We wish to challenge all these claims. In our view (a) the "new" bands can all be assigned to other known species (a conclusion independently reached by Turner et al.⁵), and (b) the evidence against a stable trigonal isomer of any species M(CO)₅ is circumstantial, but in our view overwhelming, and we wish to add yet further arguments to those^{2,6} of our previous reports.

(a) The evidence for the new isomer is that bands at 1964 and 1937 $\rm cm^{-1}$ appear under certain conditions in Cr:CO: Ar matrices but not in pure Cr:CO matrices; these latter show bands at 1962 and 1933 cm^{-1} (assignable to the E and A_1^1 bands of a square pyramidal $Cr(CO)_5$ fragment) and a further weak band at 2020 cm^{-1} , as well as the spectrum of $Cr(CO)_6$.

(i) The new bands⁴ correspond very closely in position to bands of $M(CO)_4$ and $M(CO)_5$ species; M = Cr, Mo, $W^{.7,8}$ $Cr(CO)_4$ in hydrocarbon glass shows three bands at 2045, 1941, and 1891 cm⁻¹. A fourth band is probably concealed under the $A_1^{(1)}$ band of $Cr(CO)_5$. $Cr(CO)_4$ seems to be extremely light sensitive-much more so than Mo or W tetracarbonyls-and can be generated by photolysis of Cr(CO)5 only in low concentration.⁶ The 2045-cm⁻¹ band of $Cr(CO)_4$ is very weak and so will have escaped detection under the conditions of ref 4. It seems likely therefore that the strongest "new" band is in fact a composite of three bands, two belonging to $Cr(CO)_4$ and one to $Cr(CO)_5$. The 1891-cm⁻¹ band of the tetracarbonyl is not shown in ref 4 and has presumably been assigned to tetracarbonyl.9 It is then an unlucky coincidence that the Cr case was chosen for study in ref 4, since in the Mo and W cases the tetracarbonvls are much more stable and would almost certainly have produced clearer band patterns in the medium frequency CO stretching region.

(ii) The isotope pattern observed on cocondensation of Cr atoms, ¹²C¹⁶O, ¹³C¹⁶O, and argon is described as agreeing qualitatively with what is expected for trigonal bipyramidal $Cr(CO)_5$. Unfortunately, this is not the only possible explanation. There are some important cases where the qualitative isotope pattern criterion¹⁰ suffices to distinguish between possibilities (for example, the distinction between tetrahedral and hypothetical square planar structures for the tetracarbonyls of Pt and Pd^{11,12}). Unfortunately, this is not one of them, as there is bound to be a strong qualitative resemblance between the pattern of trigonal bipyramidal $M(CO)_5$ and that of $C_{2\nu}$ (octahedral bis-cis-vacancy) $M(CO)_4$ under the relatively low resolution reported.⁴

(b) (i) Admittedly, the failure of species $M(CO)_5$ generated photochemically under a wide range of conditions to rearrange to a trigonal bipyramidal form^{2,3,6} could be attributed⁴ to the presence of CO, or of some impurity, loosely occupying the sixth site. The former criticism, however, could not be leveled against our preparation⁷ from Mo-(CO)₅PH₃ of Mo(CO)₅ indistinguishable from that prepared by photolysis of $Mo(CO)_6$.¹³

(ii) Our species $M(CO)_5$ (M = Cr, Mo, W) all show the phenomena of photoreversal² and secondary photolysis.⁷ Moreover, species $M(CO)_4L$ (M = Mo and L = $P(C_6H_{11})_{3}$;¹⁴ M = Cr, Mo, W and L = PR₃, P(OR)₃⁷) all show photoisomerism, attributed by us to cis-trans photo isomerism in octahedral $M(CO)_4(L)$ (vacancy), and photoreversal. We therefore presume the occurrence, under photoreversal conditions, of a degenerate, undetected photo isomerism in square pyramidal $M(CO)_{5}$.¹⁷ Whether the last presumption is accepted or not, the very facts of photolysis and photoreversal imply a degree of flexibility in the neighborhood of the unsaturated species. The distortion required to convert $C_{4\nu}$ to D_{3h} is small, and it seems impossible that under all the conditions which have been studied this distortion is impeded by lattice rigidity. Incidentally,

the barrier to pseudorotation in Fe(CO)₅, which presumably goes through a $C_{4\nu}$ intermediate, is very low indeed.¹⁵

We do not discount the existence of a trigonal bipyramidal species as a primary product of photolysis (especially if this proceeds via the triplet state, as has been claimed for sensitised photolysis¹⁶). The existence of a stable isomer is quite another matter. It cannot be totally disproved, but in our view, the evidence so far made public provides no reason to credit it.

We conclude with an observation about atom condensation and photolysis as techniques in matrix isolation carbonyl chemistry. There is certainly a unique logical satisfaction in generating species directly from atoms and small fragments, but photolytic techniques permit the observation of concerted growth and decay of families of peaks under closely controlled conditions, providing precisely the kind of evidence of common origin unfortunately lacking in matrix synthesis studies, such as that⁴ under discussion.

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Photochemistry of Transition Metal Complexes. The Mechanism and Efficiency of Energy Conversion by Electron-Transfer Ouenching

Sir:

In recent reports we and others have shown that excited states of tris(2,2'-bipyridine)ruthenium(II), Ru(bipy)₃^{2+*}, and related metal complexes can be quenched efficiently by electron transfer to oxidants.¹⁻⁴ It was found, for example, that electron transfer from $Ru(bipy)_3^{2+*}$ to oxidants such as $Ru(NH_3)_{6}^{3+}$, $Fe(H_2O)_{6}^{3+}$, and various pyridinium salts occurs, giving $Ru(bipy)_{3}^{3+}$ and the reduced form of the quencher. The quenching reactions were found to proceed at nearly diffusion-controlled rates.³ The quenching of longScheme I

$$\operatorname{Ru(bipy)_{3}^{2**}}_{7_{0}} + Q \xrightarrow{k_{12}}_{k_{21}} \operatorname{Ru(bipy)_{3}^{2**}}_{2} \dots Q \xrightarrow{k_{23}}_{k_{32}} \operatorname{Ru(bipy)_{3}^{3*}}_{3} \dots Q^{-\frac{k_{34}}{k_{43}}} \operatorname{Ru(bipy)_{3}^{3*}} + Q^{-\frac{1}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{3} + Q^{-\frac{1}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{3} \dots Q^{-\frac{k_{34}}{k_{43}}} \operatorname{Ru(bipy)_{3}^{3*}}_{3} + Q^{-\frac{1}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{3} \dots Q^{-\frac{k_{34}}{k_{43}}} \operatorname{Ru(bipy)_{3}^{3*}}_{3} + Q^{-\frac{1}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{3} \dots Q^{-\frac{k_{34}}{k_{43}}} \operatorname{Ru(bipy)_{3}^{3*}}_{3} + Q^{-\frac{1}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{3} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{3} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{3*}}_{3} + Q^{-\frac{1}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{3} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{3} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{3} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{7_{0}} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{7_{0}}} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{7_{0}} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{7_{0}}} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}} \operatorname{Ru(bipy)_{3}^{2*}}_{7_{0}}} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}}} \dots Q^{-\frac{k_{34}}{k_{43}}}_{7_{0}} \dots Q^{-\frac{k_{34}}$$

Table I. Ru(bipy)₃^{2+*} Quenching Rate Constants and Reduction Potential Data for Some Neutral Organic Compounds

Quencher	$-E_{\frac{1}{2}a}$	$k_q^{\text{obsd}} (M^{-1} \text{ sec}^{-1})^{b-d}$
Quencher1. p-Nitronitrosobenzene2. p-Dinitrobenzene3. o-Dinitrobenzene4. p-Nitrobenzaldehyde5. m-Dinitrobenzene6. Methyl-4-nitrobenzoate7. cis- 4,4'-Dinitrostilbene	$\begin{array}{c} -E_{\frac{1}{2}}^{e} \\ 0.525^{e} \\ 0.69f \\ 0.818 \\ 0.863f \\ 0.898f \\ 0.947f \\ 1.00^{i} \end{array}$	$\begin{array}{c} & \chi_{q} \\ \hline (9.18 \pm 0.13) \times 10^{9} \\ \hline (6.56 \pm 0.08) \times 10^{9} \\ \hline (3.10 \pm 0.04) \times 10^{9} \\ \hline (1.96 \pm 0.03) \times 10^{9} \\ \hline (1.56 \pm 0.05) \times 10^{9} \\ \hline (6.56 \pm 0.09) \times 10^{8} \\ \hline (1.83 \pm 0.08) \times 10^{8} \end{array}$
 8. 4,4'-Dinitrobiphenyl 9. 3-Nitrobenzaldehyde 10. Methyl-3-nitrobenzoate 11. 4-Chloronitrobenzene 12. 4-Fluoronitrobenzene 13. Nitrobenzene 14. 4-Methylnitrobenzene 	$\begin{array}{c} 1.004^{h} \\ 1.016^{f} \\ 1.044^{f} \\ 1.063^{f} \\ 1.128^{f} \\ 1.147^{f} \\ 1.203^{f} \end{array}$	$\begin{array}{c} (1.18 \pm 0.03) \times 10^8 \\ (4.89 \pm 0.19) \times 10^7 \\ (1.66 \pm 0.07) \times 10^7 \\ (8.04 \pm 0.25) \times 10^6 \\ (8.32 \pm 0.61) \times 10^5 \\ <2 \times 10^5 \\ <3 \times 10^5 \end{array}$

^a Acetonitrile containing 0.1 M tetra-n-propylammonium perchlorate. ^b Acetonitrile containing 0.10 M tetraethylammonium perchlorate (TEAP). c [Ru(bipy)₃²⁺] 10⁻⁵ M. dk_q was calculated using $\tau_0 = 0.862 \pm 0.010 \ \mu$ sec measured in 0.10 M TEAP by the single proton counting technique. ^eM. E. Poever, Trans. Faraday Soc., 58, 2370 (1962). ^f A. H. Maki and D. H. Geske, J. Am. Chem. Soc., 83, 1852 (1961). & A. H. Maki and D. H. Geske, J. Chem. Phys., 33, 825 (1960). ^h J. E. Harriman and A. H. Maki, J. Chem. Phys., 39, 778 (1963). ⁱGilbert M. Brown unpublished results.

lived excited states by electron transfer to yield unstable ground state products represents a potentially important energy conversion process. Major questions arising in this regard concern the oxidation (or reduction) potentials of species such as Ru(bipy)₃^{2+*}, activation energies involved in the quenching processes, and other factors which may limit the quenching efficiency by this mechanism. In the present paper we report a study of electron transfer quenching of $Ru(bipy)_3^{2+*}$ by a series of compounds having variable reduction potentials. These results present a much more detailed picture of the excited state electron transfer process and indicate that energy conversion is an extremely efficient process for $Ru(bipy)_3^{2+*}$.

Several nitrobenzene derivatives were chosen as guenchers in this investigation. This series of quenchers was chosen because in some cases they are known to have relatively high triplet energies $(E_{\rm T}({\rm nitrobenzene}) = 60 \ {\rm kcal/mol})^5$ compared to $Ru(bipy)_3^{2+*}$ and because, as a series, they undergo reversible one-electron reductions at potentials in the range -1.5 to -0.5 V vs. SCE in acetonitrile. Rate constants for intensity quenching of the $Ru(bipy)_3^{2+*}$ emission are given in Table I together with the quencher reduction potentials. All of the nitroaromatics investigated quenched the emission and the rates were found to vary monotonically with the quencher reduction potential. No spectral evidence for ground-state complexes was detected for any of the nitroaromatics; no new emission and no permanent chemical products were observed in steady-state or flash photolysis experiments. In contrast to our previous studies³ where the net products of the excited state redox reaction could be observed by flash photolysis, no transients having lifetimes longer than 50 μ sec could be detected. The lack of free ion formation with nitroaromatics as quenchers in an electron transfer process is not surprising since the immediate product is most probably an ion-pair as shown in the quenching

scheme (Scheme I). With quenchers such as bis(N-methyl)-4,4'-bipyridinium ion or $Fe(H_2O)_6^{3+}$ the quenching products are both positively charged and the escape probability from the ion pair, $k_{34}/k_{30} + k_{34}$, is very large.^{6,7} For the combination, $Ru(bipy)_3^{3+} \cdots Q^-$, the escape probability can be calculated to be in the range 0.3-1% and therefore the concentration of free ions produced is probably undetectable.6,7

If it is assumed that $k_{34} \ll k_{30}$, the quenching scheme can be analyzed using the Stern-Volmer relationship and steady-state approximations to yield eq 1. The model used is

$$k_{q}^{obsd} = \frac{k_{12}}{1 + \frac{k_{21}}{k_{23}} \left(1 + \frac{k_{32}}{k_{30}}\right)}$$
(1)

analogous to that used by Rehm and Weller for the treatment of singlet charge-transfer exciplex phenomena.⁸ If it is assumed, as did these authors,⁸ that k_{12} , k_{21} , and k_{30} are constant for a series of closely related quenchers, eq 1 can be reduced to eq 2, where ΔG_{23} is the free energy difference

$$k_{q}^{obsd} = \frac{k_{12}}{1 + \frac{k_{12}}{K_{12}k_{30}} (e^{\Delta G^{*}_{23}/RT} + e^{\Delta G_{23}/RT})}$$
(2)

and ΔG_{23}^{*} is the free energy of activation between encounter complex and ion pair. As ΔG_{23} becomes large and negative, eq 2 reduces to eq 3. Equation 3 predicts a limiting,

$$k_{q}^{obsd} = \frac{k_{12}K_{12}k_{30}}{K_{12}k_{30} + k_{12}e^{\Delta G^{*}_{23}/RT}}$$
(3)

constant value for k_q^{obsd} if ΔG^*_{23} is 0 or a small, constant value. As ΔG_{23} becomes large and positive, $\Delta G_{23} \approx \Delta G^*_{23}$ and eq 2 reduces to eq 4. ΔG_{23} can be written in terms of reduction potentials as in eq 5. In eq 5 w_p and w_r represent

$$k_{q}^{obsd} = \frac{K_{12}k_{30}}{2} e^{-\Delta G_{23}/RT}$$
(4)

$$\Delta G_{23}(V) = E_{1/2}[\text{Ru(bipy)}_{3}^{3+}/\text{Ru(bipy)}_{3}^{2+*}] - E_{1/2}[\text{Ru(bipy)}_{3}^{3+}/\text{Ru(bipy)}_{3}^{2+*}]$$

$$E_{1/2}[Q/Q^{-}] + w_{p} - w_{r}$$
 (5)

the work required to bring the product ions $(Ru(bipy)_3^{3+})$ and Q^{-}) and reactants (Ru(bipy)₃^{2+*} and Q) together to form the ion pair and encounter complex, respectively.¹⁰ From eq 3, 4, and 5 it can be seen that a plot of log k_q^{obsd} vs. $E_{1/2}[Q/Q^-]$ should: (a) be linear at low $E_{1/2}[Q/Q^-]$ values with a slope = -(1/2.3RT), and (b) approach a constant limiting value at higher $E_{1/2}[Q/Q^{-}]$. The plot in Figure 1 indicates that such is the case; the slope of the linear portion (experiments 6-12 in Table I) is $17.6 \pm 1.0 V^{-1}$ where the error estimate was made by the method of limiting slopes. The value is in good agreement with the anticipated value of 16.9 V^{-1} .

 $E_{1/2}[\operatorname{Ru}(\operatorname{bipy})_3^{3+}/\operatorname{Ru}(\operatorname{bipy})_3^{2+*}]$ can be estimated from the data in Figure 1. From eq 4, where $\Delta G_{23} = 0$, log k_q^{obsd} = log $[K_{12}k_{30}/2]$. By extrapolation of the linear portion of the curve in Figure 1 to the value for log $[K_{12}k_{30}/2]$, $E_{1/2}[\operatorname{Ru}(\operatorname{bipy})_3^{3+}/\operatorname{Ru}(\operatorname{bipy})_3^{2+*}]$ can be calculated. From their experimental data on fluorescence quenching in acetonitrile, Rehm and Weller have estimated that $\log [K_{12} \log$



Figure 1. Plot of log k_q^{obsd} vs. quencher reduction potential, $E_{1/2}[Q/$ Q-1.

 $k_{30}/2$ = 10.6. Although the exact value to be chosen here is uncertain, a value in the region 10.0-11.0 is clearly reasonable.⁸ For the points in the linear portion of Figure 1, extrapolation of lines with limiting slopes to this region gives $E_{1/2}[\text{Ru}(\text{bipy})_3^{3+}/\text{Ru}(\text{bipy})_3^{2+*}] = -0.81 \pm 0.02 \text{ V}$ after correcting for w_p .¹⁰ From the potential of the ground state $Ru(bipy)_3^{3+}/Ru(bipy)_3^{2+}$ couple in the same medium (+1.29 V),¹² it can be seen that excitation increases the reducing power of $Ru(bipy)_3^{2+}$ by 2.10 V. Since the spectroscopically estimated excited state energy of $Ru(bipy)_3^{2+*}$ is 2.18 V, essentially all of the excitation energy can be applied to driving the electron-transfer process. As expected,⁸ this indicates that the entropy difference between the ground and excited states is small. We are currently extending our investigation to other metal complexes having longlived excited states of different orbital origin.

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Enantioselective Reduction in a Chiral Double Layer

Sir:

The double layer at an electrode-solution interface is known to influence the mechanisms of electrochemical

Table I. Cathodic Reduction of $Co(acac)_{2}$ at -1.0 V with 0.10 M Trimethyl-(-)-menthylammonium Perchlorate in Acetonitrile

$\begin{bmatrix} I - D \end{bmatrix}_{0}^{+} + \\ \begin{bmatrix} I - L \end{bmatrix}_{0}^{-} \\ M \times 10^{3} \end{bmatrix}$	Conversion, %	Optical purity ⁸ (%) ± 0.06	$k_{\rm d}/k_{\rm l}$
4.10	46.5	1.02	1.033
4.62	81.7	2.30	1.028
7.82	50.1	1.23	1.036
16.28	75.4	1.87	1.027
31.28	61.2	1.38	1.030
			Mean 1.031 \pm 0.003

reactions in two distinct ways. The relative concentrations of ions and solvent molecules in this region of solution can determine which intermolecular, secondary reaction paths are available to a reactive intermediate generated by electron transfer.¹⁻⁴ Also, serving as the reaction medium, the double layer may alter the activities of reactants and intermediates. This latter role, though more general than^{5,6} the former is less well understood particularly in the case of the compact double layer, and its consequences have not been extensively explored. We wish to report a novel example of electrochemical selectivity which reflects the influence of the double layer as a reaction medium.

The reduction of cobalt trisacetylacetonate, I, in acetonitrile, at a mercury cathode proceeds via an irreversible, oneelectron, electrochemical-chemical process to yield the oligomeric Co(II) complexes $[Co(acac)_2]_n$, n = 1-4.7 When the reaction was carried out using an optically active supporting electrolyte, tri-N-methyl-(-)-menthylammonium perchlorate, II, a small but reproducible enantioselectivity was observed. For example, racemic I was reduced at a controlled potential of -1.0 V vs. Ag AgCl and the reaction stopped prior to complete conversion. The unreacted I was recovered and found to be optically active.8 The optical purity increased with increasing conversion, obeying a pseudofirst-order rate law:

$$\begin{array}{l} I \rightarrow D \xrightarrow{k_{d}} Co(acac)_{2} + acac^{-} \\ I \rightarrow L \xrightarrow{k_{1}} Co(acac)_{2} + acac^{-} \\ k_{d}/k_{1} = \frac{\ln (I - D)/(I - D)_{0}}{\ln (I - L)/(I - L)_{0}} \end{array}$$

Table I shows the results of a representative series of experiments. The selectivity, k_d/k_l , is independent of the initial concentration of I and the extent of conversion. These apparent rate constants may, in principle, represent any one or a composite of the following elementary steps: (i) mass transport of I to the electrode surface, (ii) adsorption of I at the electrode, (iii) electron transfer, involving either "free" or adsorbed I.

Experimental conditions can control which of these steps will be rate limiting. In the experiments described here, the catholyte solution was efficiently stirred over a stationary electrode in a partitioned cell. Figure 1 shows the logarithm of the faradaic current¹⁰ as a function of stirring rate and applied potential. At high overpotential (E < -2.0 V), the rate is purely mass-transport controlled as demonstrated by the insensitivity to potential and dependence on stirring rate.¹¹ At potentials above -1.1 V the rate becomes independent of stirring and above -1.0 V a simple exponential dependence on potential (Tafel relation) is observed; characteristic of rate limiting electron transfer (activation overpotential).12

The magnitude of the enantioselectivity varies systematically with potential and electrolyte concentration as shown in Figure 2. Two conclusions may be drawn from compari-