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METAL SALT CATALYZED CARBENOIDS—XII[1]

GENERAL CONSIDERATIONS

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Abstract—A systematology for carbene transfer (MT) processes based on apparent molecularities of the product determining step is proposed. An analysis is made of potential conformation effects for copper(I) and copper(II) based carbenoids and a systematology for purposes of nomenclature is proposed for conformations of penta-coordinated systems based upon trigonal bipyramides and tetragonal pyramides. The possible role of valence state is examined and the hazards of applying spin state correlations to carbenoids in parallel with the methods used for carbenes is discussed. Basic guidelines for generating data suitable for internal and external comparisons are given.

INTRODUCTION

It is generally believed that the reactions of diazoalkanes with copper salts are relatively simple and easily explained.[3] The fallacy of this position is clearly demonstrable employing the limited data which has been presented by these laboratories[4] and those of Bethell *et al.*[5] Even a pedantic analysis of the possible reaction paths open to diazoalkane-copper salt systems, reveals that the systems have a potential for extreme complexity. It is equally clear that distinctions between the various potential processes are often small but real and will be exceedingly difficult to make. It is evident that chemists have avoided careful analyses in preference to employing extrapolations from other questionably related systems.[6] Indeed, the whole copper carbenoid concept is built upon a house-of-cards in which the foundation is the assumption that various thermolyses and photolyses of diazoalkanes lead to the generation of free carbenes. The emotional rather than empirical nature of this commitment has been noted by Kirmse,[7] amongst others. In this area, the inherent conservatism of the scientific method has been set aside in favor of the convenient but already unjustified assumption that since some photolyses of diazoalkanes furnish carbenes, therefore all photolyses of diazoalkanes must furnish carbenes. The use of the sign of quantity *all* leads to a double proposition and as are many universally affirmative propositions,[8] it is of questionable validity. We have already demonstrated that unsensitized photolyses of dimethyl diazomalonate in cyclohexene solutions, do not react solely by a "free carbene" path but rather react predominantly via some other species.[9] This exception does not destroy the validity of the assumptions made relative to other alleged carbenes but surely puts them in doubt. It would appear only reasonable to demand that the existence of a free carbene in a given process be much more rigorously established than is currently the custom. We strongly question the assumption that one can extrapolate results obtained in glasses at extremely low temperatures to processes which occur at 3-400° higher temperature.[10] The principle of Le Chatelier suggest such extrapolations to be dangerous.[11] Similarly, we find it particularly questionable to assume that processes in the vapor phase represent processes in solution. This is especially so as regards changes involving large alteration of the dielectric constant of the media. Although one may have a particular reactive species common to the whole range of temperatures and medium effects, it seems equally probable that medium and temperature play important roles in "carbene-carbenoid" chemistry. We are not the first investigators to urge caution in this area,[7] but far more emphasis is being placed on a related problem of establishing the spectroscopic spin state for carbenes at the expense of answering the more difficult problem of when a free carbene is present.

The present paper is directed towards helping establish the potential range of phenomena which may be observed in carbene transfer processes and ultimately developing analyses to better determine how carbene transfers occur. The immediate goal is to develop a somewhat flexible systematology for analyzing and reporting carbene transfer phenomena. Such an approach has long found application by organic chemists to describe reactions in which only a single C–X bond is formed or broken.[12] The present approach attempts to analyze the related question where two bonds, C–X and C–Y are made or broken in such a fashion that a group CWZ is transferred from one molecular environment to another. In a number of cases the processes are similar, if not identical, to those encountered with the single bond systems. These may, nevertheless, be beneficially grouped as various members of a general species of carbene transfer reaction.

A second aspect of the present paper, is a treatment of potential steric effects. There existed a period in the development of organic chemistry when it was overly attractive to account for apparent anomalous reactions as being a consequence of steric hindrance. However, it should be quite evident that appreciable steric effects should be operating when one transfers a bulky group CWZ from one environment to another while in the presence of transition metal ions and their associated ligands. The problem is particularly complex as a consequence of the very transitory nature of copper carbenoids. It is further complicated by the tendency of many complexes to exist as telomers or as clusters. When this is combined with the fact that in some cases the formal catalyst is not the real catalyst and the real catalyst is transient or unknown. The problem appears to be insoluble. However, if one is going to establish the manner in which a group CWZ is transferred, steric effects must be treated in detail. Some authors have attempted to treat the mechanisms of "carbenoid" reactions by analyzing steric effects far from the reaction center.[13-15] It is surely questionable to discard the need for considering the nature of steric and conformational features at the reaction center while arguing that the influence of atoms 4 or 5 atoms removed from the carbene carbon is of importance. In all of the mechanisms so far proposed and those which we shall propose, the metal is intimately involved. In order to analyze steric effects, one must obviously have knowledge of the valence state of the metal if there is a change in coordination or complex type associated with the valence states involved. Conversely one might gain knowledge of the valence state as a consequence of such changes by careful analyses of the effects of carefully planned changes in the steric requirements of the ligands or carbene.

Valence state of the catalytic species. The valence state of the copper has received considerable discussion.[16] Although it might be intellectually satisfying to have only one species active in all cases, it would be unusual to find ligands, substituents, solvents, substrates, concentrations, and temperatures of little importance.

The problem is not simple. Almost all of the reactions observed with diazoalkanes and copper catalysts are complex and furnish several products. In one case we have observed 57 products and have identified over 30.[17] It is difficult to ascribe all of the products to a single species attacking the substrate and propelling it towards the multitudinous products. Before one assigns a valence state to the catalyst it is necessary to ascertain which intermediates are involved. Since almost all workers have operated at a single catalyst concentration for a given system it is all but impossible to sort out the various processes. There is absolutely no way to determine whether the catalyst state recovered reflects the consequences of the carbenoid path or of side reactions. In a few cases where such isolations have been attempted, there is a reasonable probability that the copper would have been oxidized or reduced to the final state.

In one noteworthy case where the authors are strongly committed to Cu(I) catalysis,[18] the solution was clarified by addition of Cu(0) and then a Cu(I) complex was isolated and given in evidence. Although Cu(I) in aqueous media is known to disproportionate to Cu(0) and Cu(II),[19] there is reason to suspect that complexation in non-aqueous media might facilitate reduction of uncomplexed Cu(II) by uncomplexed Cu(0) to give a Cu(I) complex.[20]

The employment of CIDNP or ESR to demonstrate the transient existence or absence of copper(II) is likely to fail because of the inherent limitations of the techniques. We feel the simplest and perhaps most direct approach to establish valence is to examine the steric factors associated with the bimolecular carbene transfer preceses. With copper(I) there should be minimal effects because the carbene will be far from the ligands and bonded to copper in a linear or trigonal system. With copper(II), the carbene will be present as a fifth ligand in a trigonal bipyramide (TBP) or a tetragonal pyramide (TP). Alternatively it may be part of an octahedral complex where the substrate is the sixth ligand or as the fourth ligand in a square planar or tetrahedral array where it has replaced another ligand. In all of these cases, there should be a strong potential for steric effects. In a following section we shall analyze the possibilities for the TBP and TP cases. The results with dimethyl diazomalonate and acetylacetonate type complexes clearly exhibit pronounced steric effects. We therefore conclude that the carbenoid system most probably is copper(II) based (*vide infra*).

Some chemists have assigned valence states on the basis of transient colors, the absence or presence of a particular product when a certain color is present or absent, etc.[13,14] Such arguments are particularly dangerous because color may arise in a number of ways unrelated to the carbenoid. In addition, the presence or absence of a product can be the consequence of the concentration of the catalyst species[21] (*vide infra*).

Our earlier arguments regarding copper(I) trialkyl phosphite complexes are not without their weaknesses. Although inferences can be drawn from the data, the fact that the formal catalyst is destroyed clearly leaves one with an unknown catalyst in terms of valence state and associated ligands. For example, one might be more confident that the original anion is still present if it were not for the fact that the very trend in partial rate data which suggests their continued presence, is a function of the olefinic substrate employed as well. Thus, cyclohexene gives results diametrically opposed to both *cis* and *trans* 2-heptenes.[22]

The possibility exists that both valence states are catalytically active and the actual state is simply a function of whether the media is suitable for oxidation, reduction or no change. Alternatively, there may exist a need for both valences of copper where a rapid electron transfer occurs between Cu(II) and Cu(I) or perhaps even between Cu(0) or Cu(III) and another valence state.

In the last section we discuss the question of gathering data in a reliable fashion and possible approaches to the problem. We propose guidelines which quickly reveal some of the basic boundary conditions for mechanistic hypotheses. The use of these guidelines emphasizes the factors which must be considered.

DISCUSSION

A general treatment of the question of how a molecule transfers a CWZ group to a substrate. Unlike nucleophilic substitution and elimination reactions[12] there exists no systematic analysis of the simultaneous or near simultaneous formulation of two C–C bonds other than the Woodward-Hoffmann type treatments of cycloaddition reactions.[23] Such processs are well known and involve the formation of C=C bonds where no previous C–C linkage existed; the formation of rings such as cyclopropanes from olefins; and the generation of products by insertion of a unit QXY into a bond W–Z to form a product WQXYZ where Q is still bonded to X and Y and the WZ bond has been ruptured. (An obvious example of the last process is the insertion of methylene into a C–H bond to generate a C–CH_3 unit.) It is not our intent to presumptiously assemble all such reactions under a unified scheme of our design. Rather, we wish to employ a basic set of terms for our present and future needs in the area of carbenoid chemistry which are not unnecessarily restrictive. Simultaneously we wish to avoid employing the terminology which has developed in the area of heterogenous catalysis to describe mechanisms; e.g. Langmuir-Hinshallwood vs Rideal processes.[24] As we will endeavor to show, this latter nonmenclature and the accompanying mythology are not applicable to homogeneous processes.

For the purpose of classification of carbene transfer process (**MT**) we have two basic choices, (a) classification by the rate determining step (rds) and (b) classification by the product determining step (pds) (the initial M for methylene is used in preference to C for CT is the standard abbreviation of Charge Transfer). Since the reactions involved are often exceedingly complex and it is difficult to identify the rds and because one of the "readily" identifiable features of a reaction is the products, we will base our analyses on the pds. For multistep processes, each reaction is an agglomeration of pds's generating transient and non-transient species of which only one is the rds relative to a product of interest. Since our overall concern is how starting materials become products we wish to identify all steps. Since we are concerned with the group CWZ which is capable of forming a maximum of two bonds, these fall into two basic categories for carbene transfer process, (a) those in which only a single bond is made or broken, and (b) those in which two bonds are made or broken. The first category is relatively well understood and will not require any exposition here. The second group is our primary concern.

Thus **MT** processes are either synchronous ($\mathbf{MT}_{\text{sync}}$) or non-synchronous ($\mathbf{MT}_{\text{nsync}}$). For simplicities sake, of these two we will assume most processes are of the $\mathbf{MT}_{\text{nsync}}$ type and write these as **MT**, and only employ $\mathbf{MT}_{\text{sync}}$ for the less common process.

In terms of molecularities, the group CWZ always arises from species (**Q**) to which it is bonded and is going to become bonded to a substrate (**S**). For convenience we can designate the carbene as (**M**) and any metal as (μ). If the intermediate **Q** contains **M** and μ we can write the species **M**μ. However, if **M** is not formally doubly bonded to μ, but rather is attached to some other group (residium) as well, eg. N_2—as in a diazoalkane metal complex, we must designate the species as **RM**μ. Similarly we would write a diazoalkane as **RM**.

There are two basic ways **M**μ or **RM**μ can transfer **M** or **RM** to **S** to furnish a product **RMS** or **MS**, (a) dissociation to furnish **M** or **RM** which then reacts with **S** to give the product, a **MT-1** process or (b) bimolecular process **MT-2**. The **MT-1** or **MT-2** process may however involve a substrate activated by the catalyst μ. These processes we shall designate **MTE** for carbene transfer with substrate enhancement.

It is clear that these designations could be applied to other types of reactions besides carbene reactions including such diverse processes as the Wittig Reactions,[25] Diazo Transfer Processes[26] and olefin formation by aldol type condensations.[27] It is not our goal to do so, although we believe the system we propose will be sufficiently general to permit its use for other reactions.

***MT*-1 *and MTE*-1** *processes.* A well defined example of the **MT-1** process exists in the work of Seyferth[28] with compounds of the type $\phi HgCX_3$ where warming liberates CX_2 and ϕHgX. A **MTE-1** process might possibly arise from the introduction of a catalyst to an olefin–$\phi HgCX_3$ mixture where the catalyst increases the π electron density of the double bond in some fashion.

***MT*-2** *processes.* The possibilities for **MT-2** processes are numerous, however they are not unmanageable. Thus, for $\mathbf{MT\text{-}2}_{\text{sync}}$ one has the possibility of forming an intermediate possessing all of the atoms of the substrate or intermediates in which a portion of the carbenoid or proto carbenoid is lost (Scheme 1).

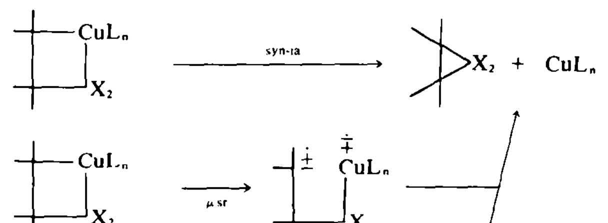
The intermediate losses the CuLn system by an internal alkylation (**ia**) and this process can be synchronous or non-synchronous where rupture occurs between metal and substrate (μ sr) or metal (μ) and carbene (μ mr); e.g. (Scheme 2).

The possibilities for $\mathbf{MT\text{-}2}_{\text{nsyn}}$ fall into two basic categories $\mathbf{MT\text{-}2}_{\text{nsync}}\mathbf{M}\mu\mathbf{S}$ and $\mathbf{MT\text{-}2}_{\text{nsyn}}\mathbf{S}\mu\mathbf{M}$ (Scheme 3).

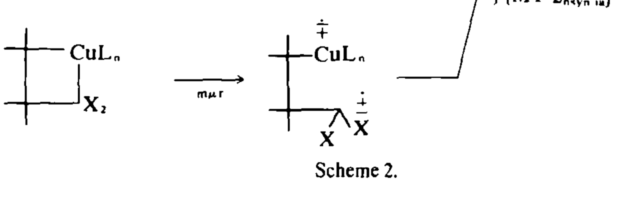
In the last case there has been a ligand transfer (**LT**) from metal to carbene carbon. If we apply this to the various C–H insertion processes known for *bis* carboalkoxy carbenes,[4,29-31] we can write the following mechanistic schemes (Scheme 4).

The third and fourth examples in Scheme 4 are simply "ene" reactions followed in one case by a LT process leading to a common intermediate which then participates in a LT process leading to a common intermediate which then participates in a MT-2_{ia} process to furnish products.

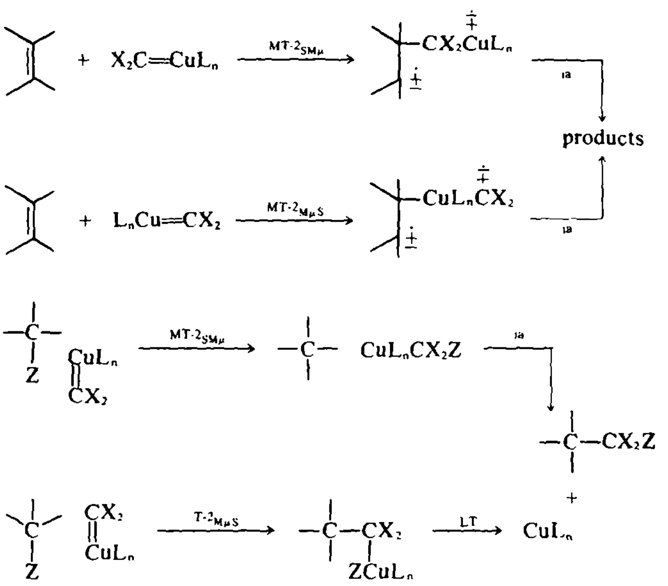
The replacement of Z by H in Scheme 3 will offer two routes to CH insertions. In addition one can envisage C-Z insertions by yet another pathway in which non-bonded electron pairs on the atom Z are attacked by the carben-



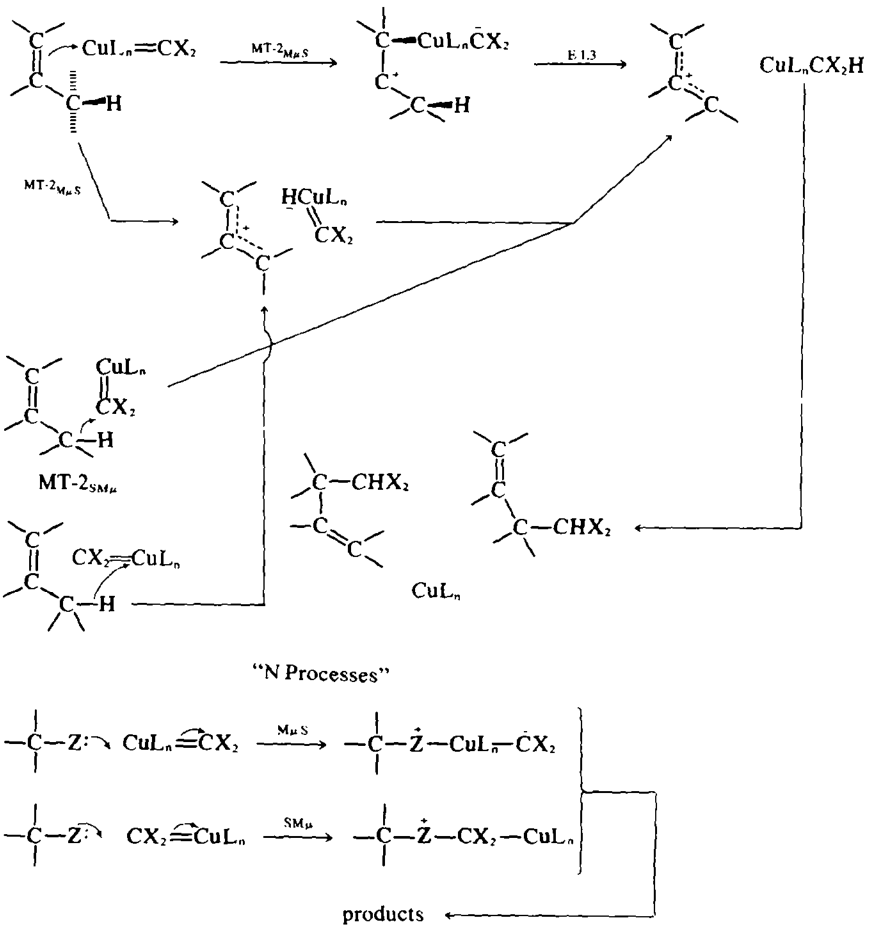
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

oid carbon or copper. These last two possibilities are especially attractive for accounting for the work of Ando[4,35] with allylic ethers and sulfides. For purposes of designation we shall call these the **N** processes to distinguish them from the **B** processes involving direct attack on the bonding electrons.

MTE-2 reactions. The real possibility exists that some substrates will be activated by complexation to the catalyst. These need not lead to enhancement towards all MT product formations but may instead lead to a favoring of one process over another. Partial rate data from the reactions of dimethyl diazomalonate with olefins as a function of catalyst concentration clearly require such a phenomenon occurring.[22,29–34] The net effect is increasing the dependence of the process upon catalyst from one to two. Since termolecular processes are of very low probability, it seems preferable to class such reactions as proceeding by enhancement of substrate where the enhancement is the result of the formation of a substrate-catalyst complex which then reacts with carbenoid. Since the substrate-complex is simply a new substrate (S'), the analyses remain the same as those employed for the **MT-2** processes. A similar situation arises in the case of the **MTE-1** reactions.

Conformational effects

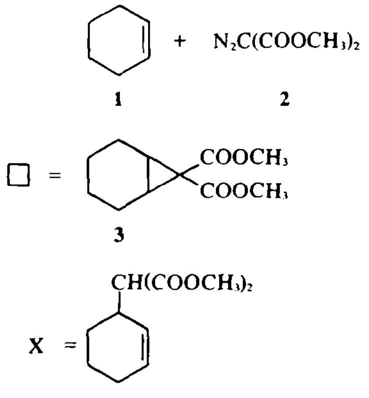
If we are going to analyse the mechanisms of carbene transfers of the **MT-2** type, we must concern ourselves with the question of what does the carbene complex look like. Clearly, simple analyses solely of the carbene portion of the intermediate are of very questionable validity. The metal atom and its associated ligands are probably closer to the reaction sites. In addition, the ligands possess considerable steric bulk. When one writes a catalyst in simple form such as CuBr or $(CH_3O)_3P$–CuI, it is misleading for that is not the form present in solution. If the contents of the solution have any ability to serve as ligands, the process is further complicated.

One might argue that if there is no proof of the valence state of the catalyst, it is impossible to examine steric effects with any rigor. However, evidence of steric effects probably offers the best means of determining the effective valence state. Frequently the coordination number of a metal is a function of valence state as is the preferred stereochemistry.[19,36] For the problem in hand, copper, this is especially true. Copper(I) forms complexes which one might crudely classify as linear, trigonal and tetrahedral (coordinating to 1, 2, 3 and 4 ligands) whereas copper(II) forms complexes which are square planar, tetrahedral, tetragonal pyramidal, presumably trigonal bipramidal and octahedral (coordinating to 4, 5 and 6 ligands).[19,36]

With copper(I) complexes of carbenes, one might expect to form essentially linear and trigonal copper carbenoids. Such complexes should be extremely insensitive to ligand steric effects because the ligands will be directed into a volume of space not required by any reacting substrate. Conversely, with copper(II) complexeses it is impossible to accommodate bulky ligands without causing appreciable interactions with a carbene ligand even if the resulting carbenoid should be tetrahedral. The data in Table 1 clearly reveals that there is an appreciable steric effect occuring as a consequence of the change from acetylacetone to *bis* pivaloyl methane as the ligand acid.

This led us to analyze the steric effects in greater detail employing the assumption that the copper of the carbenoid must be *penta* or *hexa* coordinated.

If one assumes the presence of a double bond between a metal d-orbital and a p-orbital on carbon or only a single bond with a p-orbital on the carbene, the resulting carbenoid should exhibit free rotation within the limitations imposed by potential energy barriers created by substituents. Such behavior has in fact been observed for a Rh-carbene complex.[37] The real, as vs an idealized, bonding picture is obviously complex. However, using the very simple Huckel picture, it is possible to ascertain that both combination of a carbenoid through an ether linkage –O–Cu–CX_2 or a carbonyl group C=O–Cu–CX_2 should furnish reasonable bonding employing only bonding and non-bonding orbitals to be capable of sustaining copper in the +1, +2 or +3 states (Schemes 5 and 6). The first system corresponds to a backbonding arrangement where the *n*-orbitals of O are employed because the required orbital is orthogonal to the p-orbital on carbon. The second assumes the p-orbital on C is available. Extension of the conjugation further will lead to additional orbitals but will always generate only occupied bonding or non-bonding orbitals, not anti-bonding orbitals. The situation is, of course, far more complex because of the d-orbital and we suspect that in reality the highest occupied orbital might on occasion be degenerate. Thus the compounds below will be assigned the following symbols.



$\Delta = (CH_3OOC)_2C = C(COOCH_3)_2$

5

$(CH_3OOC)_2CH$—$CH(COOCH_3)_2$

6

X = Total Insertion
Z = Total Product

Fig. 1.

Table 1. Copper(II) catalyst vs products in the reaction of diazomalonate in cyclohexene

CATALYST LIGAND	Product yield[a] (and relative to norcarane) (3)	(4)	(5)	(6)
Dipivaloylmethane	0.051 (1.00)	0.004 (0.09)	0.386 (7.52)	0.228 (4.43)
Acetylacetone	4.54 (1.00)	0.145 (0.03)	0.461 (0.10)	0.053 (0.01)
Acetylacetone-f_3	0.484 (1.00)	0.039 (0.08)	0.016 (0.03)	0.023 (0.05)
Acetylacetone-f_6	1.054 (1.00)	0.054 (0.05)	0.986 (0.94)	0.041 (0.04)

[a] relative to internal standard; 4.54 - 80 percent.

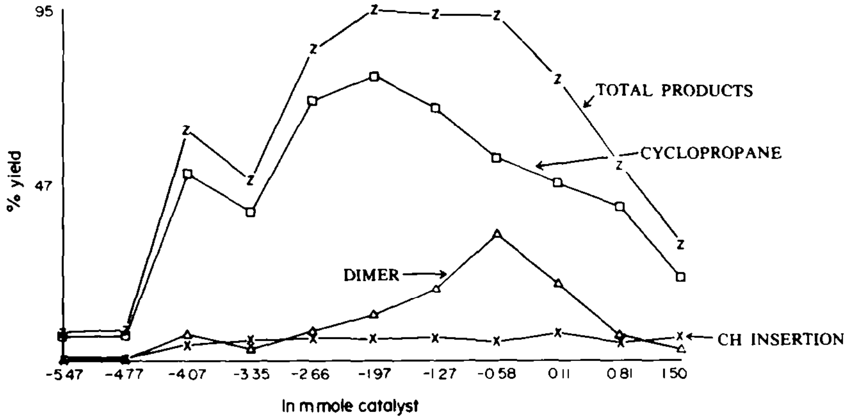
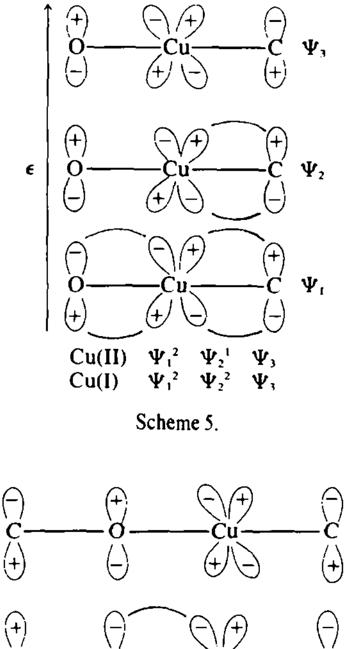
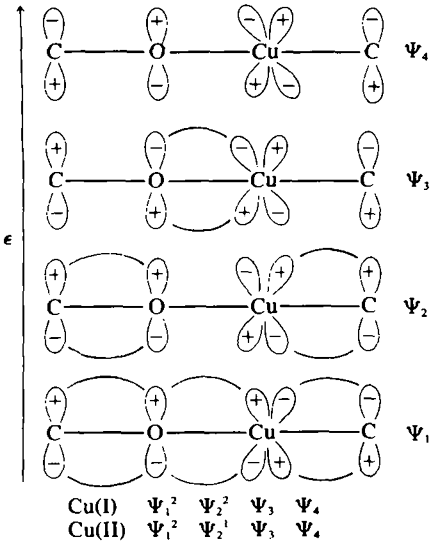


Fig. 2. Product distribution and yields as a function of Cu(AcAc)$_2$ concentration in the reaction of dimethyl diazomalonate with cyclohexene.



Scheme 5.

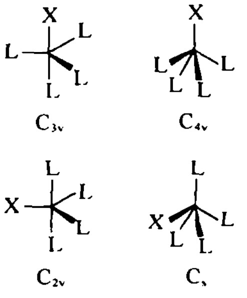


Scheme 6.

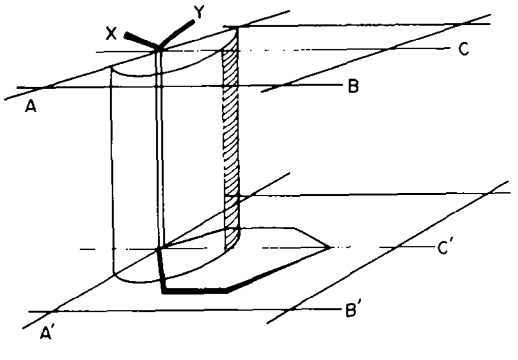
spectroscopically one might envisage singlets, doublets, triplets, transient quadruplets, etc.[38,39] Since at present one is not able to evaluate the spin states of transient complex metalo-organic species, we prefer to avoid answering the question of spin multiplicity, we prefer to emphasize the origin of the species by calling it singloid or triploid. The singloid and triploid assignments should be reserved for those carbenoid reactions which exhibit near perfect product mimicry of the related carbene species. The doubloid terminology is reserved to describe the presence of only a single unpaired electron [Cu(II) carbene complex]. This is also consistent with the fact that in the only well studied case, copper-diazomalonate systems, a dichotomy seems to exist where the cyclopropanations mimic singlet processes and the allylic C–H insertions mimic triplet processes.[31-34] Thus the term doubloid is meant to suggest equally weighted singloid and triploid processes.

One might wonder why *bis* (methoxycarbonyl) carbeno-copper complexes exhibit any triploid character whereas the carbeno and methoxycarbonyl carbeno analogs do not.[40,41] We suspect that the presence of the additional conjugative ability of the carbene substituents facilitates the formation of "stable" Cu(II) complexes which are indeed doublets whereas in the absence of such substituents Cu(I) is more stable and this leads to singlet carbenoids. The difference may arise from Jahn-Teller instabilities often encountered with d^9 systems.[42] We shall undoubtedly have to await the development of a MINDO/3 type calculation capable of handling copper before the answer will be known.

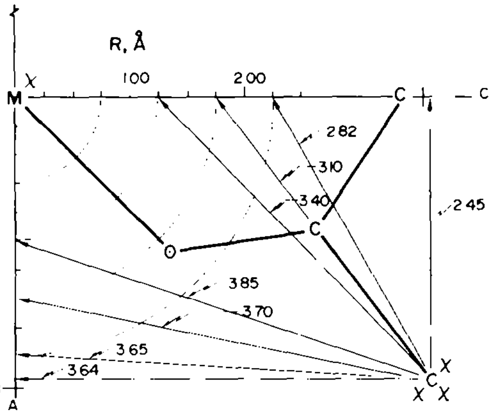
From existing crystallographic data it is clear that the 6-membered rings in acetylacetonato complexes are not regular, or even approximately regular hexagons.[43] Thus, it immediately becomes obvious that a fifth ligand which is trigonal (such as a carbene) will not be subjected to the same field effects when it is lined up in such a fashion as to generate a plane bisecting the 6-membered rings and when it is oriented perpendicular to that plane to form a new plane equidistant from the two chelate ring residues (Schemes 7–9).



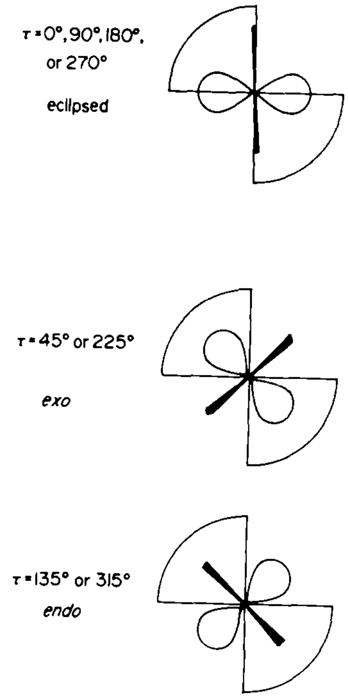
Scheme 7. Idealized geometries for ML$_4$X complexes.



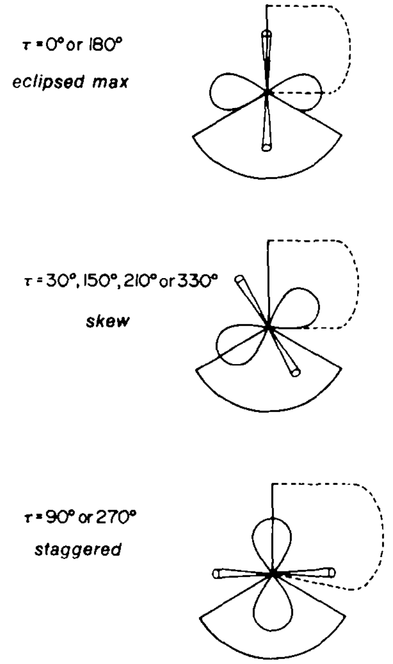
Scheme 8.



Scheme 9.

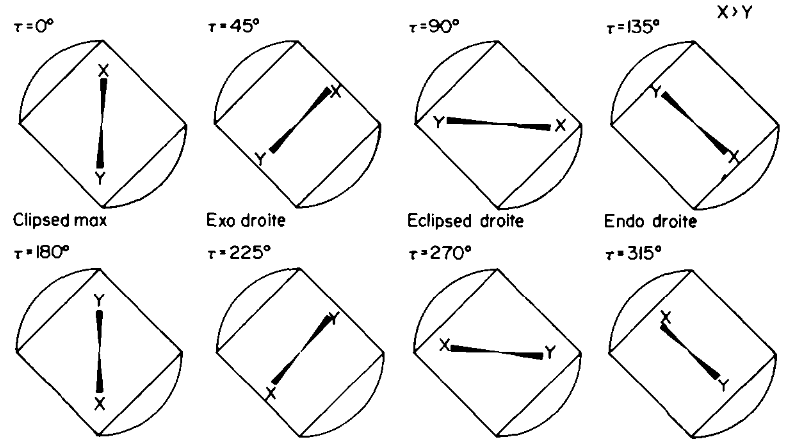


Scheme 10. The oientation of the p-orbital of C in TP carbenoids as F(τ).

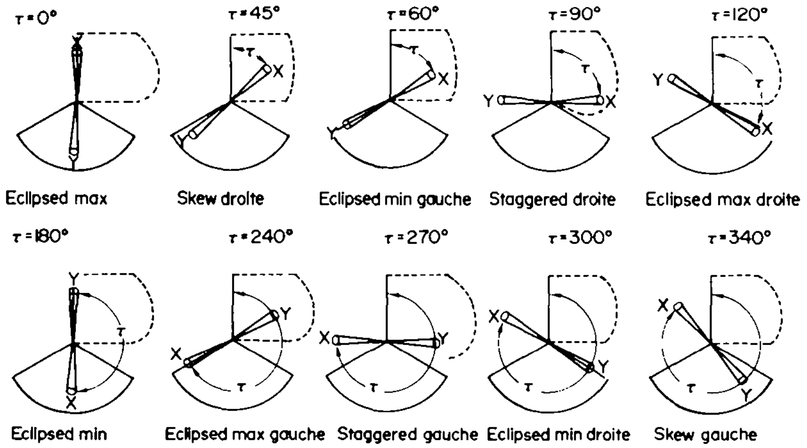


Scheme 11. The orientation of the p-orbital on C in TBP carbenoids as F(τ).

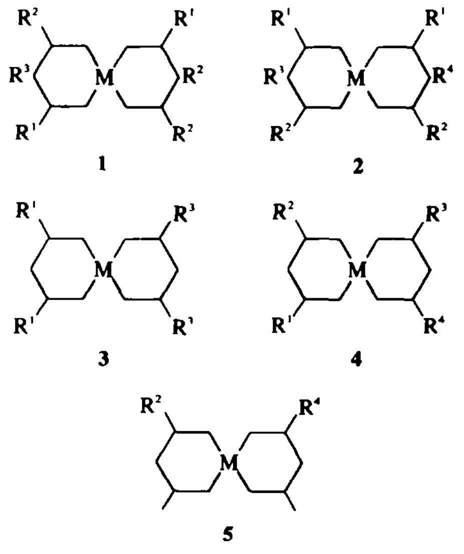
The exact magnitude of these differences is obviously unknown because there are no stable copper carbenoids known and one does not even know what is the proper bond length for a copper-carbene double bond. However, an alternate analysis is available through determining the distances to cylinderical sections projected from the plane of the chelate system to the parallel plane containing the carbenoid substituents (Schemes 8 and 9). It is clear from these diagrams that real effects should be operative for tetragonal pyramidal and octahedral carbenoids. Extrapolation to trigonal bipyramids indicates that similar effects should be operative. Extrapolation to trigonal bipyramids indicates that similar effects should be operative. Because reactions occur at orbitals and not nuclei, it is desirable to ascertain where the p, d and/or π orbitals necessary for carbene transfers will be preferentially. If they are forced into unfavorable conformations for MT processes, then the reactions should be unfavorable relative to a standard process where such effects are minimal. Schemes 10 and 11 summarize the situation for both TP and TBP cases and it is clear that the effect of substituents should be real and observable. We have extended these considerations somewhat beyond our current needs to arive at a general nomenclature for the various conformations when the carbenoid is unsymmetrical and for complexes in which the various ligand branches are not the same (Schemes 12–14). This becomes a necessity for analyzing future results when we will employ such ligands. Basically the systematogy is simple and rests upon known and IUPAC approved principles of assigning preference by the Cahn-Ingold-Prelog sequencing rules[44] for ligand substituents and carbene. We have arbitrarily placed the chelate rings of the bidentate ligand system into the second and fourth quadrants with the largest substituent located at 0°. A problem obviously arises when the resulting complexes are potentially chiral. In that case we propose that the antipode placing the largest group at 0° and its residual group of the chelate ring at 270° be employed. With tridentate and tetradentate ligands the problem becomes more complex but the initial chelate ring should lie in the fourth quadrant and subsequent rings in the third and



Scheme 12. Informations of tetragonal pyramides having two bidentate ligands and a doubly bound trigonal ligand.



Scheme 13. Conformations of a trigonal bipyramides having two bidentate ligands and a doubly bound trigonal ligand x > y.



Scheme 14.

second quadrants. Our present concern lies with *bi* and tetradentate ligands based upon acetylacetone structures.

Such an approach is suitable for all of the basic C_4 type penta coordinated and hexa coordinated system we shall be concerned with (Scheme 14). Extrapolation to TBP complexes is straightforward and involves the same orders of precendence. In the case of the TBP and TP complexes of the lower symmetries for ML_4X complexes (C_{2v}) and (Cs) can be treated similarly but for our purposes they represent aberrant forms of the C_{3v} TBP in which there have been distortions of bond angles.[45]

EXPERIMENT DESIGN

Certain features of catalyzed decompositions should be immediately evident from the catalyst concentration vs product yield data we have previously published.[21,31,33] The mechanistic consequences are extensive and are discussed in a following paper as are the synthetic consequences.[32-34] However, the general effect is to call into doubt any comparisons made between various heterogeneous or homogeneous catalyst systems. It is evident from the graph (Fig. 2) that the yield observed is a function of catalyst concentration. Since all evidence indicates that the catalytic reactions between diazo compounds and copper salts occurs in solution, and not on the surface of the solid material,[16,46] anything which alters the amount of copper in solution will affect the yield. Comparison between two catalysts of differing solubility will involve two entirely different sets of reaction conditions which possess very little common ground for comparison. With the exception of our experiments with cyclohexadienes, a very nearly common copper concentration was always associated with maximum yields of cyclopropane and allylic C–H insertion[16a] products.[34,47] Thus it would seen only reasonable that comparisons between catalysts be made at the same copper concentrations. In addition, where a maximization of a particular product is involved, the concentration should corespond with the maxima. Thus comparisons for cyclopropanations should occur at maxima and dimerization and similar processes which do not go through a maximum should be examined at a common catalyst concentration.

Since yield is also a function of the rate at which the addition of reagents is performed,[48] it is imperative that this variable be carefully controlled and reproduced for comparisons. Again this variable has an optimum value and the optimum value should be employed.

Similarly, one must exhibit great care in performing all comparison experiments at very near the same temperature for the processes are temperature sensitive.[29,32]

A direct consequence of the above provisos is that it is currently extremely hazardous to extrapolate the observations of one laboratory to those of another even when apparent correlations exist.

A further precautionary measure involves the state of the glassware employed. When a flask is employed which has seen previous service with copper salts, small but catalytically effective amounts of copper are complexed to the glass. Thus one can observe catalytic processes with "no" catalyst present.[33] A similar effect can be observed when copper(O) is heated with the olefin prior to reaction of diazo compound and then removed.[16a] Thus extreme care must be taken at low catalyst concentrations to subtract out the contribution from trace copper contaminations and from competing pure thermal reactions.

It is because of all of these limitations that we will make only the broadest comparisons between our work and that performed elsewhere.

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