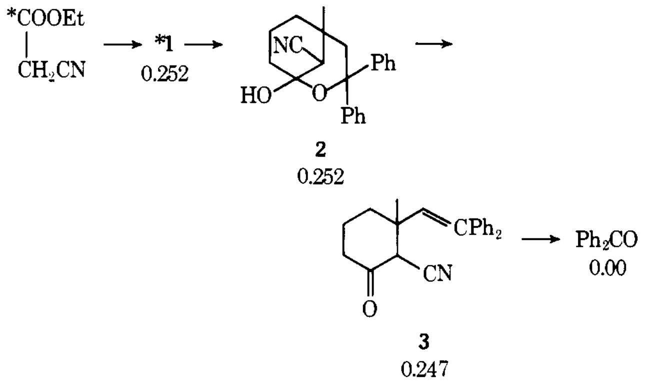
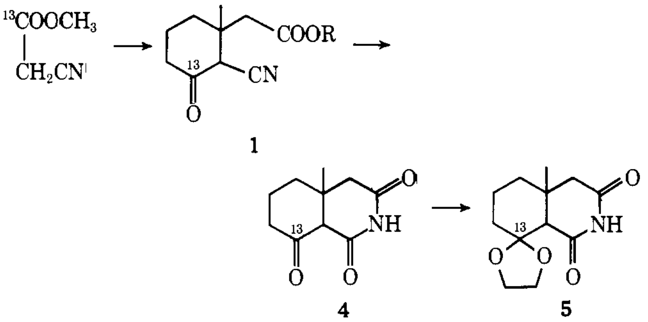
Scheme II



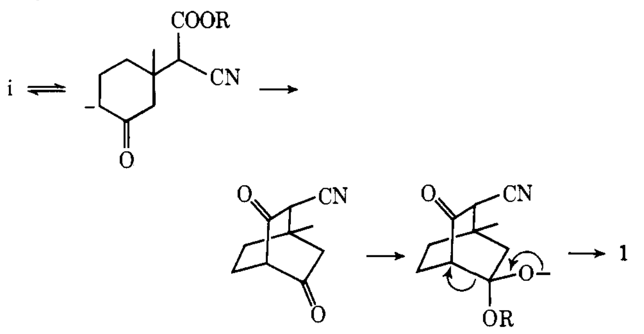
(figures represent specific molar activity in mCi/mol)

spectra of these enriched samples with the natural abundance spectra of **1**, **4**, and **5**, to which unambiguous assignments could be made,[8] showed that only one carbon in each compound was enriched: the ketone carbonyl of **1** (δ 201.075) and **4** (δ 173.33) and the corresponding ketal carbon of **5** (δ 109.10). Confirming the ^{14}C results, no enrichment was detected in the ester carbonyl (δ171.09) of **1**.



These findings invalidate the Johnson mechanism[5] as well as a reasonable alternative in which the cyano group is transferred directly from i to **1** through an iminocyclobutane intermediate and also several other mechanisms proposed for abnormal Michael additions.[9,10] They are consistent only with the bicyclo[2.2.2]octane intermediate shown in Scheme III, the so-called "para-bridged" mechanism suggested originally by Farmer and Ross[11] and considered[5] for the ethyl cyanoacetate adduct but judged unlikely (there being no opportunity for stabilization of the intermediate bridged β-diketone as the enolate anion).

Scheme III



Our tracer studies provide the first unambiguous evidence that the bicyclo[2.2.2]octane route is not only a viable mechanism but apparently the sole pathway for formation of abnormal Michael products from 3-methyl-2-cyclohexenone.[12] The present case provides another illustration of the importance of subjecting even those mechanisms which appear obvious to experimental test.

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(8) We are particularly indebted to Professor R. H. Cox for his aid in obtaining and interpreting the cmr spectra. The Fourier transform nmr spectrometer on which the spectra were obtained was purchased with the aid of a grant from the National Science Foundation, to whom we express our warm appreciation.
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An Electron Spin Resonance Study of the Oxidative Homolytic Cleavage of Metal-Metal and Metal-Carbon Bonds

Sir:

The metal-metal bonds of a variety of transition metal binuclear carbonyl complexes can be readily cleaved by the action of one-electron oxidizing agents ($NOPF_6$, ferric complexes, etc.) with the production of diamagnetic cationic species containing a solvent molecule in the coordination sphere of the metal.[1] One-electron oxidants can also cleave the metal-metal bonds of organoditin compounds[2] as well as the metal-carbon bonds of many metal alkyls.[3] The latter reactions are traditionally referred to as electrophilic substitutions although a single-electron mechanism has been established in a few instances.[3] A single electron transfer from a neutral diamagnetic organometallic compound must necessarily lead in the primary mechanistic step to a cationic paramagnetic intermediate[4] which can undergo fragmentation into a diamagnetic cation and a reactive metal- or carbon-centered radical. We wish to present esr evidence for the formation of such radicals from a variety of organometallic compounds containing metal-metal or metal-carbon σ bonds using tetracyanoethylene (TCNE) as the one-electron oxidizing agent and for their further reactions.

A 10^{-3} *M* tetrahydrofuran solution of manganese decacarbonyl and TCNE displays, in the absence of oxygen, a complex esr spectrum which is the superposition of the spectra of the TCNE radical anion,[5] indicative of a one-electron transfer from $Mn_2(CO)_{10}$, and of another species. A large excess of $Mn_2(CO)_{10}$ eradicates the $TCNE\cdot^-$ lines yielding the unencumbered spectrum of the second species (Figure 1) which can be analyzed in terms of a hyperfine structure due to four distinct nitrogens, of which two are almost equivalent, and to only one manganese atom (Table I). The small manganese splitting ($a^{Mn} = 2.163$ G), the *g* value (Table I), the narrow line widths (0.25 G), and the absence

Table I. Esr Spectral Parameters of Transition Metal Substituted Allylic Radicals Derived from Tetracyanoethylene and Binuclear Carbonyls[a]

$XN{=}C{=}C(CN)C(CN)_2$ X	Temp, °C	$\langle g \rangle$	Isotropic hyperfine coupling constants, G $a(N_{1,1})$[b]	 $a(N_2)$	 $a(N_3)$	 $a(M)$[c]
$(\pi\text{-}C_5H_5)Cr(CO)_3$	−25	2.00163	1.690	1.205	2.660	2.52
$(\pi\text{-}C_5H_5)Mo(CO)_3$	g	2.00190	1.729	1.122	2.575	0.78
$Mn(CO)_5$[d]	g	2.00198	1.734[e]	1.201	2.530	2.163
$Mn(CO)_5$	g		1.702	1.176	2.555	2.158
$(\pi\text{-}C_5H_5)Fe(CO)_2$	g	2.00077	1.719	1.269	2.696	f
$(n\text{-}Bu)_3Sn$	g	2.00256	1.771	1.151	2.023	0.68

[a] In tetrahydrofuran solutions. [b] Average of $a(N_1$ syn) and $a(N_1$ anti). [c] Metal isotropic hyperfine splitting. [d] In benzene–acetonitrile solution. [e] $\Delta a(N_{1,1}) = 0.08$; determined by computer simulation of the spectrum as a function of Δ. [f] Not determined. [g] Room temperature.

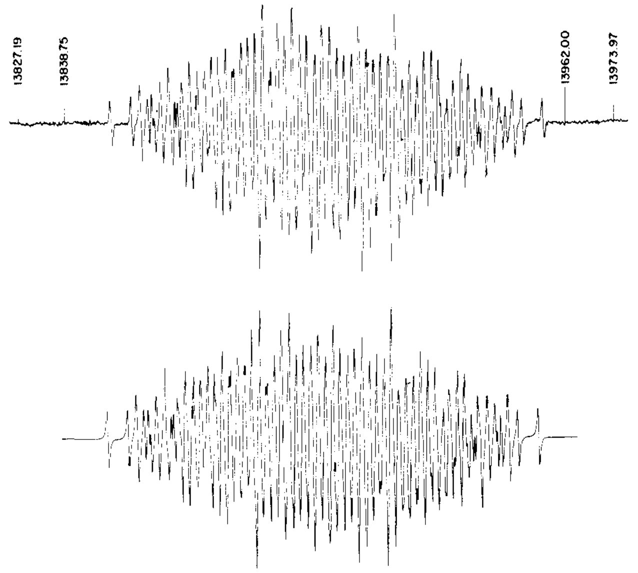
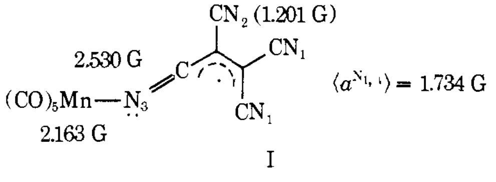


Figure 1. Experimental and calculated esr spectra of the $(CO)_5MnN{=}C{=}C(CN)\dot{C}(CN)_2$ radical in benzene-acetonitrile solution. The proton nmr field markers are in kilohertz.

of appreciable magnetic anisotropies indicate a radical species in which the unpaired electron is largely confined to an organic moiety. The radical is identified as the iminotricyanoallyl radical I formed by the addition of a $\dot{M}n(CO)_5$ radical to a nitrogen terminus of a neutral TCNE molecule.[6]



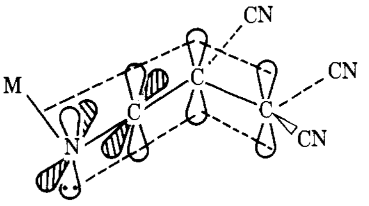
I

$$Mn_2(CO)_{10} + TCNE \xrightarrow[\text{slow}]{} [Mn_2(CO)_{10}]^{\cdot +} + TCNE^{\cdot -} \quad (1)$$

$$[Mn_2(CO)_{10}]^{\dot{+}} \xrightarrow[\text{fast}]{\text{solv}} \dot{M}n(CO)_5 + [Mn(CO)_5(\text{solv})]^{+} \quad (2)$$

$$Mn(CO)_5 + TCNE \xrightarrow[\text{fast}]{} (CO)_5MnN{=}\dot{C}C(CN){=}C(CN)_2 \longleftrightarrow (CO)_5MnN{=}C{=}C(CN)\dot{C}(CN)_2 \quad (3)$$

The foregoing assignment is supported by recent esr results for a related organic 1,1-dicyanoallyl radical as well as by INDO MO calculations[7] for related organic species. Thus, the average coupling of the terminal nitrilic nitrogen atoms in I ($\langle a^{N_{1,1}} \rangle = 1.734$ G) compares well with the corresponding coupling for the 1,1-dicyano-2-*tert*-butylallyl radical[8] ($\langle a^{N_{1,1}} \rangle = 1.76$ G). INDO calculations for the 1,1,2-tricyanoallyl radical $\dot{C}H_2C(CN){=}C(CN)_2$[9] give $\langle a^{N_{1,1}} \rangle = 2.62$ and $a^{N_2} = -1.04$ G supporting the assignment of the 1.201 G splitting to the nitrogen of the cyano group attached to the central allylic carbon. Similar calculations for the hypothetical iminoallyl radical $HN{=}\dot{C}\text{-}CH{=}CH_2$,[10] which also contains an NC double bond orthogonal to the allylic π system as in the isoelectronic methyleneallyl radical $CH_2{=}\dot{C}CH{=}CH_2$,[11] yield $a^N = 10.8$ G for a bent HNC structure with $\angle HNC = 120°$ normal to the allylic plane, and $a^N = 3.7$ G for a linear HNC fragment, suggesting that the largest N splitting of I should be associated with the imino nitrogen. Furthermore, the bent HNC structure is calculated to be more stable by 26 kcal/mol than the linear structure. On this basis, we propose that a similar out-of-plane bent structure II applies to radical I and its analogs (*vide infra*). The unusual stability of this novel class of organometallic radicals may be attributed to (i) the delocalization afforded by the three cyano groups, (ii) the π conjugation of the lone pair orbital on the imino nitrogen, and (iii) the hyperconjugation of the nitrogen-metal σ bond with the π allylic MO system.[12] The proposed bent M-N-C structure with the metal atom eclipsing the π MO system is analogous to the preferred conformations established for a series of allylic radicals with $-CH_2SR$[13] and $-CH_2MR_3$ (M = Si, Ge, and Sn)[14] groups attached to a terminal allylic carbon.



II

The identification of radical I as an adduct of $\dot{M}n(CO)_5$ to neutral TCNE is further substantiated by its detection (together with $TCNE^{\cdot -}$) in the reactions of TCNE with $NaMn(CO)_5$ as well as with $(CO)_5MnCH_2C_6H_5$. In the former reaction the $\dot{M}n(CO)_5$ radical is formed by a simple electron transfer from the manganate anion. Radical I, however, is observed only if the manganate anion is slowly added to TCNE and not if the addition is carried out in the opposite order. Clearly, the $\dot{M}n(CO)_5$ radical is more likely to encounter a neutral TCNE molecule in the first case than in the second. The formation of I in the latter reaction is significant, since it establishes the radical nature of a large class of reactions involving the interaction between TCNE and metal-carbon σ bonds.[15] The most frequent and abundant products in these reactions were found to be keteneiminato complexes III. These products can now be regarded as arising by the coupling of iminoallylic radicals such as II with alkyl radicals R.

$$\underset{}{M{—}R} + TCNE \longrightarrow \underset{\text{III}}{M{—}N{=}C{=}C(CN)C(CN)_2R} \quad (4)$$

Radicals II are also formed in the reactions of TCNE with the cyclopentadienyl carbonyl dimers of Cr, Mo, W, and Fe as well as with the corresponding benzyl derivatives (Table I), but not with $Re_2(CO)_{10}$, $Co_2(CO)_8$, and $[\eta^5\text{-}C_5H_5Ni(CO)]_2$ which give $\mathrm{TCNE}\cdot^{-}$ as the only detectable paramagnetic species in solution. Radical II with $M = \eta^5\text{-}C_5H_5Cr(CO)_3$ is the most labile and decays rapidly above −25°. At similar low temperatures, the same radical can also be produced (together with $\mathrm{TCNE}\cdot^{-}$) from $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2Hg$ and TCNE underscoring the generality of the oxidative homolytic scission of metal–metal bonds. The esr spectra of these species are simpler than that of I, since the corresponding metal nuclei in largest natural abundance have no nuclear spin. However, satellite lines due to ^{53}Cr and ^{95,97}Mo have been observed. The metal–metal bonds of main-group organometallic compounds can also undergo oxidatively promoted homolysis judging by the ready formation of radical II with $M = (n\text{-Bu})_3Sn$ in the reaction of TCNE and hexa-*n*-butylditin (Table I).[16] This radical is extraordinarily stable, and it appears to have been isolated in pure form, although not recognized as II, in a recent preparative study.[17] The hexaphenyl derivative and the silicon analogs do not give II but only $\mathrm{TCNE}\cdot^{-}$ as was already reported.[18] The details of this work together with additional radical reactions of TCNE and other organic electron acceptors with organometallic compounds will be reported elsewhere.

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(10) Trigonal allyl geometry: CC = 1.38, CH = 1.08, CN = 1.40, and NH = 1.01 Å.

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(16) The small ^{115,117}Sn and N_3 splittings (*cf.* Table I) suggest an expanded Sn–N–C bond angle. A collinear arrangement of these atoms would maximize a π (d–p) interaction between the d orbitals on Sn and the nitrogen lone pair in a pure p orbital. Such π (d–p) conjugation is not accessible to the transition metal analogs, since the d orbitals are engaged in bonding to the metal ligands.

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Spin Selectivity in Low Temperature Solid State Photochemistry

Sir:

A few years ago it was suggested[1] that microwave radiation capable of changing the direction of the unpaired spins of a photochemically active triplet state (*i.e.*, microwaves in resonance with its zero-field (zf) transitions) could affect the rate and yield of solid state photochemical reactions involving this state. In this communication we report on the observation that the rate of the biphotonic photochemistry of pyrimidine[2] in benzene at 1.6°K is found to decrease when the system is exposed to microwaves in resonance with its zf transitions or to a static magnetic[3] field. The theoretical treatment of this problem given in this communication reveals that this could arise from having unequal intersystem crossing (ISC) rates, unequal decay rates, or unequal photochemical reaction rates for the three zf levels of the triplet state. In the system studied, in addition to unequal ISC and decay rates, *the different spin levels are found to have different photochemical reaction rates.*

The phosphorescence intensity of pyrimidine in benzene at liquid helium temperatures decreases as a function of time under 3130 Å excitation.[2] A new uv absorption band with an optical density of >0.10 that of the unreacted pyrimidine is found to appear at 3600 Å upon melting an irradiated thin sample for 12 hr. The overall rate of the reaction (determined from the decrease in the phosphorescence intensity with uv exposure time) is found to be first order in optically clear crystals. (Nonlinear effects due to scattering of the exciting light are found when polycrystalline samples are used.) At low intensity, the rate constant of the reaction is found to be second order in the exciting light intensity, suggesting a biphotonic reaction as was found for other systems.[4,5]

The effect of resonant microwaves[6] and static magnetic field (10 kG) on decreasing the rate of the photochemical disappearance of pyrimidine is shown in Figure 1. These perturbations cause a decrease in the value of the rate constant of the observed photochemical change by a factor of $\frac{1}{2}$–$\frac{1}{3}$.

In the absence of spin–lattice relaxation between the three zero-field (zf) levels, a set of rate equations may be derived for the following biphotonic mechanism.

$$S_0 \underset{\beta_i}{\overset{\alpha_i I}{\rightleftarrows}} T_i \xrightarrow{\gamma_i I} \text{product}$$

The rate equations for populating any zf level *i* of the triplet state (T) and the ground state (S_0) are given by

$$\frac{dT_i}{dt} = \alpha_i IS - \beta_i T_i - \gamma_i IT_i \qquad (1)$$