\cdot *}$

A radical-chain process initiated by the oxidation of Ph_2CN_2 to Ph_2CN_2 ⁺ has been proposed by Jugelt and Pragst for the electrolytic decomposition.¹² However, the main reaction product was reported to be tetraphenylethylene rather than the azine, thus indicating that different reactive intermediates must be involved in electrolytic oxidation and tetraphenylethylene induced decomposition of diphenyldiazomethane. The formation of the azine radical cation by interaction of both traditional metal catalysts for diazoalkane decomposition, and tetraphenylethylene, raises the possibility that one-electron oxidation of diazoalkanes is an important step in their catalytic decomposition. We are exploring this possibility by investigating the kinetics of the formation of the azine radical cation and the relationship of its formation with the kinetics of decomposition of the diazo compound.

It was of obvious interest to compare tetraphenylethylene with copper catalysts in cyclopropanation reactions. For this purpose, it was necessary to perform experiments with other diazoalkanes, since in our hands copper-catalyzed decomposition of diphenyldiazomethane does *not* give rise to cyclopropanes.¹³

When solutions of tetraphenylethylene (3 mmol) and α diazoacetophenone PhCOCHN₂ (10 mmol) in cyclohexene (75 ml) were degassed, nitrogen evolution was observed. Reaction was complete in 10 hr, and the major product was 7-benzoylnorcarane, isolated in yields of 42-44%. This should be compared with the 44-62% yields obtained with various copper catalysts.¹⁴

Diazomethane and diazofluorene also give rise to cyclopropanes upon tetraphenylethylene-catalyzed reaction with cyclohexene. When diazomethane (58.2 mmol) was swept with a stream of nitrogen into a saturated solution of tetraphenylethylene (a stirred suspension of 1.50 mmol) in cyclohexene, norcarane was formed in 15 \pm 5% yield, compared with the 24% yield obtained upon copper catalysis.¹⁵ Since photolysis of diazomethane in cyclohexene yields methylcyclohexenes as major products in addition to norcarane,¹⁶ formation of norcarane without methylcyclohexenes upon tetraphenylethylene catalysis indicated that we are dealing with a carbenoid reaction and rules out stray light as the source of norcarane. The absence of the known compound tetraphenylcyclopropane as a reaction product implies that no intermediates are formed with covalent bonding between diazomethane and tetraphenylethylene. From a degassed reaction mixture consisting of diazofluorene (1.7 mmol) and tetraphenylethylene (1.8 mmol) dissolved in cyclohexene (20 ml), a 43.5% yield of spirobicyclo[4.1.0]hexane-7,9-fluorene was isolated in addition to a 37.2% yield of bifluorenylidene. With a cupric chloride cat-



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alyst (20 mg) the corresponding yields were 32.7 and 30.5%, respectively.

When experiments with α -diazoacetophenone, diazomethane, and diazofluorene were repeated without the presence of tetraphenylethylene, no cyclopropanation products were detected.

In the tetraphenylethylene-catalyzed cyclopropanations with diazoacetophenone, diazomethane, and diazofluorene, no paramagnetic species were detected by esr spectroscopy during the reaction or after decomposition of the diazo compound was complete. Thus the relationship between these reactions and the tetraphenylethylene-catalyzed decomposition of diphenyldiazomethanene remains to be established by detailed kinetic studies and trapping experiments.

The catalyst employed in our experiments is commercial tetraphenylethylene (Aldrich) purified by recrystallization followed by column chromatography. Since the synthesis of tetraphenylethylene normally employs copper metal,¹⁷ we explored the possibility that a copper impurity was responsible for the observed decomposition of diazo compounds. Decomposition of diazo compounds by copper complexes present in only 10^{-2} M ratio has been reported.¹⁸ Analysis of our purified tetraphenylethylene by atomic absorption spectroscopy indicated a copper content of 0.01 weight %. When a quantity of cupric chloride (the most likely form for a copper impurity in tetraphenylethylene) equivalent to ten times the impurity found in tetraphenylethylene was employed as a catalyst for diphenyldiazomethane decomposition, the first half-life of the reaction is greater than four times that observed with tetraphenylethylene. Also the rate of the copper-catalyzed reaction was the same in the presence and absence of air. Copper was definitely precluded as the active catalyst when a sample of tetraphenylethylene prepared by Meyers via a copper-free synthesis¹⁹ showed catalytic properties identical with those of commercial material.

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- (8) Electrolytic oxidation of an acetonitrile solution 0.002 M in benzophenone azine with 0.1 *M* tetrabutylammonium perchlorate as supporting electrolyte was carried out at 2.0 V in a vacuum electrolysis cell designed by S. I. Weissman and C. Cheng employing a platinum anode and mercury cathode
- (9) At room temperature the first half-life for decomposition of Ph₂CN₂ in a tetrahydrofuran solution under air 0.015 M in both Ph₂CN₂ and Ph₂C=CPh₂ is 23 hr. In a refrigerator, decomposition was not complete after 2 weeks, compared to the 2 hr required for a similar degassed solution.
- (10) These experiments were carried out by adding the metal salt to degassed solutions of diphenyldiazomethane in tetrahydrofuran. The resulting green solutions were immediately decanted directly into esr sample tubes without exposure to air and the spectra recorded. In the metal-containing systems the esr signal of the azine radical cation per-sists only briefly, disappearing within minutes (Zn) to hours (Cu^{ll}).
- (11) No charge-transfer complex between diphenyldiazomethane and tetraphenylethylene has been detected by optical absorption spectroscopy, the experiments having been carried out without degassing on solutions 10^{-3} *M* in both compounds. Direct electron transfer from Ph₂CN₂ to Ph₂C=CPh₂ is too endothermic (*ca.* 3 eV) to be considered likely. The esr spectrum of the radical anion of tetraphenylethylene has not been

observed in our experiments. The predominant counterion is probably the dianion of tetraphenylethylene, formed by disproportionation of the radical anlon.

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Cautions Concerning Uses of Copper(II) Selective **Broadening in Nuclear Magnetic Resonance** Spectroscopy for Determination of Ligand Binding Sites

Sir:

Sites of Cu(II) binding to molecules such as nucleic acid bases, histidine and derivatives, and peptides have often been characterized by selective broadening in proton magnetic resonance spectra of ligand hydrogens located nearest to Cu(II). Typically the ligand is present in a 100-fold or greater excess over Cu(II). To apply the method successfully to small molecules, two criteria must be met: there must be rapid chemical exchange of Cu(II) among all sites and there must be no scalar coupling to contribute to line broadening so that only the dipolar contribution with its inverse sixth power dependence of distance between paramagnetic ion and affected nuclei prevails.

In the case of rapid chemical exchange and in the absence of significant outer sphere effects, the inverse spinlattice and transverse relaxation times due to the presence of paramagnetic ion become¹

and

$$T_{2p}^{-1} = pq T_{2m}^{-1}$$

 $T_{1n}^{-1} = pq T_{1m}^{-1}$

where p is the ratio of molar concentrations of metal ion to ligand and q is the average number of ligands bound in an identical way. Thus $T_{1p}/T_{2p} = T_{1m}/T_{2m}$. The relaxation times of nuclei bound to paramagnetic ions may be described by the Solomon-Bloembergen equations² which for Cu(II) and protons on small ligands at 100 MHz become

$$T_{1m}^{-1} = 6a \tau_r \gamma^{-6}$$
 (1)

$$T_{2m}^{-1} = 7a\tau_{r}r^{-6} + bA^{2}\tau_{s}$$
(2)

where a and b are a collection of constants for the dipolar and scalar parts, respectively, τ_r is the rotational correlation