



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.

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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

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

When experiments with α -diazacetophenone, 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 diphenyldiazomethane 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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- The reaction described occurs in all solvents thus far employed: tetrahydrofuran, benzene, methylene chloride, and dimethoxyethane.
- 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.
- At room temperature the first half-life for decomposition of Ph_2CN_2 in a tetrahydrofuran solution *under air* 0.015 *M* in both Ph_2CN_2 and $\text{Ph}_2\text{C}=\text{CPh}_2$ is 23 hr. In a refrigerator, decomposition was not complete after 2 weeks, compared to the 2 hr required for a similar degassed solution.
- 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 persists only briefly, disappearing within minutes (Zn) to hours (Cu^I).
- 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 Ph_2CN_2 to $\text{Ph}_2\text{C}=\text{CPh}_2$ 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 anion.
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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 spin-lattice and transverse relaxation times due to the presence of paramagnetic ion become¹

$$T_{1p}^{-1} = pqT_{1m}^{-1}$$

and

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

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

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

$$T_{2m}^{-1} = 7a\tau_r r^{-6} + bA^2\tau_s \quad (2)$$

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