



**Figure 2.** The 220-MHz NMR spectrum of pantetheine in  $D_2O$  solution at  $18^\circ$ . Methylene resonances of the cysteamine portion of the molecule are seen as deformed triplets at 2.65 ( $CH_2S$ ) and 3.30 ppm downfield from internal TSP. Deformed triplets occur at 2.51 ( $CH_2CO$ ) and 3.45 ppm for the  $\beta$ -alanine residue. The average coupling constants were measured on expanded spectra.

**Table II.** Enthalpy and Entropy Changes for the Rotameric Equilibrium *Gauche*  $\rightleftharpoons$  *Trans* for CoA and Pantetheine

Compound	Solvent	$\beta$ -Alanyl moiety		Cysteamine moiety	
		$\Delta H$ , kcal/mol	$\Delta S$ , eu	$\Delta H$ , kcal/mol	$\Delta S$ , eu
CoA <sup>a</sup>	$D_2O$	$7.6 \pm 2.2$	23	$-0.88 \pm 0.26$	-2
Pantetheine <sup>a</sup>	$D_2O$	$1.44 \pm 0.4$	25	$0.71 \pm 0.03$	2
$\beta$ -Mercaptoethylamine <sup>b</sup>	$DCCl_3$			$-0.49 \pm 0.24$	
$\beta$ -Alanine <sup>b</sup>	$DCCl_3$	$-0.43 \pm 0.15$			

<sup>a</sup> Calculated from rotamer populations at two temperatures, 63 and  $18^\circ$ , using  $\Delta G = RT \ln K_{eq} = \Delta H - T\Delta S$  where  $K_{eq} = n_t/n_g$ .

<sup>b</sup> Calculated from observed rotamer populations at  $34^\circ$ , assuming  $\Delta S = R \ln 2$ .

For the  $\beta$ -alanine moiety we have adopted the values of  $J_g$  and  $J_t$  used for the cysteamine moiety. This seemed reasonable based upon the known dependence of the magnitude of the average vicinal coupling constant on the sum of the atom electronegativities about the carbons bearing the coupled protons;<sup>5</sup> the electronegativities of carbon and sulfur are identical. Indeed, the adopted values accurately predicted  $J_{av}$  for the *gauche*  $NCH_2CH_2C=O$  fragment of *N-tert-butyl-4-piperidone* ( $(J + J')/2$ )<sub>calcd</sub> = 6.0; obsd = 6.0 Hz.

Using the above values for  $J_g$  and  $J_t$  the rotamer populations (Table I), and entropy and enthalpy changes (Table II) associated with the rotameric equilibria in CoA and pantetheine were calculated. For the  $\beta$ -alanyl moiety of CoA the data provide strong evidence for a highly favored *gauche* orientation, counter to that reported for  $\beta$ -alanine.<sup>6</sup> Also for the  $\beta$ -alanyl moiety of pantetheine at room temperature, its sensitivity to temperature changes further indicates an enthalpy favoring the *gauche* rotamer. The magnitudes of  $\Delta H$  in both CoA and pantetheine, large for ethylene fragments with no attached bulky groups, is consistent with observed enthalpy differences arising from hydrogen bonding. For the cysteamine portion of both CoA and pantetheine the data in Table I show a rotational preference for a *trans* orientation. Here the enthalpy difference between the two states is about the same as that for cysteamine, consistent with normal rotational preferences and inconsistent with intramolecular hydrogen bonding as a conformation-determining factor for this portion of the molecule. Also consistent with a hydrogen bonding hypothesis is the fact that in  $DMSO-d_6$ , a strong disrupter of hydrogen bonds, the *trans* rotamer is strongly preferred in both pantetheine and CoA for the  $\beta$ -alanine moiety.

Although conformations involving hydrogen bonding between the  $\beta$ -alanyl N-H hydrogen atom and a phosphate oxygen atom base, or sugar hydroxyl groups must be considered for CoA because of the much larger  $\Delta H$  for the  $\beta$ -alanyl rotamer equilibrium as compared to that of pantetheine, the evidence for a preferred *gauche* conformation of the  $\beta$ -alanyl fragment of pantetheine where none of these groups are present strongly suggests that any hydrogen bonding occurs internally within the pantetheine moiety in aqueous solution. It is clear that folded conformations in aqueous medium, maintained primarily by hydrogen-bonding forces proposed here, may be important in the recognition of coenzyme A by enzymes as well as in defining the relative positions of groups at the active sites in known multienzyme complexes utilizing the pantetheine prosthetic group.

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G. Edwin Wilson, Jr.,\* Thomas J. Bazzone  
Chan H. Kuo, Peter L. Rinaldi

Department of Chemistry, Polytechnic Institute of New York  
Brooklyn, New York 11201

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## On Purported Trigonal Bipyramidal $Cr(CO)_5$

Sir:

For some years now, the vexed question of the equilibrium geometry of the pentacarbonyls  $M(CO)_5$  ( $M = Cr, Mo, W$ ) would appear to have been solved. Square pyramidal species have been repeatedly described<sup>1-3</sup> and bands formerly attributed to a  $D_{3h}$  isomer of  $Mo(CO)_5$ <sup>1</sup> have been reassigned to polymeric species.<sup>2,3</sup> Very recently, Ozin<sup>4</sup> has presented evidence for a new more stable isomer of  $Cr(CO)_5$ , formed by vapor deposition matrix isolation methods followed by annealing. It is further claimed that the species described by Turner as  $Cr(CO)_5$  in CO and other matrices should be reformulated as  $Cr(CO)_5S$ , where S is an O-bonded or sideways bonded isocarbonyl, that the more stable isomer of  $Cr(CO)_5$  is of trigonal bipyramidal geometry, and that isotopic substitution data confirm this assignment.

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.<sup>5</sup>), 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<sup>2,6</sup> of our previous reports.

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

(i) The new bands<sup>4</sup> correspond very closely in position to bands of  $M(\text{CO})_4$  and  $M(\text{CO})_5$  species;  $M = \text{Cr}, \text{Mo}, \text{W}$ .<sup>7,8</sup>  $\text{Cr}(\text{CO})_4$  in hydrocarbon glass shows three bands at 2045, 1941, and 1891  $\text{cm}^{-1}$ . A fourth band is probably concealed under the  $A_1^{(1)}$  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.<sup>6</sup> The 2045- $\text{cm}^{-1}$  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- $\text{cm}^{-1}$  band of the tetracarbonyl is not shown in ref 4 and has presumably been assigned to tetracarbonyl.<sup>9</sup> 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 criterion<sup>10</sup> suffices to distinguish between possibilities (for example, the distinction between tetrahedral and hypothetical square planar structures for the tetracarbonyls of Pt and Pd<sup>11,12</sup>). 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.<sup>4</sup>

(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<sup>2,3,6</sup> could be attributed<sup>4</sup> to the presence of CO, or of some impurity, loosely occupying the sixth site. The former criticism, however, could not be leveled against our preparation<sup>7</sup> from  $\text{Mo}(\text{CO})_5\text{PH}_3$  of  $\text{Mo}(\text{CO})_5$  indistinguishable from that prepared by photolysis of  $\text{Mo}(\text{CO})_6$ .<sup>13</sup>

(ii) Our species  $M(\text{CO})_5$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) all show the phenomena of photoreversal<sup>12</sup> and secondary photolysis.<sup>7</sup> Moreover, species  $M(\text{CO})_4\text{L}$  ( $M = \text{Mo}$  and  $\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$ ; <sup>14</sup>  $M = \text{Cr}, \text{Mo}, \text{W}$  and  $\text{L} = \text{PR}_3, \text{P}(\text{OR})_3$ )<sup>7</sup> 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  $M(\text{CO})_5$ .<sup>17</sup> 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.<sup>15</sup>

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 photolysis<sup>16</sup>). 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 that<sup>4</sup> under discussion.

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John D. Black, Paul S. Braterman\*

Department of Chemistry, University of Glasgow  
Glasgow G12 8QQ, Scotland

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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.<sup>1-4</sup> 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.<sup>3</sup> The quenching of long-