acetonitrile crystal I.[14] Detailed esr results[15] for this electron-excess center in CD$_3$CN single crystals are consistent with a structure in which the unpaired electron occupies a supramolecular σ-bonding orbital. This is derived by addition of the separate molecular antibonding π orbitals which overlap with their axes in the plane of the two antiparallel molecules.

Finally, we recall that the symmetry properties of what are essentially supramolecular orbitals have been used extensively in the formulation of the Woodward–Hoffmann rules for concerted chemical reactions.[16] This communication indicates that the esr method can provide definitive structural information about such orbitals in suitable systems.

Acknowledgment. We wish to acknowledge a useful discussion with Dr. Ralph G. Pearson on the structure of the acetonitrile dimer radical anion. We also thank Dr. J. E. Bloor for the use of the computer program and advising us on the calculations.

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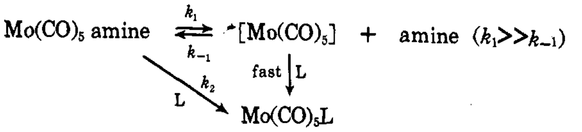
The Nature of the Intermediate Procreated in Substitution Reactions of Group VI Metal Carbonyls

Sir:

The possibility that a five-coordinated intermediate, [Mo(CO)$_5$], is generated by the decomposition of Mo(CO)$_5$–amine complexes in the presence of Lewis bases (L) to form substituted Mo(CO)$_5$L species (L = phosphines and arsines) has been discussed elsewhere.[1] A similar process is reported for the tungsten analogs.[2]



$$\begin{tikzcd}
\mathrm{Mo(CO)_5\ amine} \arrow[r, shift left, "k_1"] \arrow[dr, "k_2", "L"'] & {}^{*}[\mathrm{Mo(CO)_5}] + \mathrm{amine}\ (k_1 >> k_{-1}) \arrow[l, shift left, "k_{-1}"] \arrow[d, "\mathrm{fast}"', "L"] \\
 & \mathrm{Mo(CO)_5L}
\end{tikzcd}$$

This reaction can also occur *via* an S$_N$2 process; however, the second-order process is easily suppressed by employing low concentrations of the Lewis base.

The nature of the intermediate in these reactions is of particular interest, since it is this same intermediate which is believed to be present in both the photochemical[3] and thermal[4] substitution reactions of the group VI hexacarbonyls. This communication describes some experiments which lead to a differentiation between two of the commonly considered possible forms suggested for [Mo(CO)$_5$] in solution, namely, the trigonal bipyramid and the square pyramid.

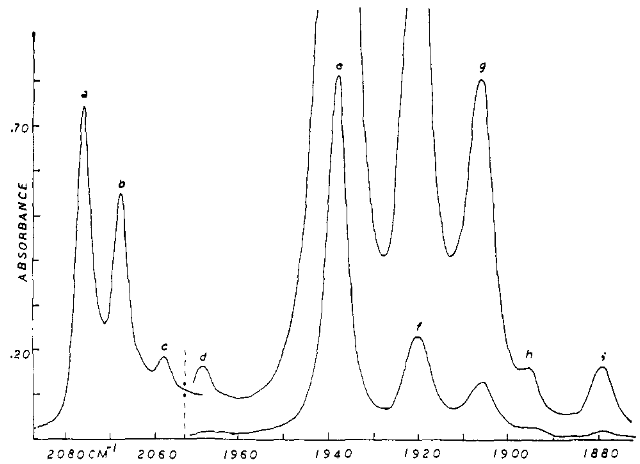


Figure 1. Infrared spectra of ^{13}CO-enriched Mo(CO)$_5$NHC$_5$H$_{10}$ in hexane solution. Peaks a, e, and f are for the all-^{12}CO species; peaks b, d, and g are for the ^{13}CO$_{eq}$ species; peak i is for the ^{13}CO$_{ax}$ species; and peaks c and h are for the di-^{13}CO$_{eq}$ species.[6]

A method for discriminating between these two possibilities arises from the ability to preferentially substitute ^{13}CO for equatorial carbonyl groups over axial carbonyl groups in Mo(CO)$_5$NHC$_5$H$_{10}$. This is accomplished using ultraviolet irradiation in tetrahydrofuran solution. Mo(CO)$_5$NHC$_5$H$_{10}$ was irradiated in solution in a quartz vessel at 25° for 1.7 hr using a Hanovia 550-W lamp in the presence of excess ^{13}CO. The THF was removed under vacuum conditions at room temperature and the ^{13}CO-enriched product was extracted in hexane solution. The infrared spectrum in the CO stretching region showed an abundance of ^{13}CO in the equatorial position (Figure 1). There was 40.5 ± 0.5% enrichment of the equatorial position with a single ^{13}CO group (peak b) and 3.7 ± 0.2% enrichment of the axial position (peak i).[5] Since statistically the equatorial position should be populated more than the axial position by a factor of 4, the enhancement in equatorial enrichment is approximately 2.8 times as great as the axial enrichment.

If the labeled Mo(CO)$_4$(^{13}CO)NHC$_5$H$_{10}$ species reacts to produce a five-coordinate intermediate, then the nature of the intermediate can be deduced from the distribution of the ^{13}CO in the product Mo(CO)$_5$L. Clearly, if *in the transition state and in the intermediate* the axial and equatorial CO groups maintain their integrity, the distribution of ^{13}CO in the product Mo(CO)$_5$L will be the same as that in the starting material Mo(CO)$_5$NHC$_5$H$_{10}$.

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(5) The percentages of ^{13}CO$_{eq}$ and ^{13}CO$_{ax}$ were determined from the relative band areas in the corresponding ^{13}CO and ^{12}CO species, *e.g.*, bands a and b (Figure 1) for the equatorial abundance and bands f and i for the axial abundance. This procedure is approximately correct, since the ratios of these bands in the parent natural-abundance ^{13}CO species for both the amine and arsine complexes are very close to the ratio expected for the presence of 1% ^{13}CO. In addition, the coupling of axial and equatorial modes, as indicated by the L_{ij} matrix elements, in both the amine– and arsine–carbonyl complexes is roughly the same. Imbedded in this method also is the assumption that the intensities for a ^{12}CO or ^{13}CO group are the same. This is in agreement with experimental results [see, *e.g.*, G. Bor and G. Jung, *Inorg. Chim. Acta*, **3**, 69 (1969)]. Spectra were recorded employing a linear absorbance scale.[6]

(6) Frequencies were calculated with an iterative computer program using an energy-factored block matrix for the carbonyl stretching vibrations as described elsewhere [see, *e.g.*, D. J. Darensbourg, *ibid.*, 4, 597 (1970)]. Agreements between calculated and observed frequencies were generally within ±0.5 cm^{-1}.

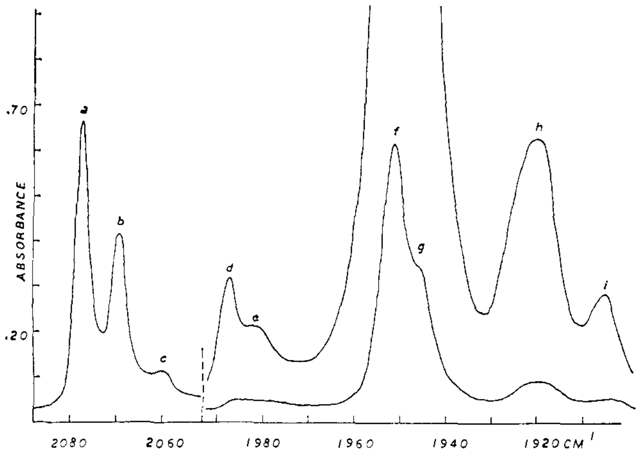

Figure 2. Infrared spectra of ^{13}CO-enriched $Mo(CO)_5As(C_6H_5)_3$ originating from the reaction of $Mo(CO)_5NHC_5H_{10}$ and $As(C_6H_5)_3$ in hexane solution. Peaks a, d, f, and g are for the all-^{12}CO species; peaks b, e, and h are for the $^{13}CO_{eq}$ species; peak i is for the $^{13}CO_{ax}$ species; and peak c is for the di-$^{13}CO_{eq}$ species.[6]

The substitution reaction with triphenylarsine to form $Mo(CO)_5As(C_6H_5)_3$ was performed using the ^{13}CO enriched $Mo(CO)_5NHC_5H_{10}$ sample. Care was taken to avoid complications due to the second-order reaction process. This was checked by simultaneously performing identical decomposition kinetic experiments with $Mo(CO)_5NHC_5H_{10}$ in the absence and presence of triphenylarsine. These reactions were followed employing infrared spectroscopy in the carbonyl stretching region. The experiments were run at 38° in hexane with concentrations of $Mo(CO)_5NHC_5H_{10}$ and $As(C_6H_5)_3$ being 4.72×10^{-3} and 1.50×10^{-2} M, respectively. Under these conditions no contribution from k_2 was observed and the sole reaction product was $Mo(CO)_5As(C_6H_5)_3$, obtained in 100% yield. The rate constants k_1 were found to be 1.15×10^{-4} and 1.20×10^{-4} sec^{-1}, respectively, for the two cases. During this reaction there was *no* change in the relative abundance of axial and equatorial carbonyl groups in the $Mo(CO)_5NHC_5H_{10}$ species.

The infrared spectrum in the CO stretching region for the substitution product $Mo(CO)_5As(C_6H_5)_3$, enriched in ^{13}CO, is shown in Figure 2. Now 34.0 ± 0.5% of the molecules have a single equatorial ^{13}CO (peak b) and 7 ± 1% of the molecules are axially substituted with ^{13}CO (peak i). Therefore, *the experiment unequivocally indicates a redistribution of equatorial and axial carbonyl groups during the substitution process.*

This equilibration may occur in the transition state. Although it is difficult to envisage a transition state in which all the CO's are equivalent, a possible model is illustrated by Brown for the $Mn(CO)_5X$ species.[7] Owing to the bulkiness of the piperidine base, this possibility is highly unlikely. The alternative is, assuming a dissociative process, an equilibration of the axial and equatorial CO groups in the five-coordinate intermediate through either a trigonal bipyramid or a highly distorted square pyramid.[8] From the ^{13}CO distribution in $Mo(CO)_5As(C_6H_5)_3$, it appears that there has been almost a complete statistical scrambling of the axial and equatorial positions (prediction would be for 35.3 ± 0.6% ^{13}CO equatorial and 8.8 ± 0.2% ^{13}CO axial in the product based on the percentages in $Mo(CO)_5NHC_5H_{10}$).[10]

The accuracy of this experiment would be greatly improved if it were possible to preferentially label the axial position in the starting material. Studies are in progress in our laboratories for elucidating the photochemical conditions necessary for specifically labeling metal carbonyl species.

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[7] T. L. Brown, *Inorg. Chem.*, 7, 2673 (1968).

[8] A similar observation was made when tungsten hexacarbonyl was irradiated in a frozen hydrocarbon medium. Infrared spectra indicate that the pentacarbonyl species produced in the frozen-glass state most likely has a square-pyramidal configuration, whereas when the solid is melted a trigonal-bipyramidal configuration is produced.[9]

[9] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, 84, 3589 (1962); 85, 1013 (1963).

[10] If the reaction proceeds through a trigonal-bipyramidal intermediate, the per cent distribution between equatorial and axial carbonyl groups is expected to be 83% $^{13}CO_{eq}$ and 17% $^{13}CO_{ax}$, starting with the mono-equatorially labeled species. This is very close to the expected statistically scrambling distribution of CO groups in a pentacarbonyl species (80% $^{13}CO_{eq}$ and 20% $^{13}CO_{ax}$).

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A New Highly Anisotropic Dinitroxide Ketone Spin Label. A Sensitive Probe for Membrane Structure

Sir:

Recently we introduced a short versatile procedure for the conversion of a ketone group into a stable mononitroxide free radical.[1] Such nitroxides have enjoyed wide use as spin labels, the esr spectra of which yield valuable information, *inter alia*, about the orientation, motion, and polarity within the molecular structure of membranes and membrane models.[2] We now describe a procedure, patterned after our previous one,[1] for the conversion of a ketone group into a stable dinitroxide spin label. We also describe experiments which show such dinitroxides to have potential as new sensitive probes for membrane structure studies.

Amino acid **2**, prepared from amino ketone **1**[3] by the method of Rassat,[4] was reduced with $LiAlH_4$ in refluxing ether to afford dinitroxide precursor **3**, mp 119–120°.[5] A solution of **3** (0.5 g), 5α-cholestan-3-one

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[1] J. F. W. Keana, S. B. Keana, and D. Beetham, *J. Amer. Chem. Soc.*, 89, 3055 (1967).

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[3] Available from Aldrich Chemical Co.

[4] A. Rassat and P. Rey, *Bull. Soc. Chim. Fr.*, 815 (1967).