A more detailed report will be forthcoming at a later date.

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Autocatalytic Decomposition of Alkylcopper(I) Species. Electron Spin Resonance Spectrum of Binuclear Copper(0) Intermediates

Sir:

We have examined alkyl derivatives of transition metal complexes formed by metathesis between various Grignard reagents and transition metal halides and other salts in tetrahydrofuran (THF) solutions.[1] In this report we wish to present evidence for the *autocatalytic* decomposition of organocopper(I) species in homogeneous solutions. We also wish to show catalysis by other "zero"valent metal complexes and the presence of novel mixed valence copper(0) species during the decomposition.

The studies were carried out by mixing a solution of the Grignard reagent (*e.g.*, ethylmagnesium bromide) and copper(I) chloride in stoichiometric amounts in THF at −78°.[2] The resulting homogeneous and colorless solution was stable for prolonged periods at this temperature. From the negative Gilman color test I,[3] we deduce that the ethylcopper(I)[4] species was formed according to eq 1.[5]

$$\mathrm{CH_3CH_2MgBr + Cu^ICl \xrightarrow[\text{THF}]{-78^\circ} CH_3CH_2Cu^I + MgBrCl} \quad (1)^6$$

When the Grignard reagent and copper(II) chloride were mixed (in a 2:1 molar ratio) under the same conditions, a transitory orange color was observed and 0.5 mol of *n*-butane was generated spontaneously. The properties of the resulting colorless solution were indistinguishable from that formed directly from copper(I) chloride. We infer that alkylcopper(II) species under these conditions were only formed as highly metastable species,[7] and afforded alkylcopper(I).

The decomposition of *n*-propylcopper(I) in THF solution produced propylene and propane in approximately equal amounts consistent with the results obtained from *n*-butyl(tri-*n*-butylphosphine)copper(I) in diethyl ether.[5a]

$$\mathrm{CH_3CH_2CH_2Cu \xrightarrow[\text{THF}]{} [\underset{51\%}{CH_3CH{=}CH_2} + \underset{49\%}{CH_3CH_2CH_3}] + Cu} \quad (2)$$

Careful examination of the rate of decomposition of ethylcopper(I) at 0° (Figure 1) revealed an induction period followed by a rapid decomposition (dark circles). The induction period was removed when a solution of partially decomposed ethylcopper(I) was deliberately added[8] to a solution of ethylcopper(I) (open circles). Other alkylcopper(I) compounds have varying degrees of stability but otherwise showed the same kinetic behavior.[9]

We attribute the autocatalytic decomposition of alkylcopper(I) species to the presence of copper(0) intermediates during decomposition. This induced decomposition can be shown in an alternative experiment illustrated in Figure 2, in which catalytic amounts of soluble silver(0), palladium(0), and copper(0) species[11] stimulated the decomposition of *n*-propylcopper(I) in a rather dramatic way.[10] This behavior is not restricted to organocopper species since the more stable alkylmanganese compounds also show a marked catalytic decomposition.[1]

The visible absorption spectrum and the electron paramagnetic resonance (epr) spectrum of organocopper species in THF solution showed interesting changes during these transformations. If a solution of ethylcopper(I) in THF was held at −10° for approximately 30 min, it gradually turned purple[12,13] and remained homogeneous, but no decomposition was apparent. The change is probably due to association of the organocopper(I) species into clusters.[14,15] No epr (microwave) absorption occurred during this period of color change. Raising the temperature to 0° shortened the period of quiescence and accelerated the rate of decomposition of ethylcopper(I) [Figure 1]. The epr

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(1) M. Tamura and J. Kochi, to be published.

(2) The reaction can also be carried out practically by using an excess of Grignard reagent. House, *et al.*, have shown that dialkylcuprate(I) is not formed from a Grignard reagent and copper(I) iodide in diethyl ether [H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966)].

(3) H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, **47**, 2002 (1925).

(4) The oxidation state of copper is given only as a formalism.

(5) For some studies of organocopper(I) species see: (a) G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, **92**, 1426 (1970); **91**, 6542 (1969); (b) G. Costa, A. Camus, L. Gatti, and N. Marsich, *J. Organometal. Chem.*, **5**, 568 (1966); **8**, 339 (1967); G. Costa, G. de Alti, L. Stefani, and G. Boscarato, *Ann. Chim. (Rome)*, **52**, 289 (1962); (c) K. H. Thiele and J. Köhler, *J. Organometal. Chem.*, **12**, 225 (1968); (d) R. J. DePasquale and C. Tamborski, *J. Org. Chem.*, **34**, 1736 (1969); (e) A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 2186 (1968); (f) A. Camus and N. Marsich, *J. Organometal. Chem.*, **14**, 441 (1968); **21**, 249 (1970); (g) H. Gilman and J. M, Straley, *Recl. Trav. Chim. Pays-Bas*, **55**, 821 (1936); (h) C. E. H. Bawn and F. J. Whitby, *J. Chem. Soc.*, 3926 (1960); C. E. H. Bawn and R. Johnson, *ibid.*, 4162 (1960).

(6) Coordination by THF around copper is assumed, but not specifically included.

(7) Dialkylcopper(II) may be an intermediate which decomposes to alkylcopper(I) with the liberation of dialkyl. Alternatively, the reaction may proceed *via* prior reduction of copper(II) followed by subsequent reaction of the Grignard reagent with copper(I).

(8) These reactions were carried out in an all-glass apparatus consisting of two compartments.

(9) (a) For example, 15 and 100 hr are required for the decomposition of methyl- and neopentylcopper(I), respectively, at room temperature. The induction periods for the decomposition of *n*-propyl-, ethyl-, and isopropylcopper(I) at 0° are 200, 30, and <5 min, respectively. (b) The induction period varied somewhat with different batches of copper salts due to small but variable amounts of iron impurities which are also exceedingly efficient catalysts.[1,10] The rate of the decomposition was, however, independent of the presence of excess Grignard reagent (up to fivefold excess) or magnesium bromide (twofold).

(10) The decomposition of *n*-butyl(tri-*n*-butylphosphine)copper(I)[5a] in diethyl ether also shows a slight induction period which is removed by catalytic amounts of iron(0) species.[1]

(11) The preparation of soluble silver(0), palladium(0), and copper(0) species will be described separately.[1]

(12) (a) Colored (red) solutions of alkylcopper species in di-*n*-butyl ether were originally investigated by Noller, *et al.*; (b) V. D. Parker, L. H. Piette, R. M. Salinger, and C. R. Noller, *J. Amer. Chem. Soc.*, **86**, 1110 (1964).

(13) Solutions of *n*-propylcopper(I) showed a broad absorption band centered at 575 nm. The apparent absorptivity ($\log \epsilon \cong 2$) based on the copper charged was difficult to reproduce and changed with time.

(14) Further studies of these species are in progress.

(15) (a) Arylcopper(I) clusters have been recently described; (b) A. Cairncross and W. A. Sheppard, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1967, Abstract ORGN-118; (c) *cf.* also L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Amer. Chem. Soc.*, **90**, 7357 (1968).

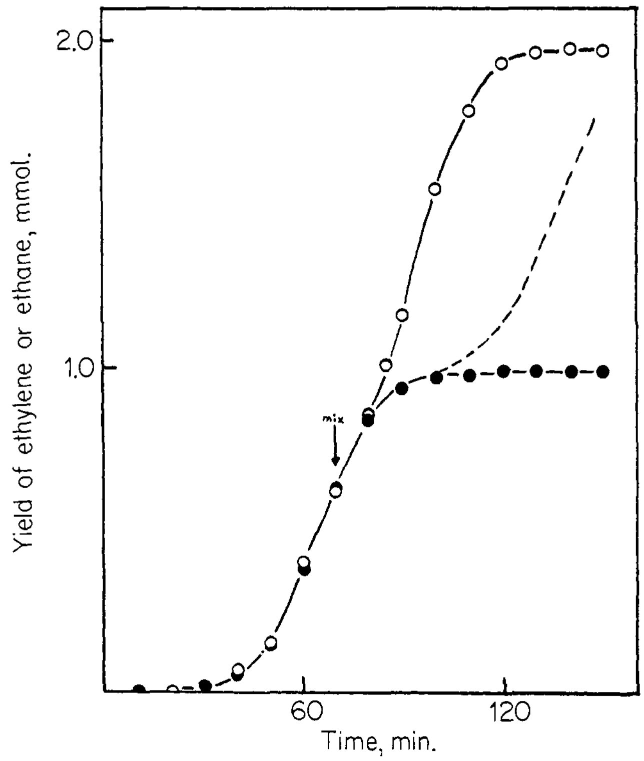

Figure 1. The decomposition of ethylcopper(I) in THF at 0° (dark circles); catalyzed decomposition (open circles); arrow at the point at which the half-decomposed mixture was added to ethylcopper(I). The dotted line represents the course of the decomposition expected in the absence of added copper(0).

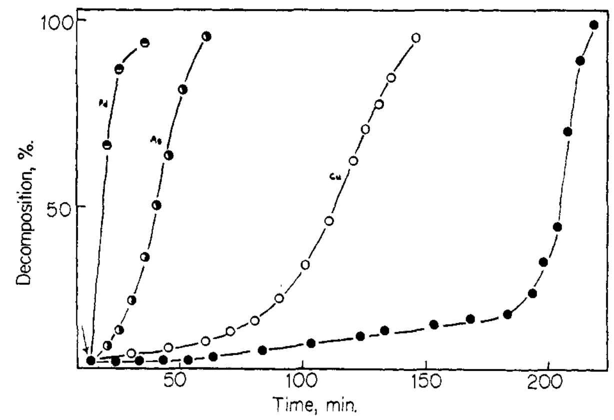

Figure 2. The decomposition of *n*-propylcopper(I) in THF at 2.0° (●). The decomposition of *n*-propylcopper(I) after addition of 10 mol % soluble Pd^0 (●), Ag^0 (◑), Cu^0 (○), at point of arrow.

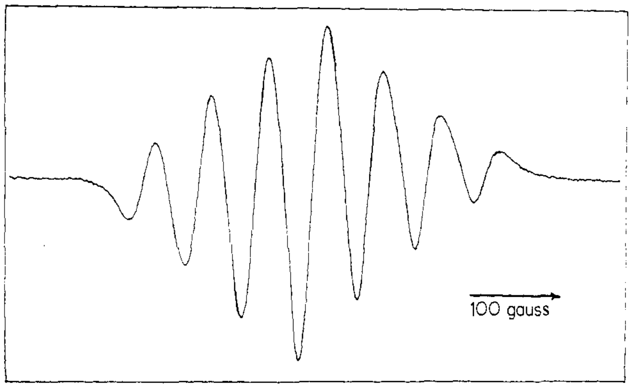

Figure 3. The epr spectrum of the binuclear copper(0) complex formed during decomposition of ethylcopper(I) in THF at 0°.

spectrum shown in Figure 3 was obtained only *during decomposition* of ethylcopper(I). The amplitude of the spectrum reached a maximum at approximately half-decomposition and disappeared when the reaction was complete. The lifetime of the paramagnetic species could be sustained for longer periods if the solution was quickly chilled.

The high signal-to-noise ratio of the spectrum shown indicates that the paramagnetic species was not a minor component in the reaction. The same spectrum was obtained starting from copper(I) chloride, lithium chlorocuprate(II), lithium chlorocuprate(I), or copper(II) bromide or chloride. Furthermore, ethylcopper(I) prepared from the following combinations of reactants, diethylmagnesium–copper(II) perchlorate, ethyllithium–copper(II) trifluoromethanesulfonate, and diethylmagnesium–copper(II) trifluoromethanesulfonate, also afforded the same epr spectrum. We conclude, thus, that neither halide nor magnesium is required for the formation of the paramagnetic species.[16]

The presence of hyperfine splitting consisting of seven equally spaced components (with approximately the correct intensity distribution of 1:2:3:4:3:2:1) indicates that the paramagnetic species has two copper nuclei undergoing spin exchange in (nearly) the same ligand field.[17–19] The *g* value of 2.0024 is close to the spin-only value and is consistent with an electron associated primarily with an s orbital (of a copper(0) species) and showing a minimum of spin–orbit coupling characteristic of copper(II) complexes.[21] Both of these parameters vary in a small but discrete manner with the alkyl moiety (Table I) and indicate that alkyl groups are within the coordination sphere of the two copper nuclei. The observed line width of 26 G, how-

Table I. Magnetic Parameters of Binuclear Copper(0) Species

Grignard reagent	Temp, °C	$\langle g \rangle_{iso}$	$\langle a_{Cu} \rangle_{iso}$, G	$\langle \Delta H_{msl} \rangle$, G
CH_3CH_2MgBr	0	2.0024	61	26
$CH_3CH_2CH_2MgBr$	0	2.0049	64	29
$CH_3CH_2CH_2CH_2MgBr$	−2	2.0055	64	30

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[16] Experiments with copper(II) fluoride and hydridomagnesium bromide were unsuccessful.

[17] Copper consists of two isotopes, ^{63}Cu and ^{65}Cu, both with nuclear spins of $^3/_2$ and similar magnetic moments.

[18] For a discussion of metal–metal interactions and mixed valence complexes see: (a) G. F. Kokoszka and G. Gordon, *Transition Metal Chem.*, 5, 181 (1969); (b) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967).

[19] (a) The value of the isotropic coupling constant of 61 G, however, appears to be too small for a mixed valence complex consisting solely of Cu^{I}–Cu^{0}. In the neutral gaseous copper atom, optical measurements indicate the magnitude of the contact term to be 0.197 cm^{-1} or 2110 G.[20] Half of this value is still at least an order of magnitude removed from the observed splitting and suggests that the electron is not completely localized on the copper nuclei. (b) At this juncture we cannot eliminate the alternative possibility that the paramagnetic species is an alkyl radical complex with a binuclear Cu^{I}Cu^{I} species [*cf.* J. Kochi and F. Rust, *J. Amer. Chem. Soc.*, **83**, 2017 (1961)].

[20] J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961.

[21] For the epr study of a binuclear Cu^{II}–Cu^{I} complex see: C. Sigwart, P. Hemmerich, and J. T. Spence, *Inorg. Chem.*, **7**, 2545 (1968).

ever, places an upper limit to the magnitude of the hyperfine splitting due to such ligands.[22]

The presence of binuclear copper species during the catalytic decomposition of alkylcopper(I) suggests that they play important roles in the mechanism. One such possibility which lies within the framework of the results obtained by Whitesides, *et al.*,[5a] is included in the following scheme (eq 3–5).[23]

$$RCu^{I} + Cu^{0} \longrightarrow [RCu^{I}Cu^{0}] \qquad (3)^{6}$$

$$[RCu^{I}Cu^{0}] \xrightarrow{\text{fast}} R(-H) + Cu^{0} + Cu^{I}H \qquad (4)$$

$$RCu^{I} + Cu^{I}H \longrightarrow RH + 2Cu^{0}, \text{etc.} \qquad (5)$$

Finally, we wish to emphasize that the thermal stability of organometals of the transition series depends on the solvent. For example, we find organocopper(I) species are appreciably more stable in THF than in diethyl ether solutions (even with the aid of phosphine ligands).[24] The added stability of organometals in this and related solvents enables kinetic studies to be carried out with greater facility. Furthermore, we were unable to observe the presence of binuclear copper intermediates during the decomposition of organocopper(I) derivatives (with and without tributylphosphine ligands) in diethyl ether.

Acknowledgment. We wish to thank Professor John S. Griffith for many helpful discussions and the National Science Foundation for their financial support.

[22] Each hyperfine component of the spectrum has a different line width which increases with an increase in m_I, more or less monotonically. It suggests the presence of a small anisotropy of the g and a tensor and a positive $\Delta g/\Delta a$ value. As the temperature is lowered the line widths become broader, but even at −102° (a temperature well below the freezing point of THF) the spectrum retains some of the character of the seven-line splitting. The latter is inconsistent with a copper(II) species.

[23] In this formulation, cluster formation is not explicitly taken into account although it may be important. Our results indicate that only two copper nuclei are coupled to the electron. If other copper nuclei are involved their interaction is much less important.

[24] A property no doubt related to the ability of THF to form more stable complexes with metal ions than diethyl ether. See, *e.g.*, F. W. Walker and E. C. Ashby, *J. Amer. Chem. Soc.*, **91**, 3845 (1969); *Quart. Rev., Chem. Soc.*, **21**, 259 (1967).

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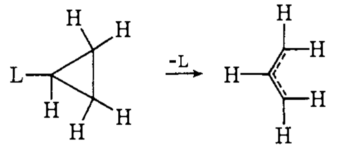
Ring Opening of Cyclopropanes over Palladium Metal

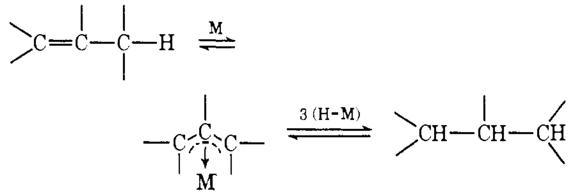
Sir:

The symmetry rules developed for the opening of cyclopropane rings correctly predict the mode of reactions yielding allyl intermediates through either disrotatory or conrotatory processes by removal of a suitable leaving group *across* the ring from the carbon–carbon bond which is broken.[1]

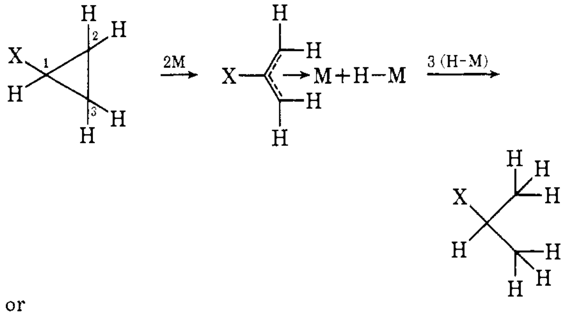


(1)

It has been proposed that heterogeneous catalytic hydrogenation and exchange with deuterium of alkenes over transition metals follow a pathway involving π-allyl adsorbed intermediates.[2] If this view of metal catalyzed processes is correct, the catalytic ring opening of substituted cyclopropanes might well be expected to occur by a process involving carbon–hydrogen bond cleavage across the ring from carbon–carbon bond breaking in an electrocyclic process[3]

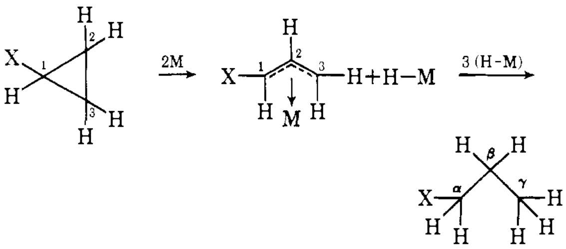


(2)



(3a)

or



(3b)

For most substituents (other than alkyl) it has been found that ring opening occurs predominantly at C_1–C_3 (reaction 3b) to yield *n*-propyl adducts,[4] indicating that if π-allyl intermediates are involved, carbon–hydrogen bond breaking must occur at C_2.

The author wishes to report evidence which indicates that π-allyl intermediates are not so involved in the heterogeneous catalytic ring opening of cyclopropanes. Compounds of the kind shown in sequence 3 above, where X = phenyl, benzyl, and acetyl, were hydrogenolyzed over palladium-on-wide-pore silica with deuterium[5] in the gas phase[6] to produce *n*-propyl products.[7] The distribution of deuterium found in the products is shown in Table I.[8]

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[1] E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 233; R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[2] (a) F. G. Gault, J. J. Rooney, and C. Kemball, *J. Catal.*, **1**, 255 (1962); (b) J. J. Rooney, *ibid.*, **2**, 53 (1963); J. J. Rooney and G. Webb, *ibid.*, **3**, 488 (1964).

[3] F. D. Mango, *Advan. Catal.*, **20**, 291 (1969), has suggested a similar process for alkenes; R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, 71 (1969); F. D. Mango and J. H. Schachtschneidner, *J. Amer. Chem. Soc.*, **89**, 2484 (1967).

[4] J. Newham, *Chem. Rev.*, **62**, 123 (1962); J. Newham and R. L. Burwell, Jr., *J. Phys. Chem.*, **66**, 1438 (1962).

[5] J. A. Roth, B. Geller, and R. L. Burwell, Jr., *J. Res. Inst. Catal. Hokkaido Univ.*, **16**, 221 (1968); 0.14% by weight palladium.

[6] A vapor mixture of deuterium and alkane was passed over the palladium catalyst at a rate of 12–15 cm³/min (see also ref 5).

[7] Compounds with X = $-CN$, $-CO_2CH_3$, and $-CH_2$-cyclopropyl did not ring open appreciably below 160° with the same active catalyst. Other products were formed in 1% quantities.

[8] The values reported are the result of integration of the nuclear