

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 $M(\text{CO})_5$ 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 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 bands of a square pyramidal $\text{Cr}(\text{CO})_5$ fragment) and a further weak band at 2020 cm^{-1} , as well as the spectrum of $\text{Cr}(\text{CO})_6$.

(i) The new bands⁴ correspond very closely in position to bands of $M(\text{CO})_4$ and $M(\text{CO})_5$ species; $M = \text{Cr}, \text{Mo}, \text{W}$.^{7,8} $\text{Cr}(\text{CO})_4$ in hydrocarbon glass shows three bands at 2045, 1941, and 1891 cm^{-1} . A fourth band is probably concealed under the A_1 band of $\text{Cr}(\text{CO})_5$. $\text{Cr}(\text{CO})_4$ seems to be extremely light sensitive—much more so than Mo or W tetracarbonyls—and can be generated by photolysis of $\text{Cr}(\text{CO})_5$ only in low concentration.⁶ The 2045- cm^{-1} band of $\text{Cr}(\text{CO})_4$ 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 $\text{Cr}(\text{CO})_4$ and one to $\text{Cr}(\text{CO})_5$. 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 tetracarbonyls 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, $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and argon is described as agreeing qualitatively with what is expected for trigonal bipyramidal $\text{Cr}(\text{CO})_5$. 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 $M(\text{CO})_5$ and that of C_{2v} (octahedral bis-cis-vacancy) $M(\text{CO})_4$ under the relatively low resolution reported.⁴

(b) (i) Admittedly, the failure of species $M(\text{CO})_5$ 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 $\text{Mo}(\text{CO})_5\text{PH}_3$ of $\text{Mo}(\text{CO})_5$ indistinguishable from that prepared by photolysis of $\text{Mo}(\text{CO})_6$.¹³

(ii) Our species $M(\text{CO})_5$ ($M = \text{Cr}, \text{Mo}, \text{W}$) all show the phenomena of photoreversal¹² and secondary photolysis.⁷ Moreover, species $M(\text{CO})_4\text{L}$ ($M = \text{Mo}$ and $\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$; $M = \text{Cr}, \text{Mo}, \text{W}$ and $\text{L} = \text{PR}_3, \text{P}(\text{OR})_3$)⁷ all show photoisomerism, attributed by us to cis-trans photoisomerism in octahedral $M(\text{CO})_4(\text{L})$ (vacancy), and photoreversal. We therefore presume the occurrence, under photoreversal conditions, of a degenerate, undetected photoisomerism in square pyramidal $M(\text{CO})_5$.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_{4v} 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 $\text{Fe}(\text{CO})_5$, which presumably goes through a C_{4v} 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 sensitized 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 Quenching

Sir:

In recent reports we and others have shown that excited states of tris(2,2'-bipyridine)ruthenium(II), $\text{Ru}(\text{bipy})_3^{2+*}$, and related metal complexes can be quenched efficiently by electron transfer to oxidants.¹⁻⁴ It was found, for example, that electron transfer from $\text{Ru}(\text{bipy})_3^{2+*}$ to oxidants such as $\text{Ru}(\text{NH}_3)_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, and various pyridinium salts occurs, giving $\text{Ru}(\text{bipy})_3^{3+}$ and the reduced form of the quencher. The quenching reactions were found to proceed at nearly diffusion-controlled rates.³ The quenching of long-

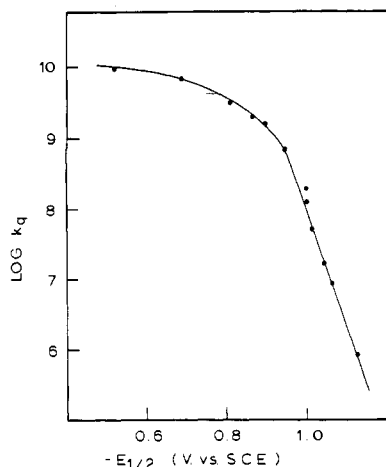


Figure 1. Plot of $\log k_q^{\text{obsd}}$ vs. quencher reduction potential, $E_{1/2}[Q/Q^-]$.

$k_{30}/2] = 10.6$. 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 $E_{1/2}[\text{Ru}(\text{bipy})_3^{3+}/\text{Ru}(\text{bipy})_3^{2+*}] = -0.81 \pm 0.02$ V after correcting for w_p .¹⁰ From the potential of the ground state $\text{Ru}(\text{bipy})_3^{3+}/\text{Ru}(\text{bipy})_3^{2+}$ couple in the same medium (+1.29 V),¹² it can be seen that excitation increases the reducing power of $\text{Ru}(\text{bipy})_3^{2+}$ by 2.10 V. Since the spectroscopically estimated excited state energy of $\text{Ru}(\text{bipy})_3^{2+*}$ 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 long-lived excited states of different orbital origin.

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Enantioselective Reduction in a Chiral Double Layer

Sir:

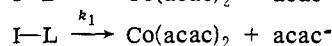
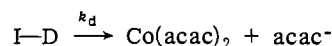
The double layer at an electrode-solution interface is known to influence the mechanisms of electrochemical

Table I. Cathodic Reduction of $\text{Co}(\text{acac})_3$ at -1.0 V with 0.10 M Trimethyl(-)-menthylammonium Perchlorate in Acetonitrile

$\frac{[\text{I}-\text{D}]_0 + [\text{I}-\text{L}]_0}{M \times 10^3}$	Conversion, %	Optical purity ⁸ (%) ± 0.06	k_d/k_1
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 ± 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, one-electron, electrochemical-chemical process to yield the oligomeric $\text{Co}(\text{II})$ complexes $[\text{Co}(\text{acac})_2]_n$, $n = 1-4$.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. $\text{Ag}|\text{AgCl}$ 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 pseudo-first-order rate law:



$$k_d/k_1 = \frac{\ln(\text{I}-\text{D})/(\text{I}-\text{D})_0}{\ln(\text{I}-\text{L})/(\text{I}-\text{L})_0}$$

Table I shows the results of a representative series of experiments. The selectivity, k_d/k_1 , 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-