

The failure of  $\text{Ni}(\text{CO})_3^-$  to follow the general trend is readily accounted for in this interpretation. Since the 3d orbitals are filled in the neutral carbonyl, the extra electron in the anion must occupy a higher orbital, presumably a ligand orbital. The lowest optical transitions of the anion would presumably involve this higher energy electron, so that this anion should not be compared with any of the others, in which the lowest transition involves a 3d-type electron.

It may be pointed out that the interpretation presented above in terms of metal-to-ligand charge-transfer transitions is readily carried over essentially unchanged to photodetachment thresholds. The qualitative analysis is identical, with the role of the ligand acceptor orbitals simply being taken instead by the free-electron continuum states. Accordingly, the question of whether the process observed was photodissociation or photodetachment is seen in fact to be of small importance for a first qualitative interpretation of these results.

It may be noted, finally, that for one anion,  $\text{Cr}(\text{CO})_4^-$ , direct comparison with condensed phase results is possible. While the solution spectrum of  $\text{Cr}(\text{CO})_4^-$  is

not available to us, the ion is reported to be light yellow.<sup>21</sup> This is entirely consistent with the gas-phase spectrum, which has a weak tail extending just into the blue end of the visible spectrum. The gas-phase result indicates that the near-uv absorption of  $\text{Cr}(\text{CO})_4^-$  results in destruction of the ion, and this is in accord with the observation that the ion in solution is light sensitive to blue light.<sup>21</sup> While stabilization of the other anions studied here in condensed phase may be difficult, it would be of considerable interest to determine whether the visible region absorption peaks observed in gas phase are also observed in condensed phase, where the ion structures might be characterized.

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(21) H. Stammreich, K. Kawai, Y. Tavares, P. Krumholz, J. Behmoiras, and S. Brill, *J. Chem. Phys.*, **32**, 1482 (1960).

## Trigonal Bipyramidal Chromium Pentacarbonyl and Its Implications to Structure and Bonding Considerations of Pentacarbonyls and Pentacarbonyl Anions

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**Abstract:** The reactions of Cr atoms with CO at 4.2–10°K are investigated by matrix isolation infrared spectroscopy. Examination of the reaction products in  $^{12}\text{C}^{16}\text{O}/\text{Ar}$  and  $^{12}\text{C}^{16}\text{O}/^{18}\text{C}^{16}\text{O}/\text{Ar}$  matrices establishes the existence of a  $\text{Cr}(\text{CO})_5$  species having a  $D_{3h}$  trigonal bipyramidal stereochemistry. The data obtained using pure  $^{12}\text{C}^{16}\text{O}$  are quite different from those in  $^{12}\text{C}^{16}\text{O}/\text{Ar}$  matrices and exhibit a number of features which strongly suggest that square pyramidal  $\text{Cr}(\text{CO})_5$ , originally thought to be the primary product of  $\text{Cr}(\text{CO})_6/\text{Ar}$  matrix photolyses, is actually  $\text{Cr}(\text{CO})_5\text{S}$ , where S is either an O-bonded isocarbonyl or a sideways-bonded carbonyl ligand. The spectral and bonding properties of 15-, 16-, 17-, and 18-electron valence shell pentacarbonyls and pentacarbonyl anions are compared and a theory is presented which rationalizes the observed stereochemical changes on passing from the 16- and 18-electron trigonal bipyramidal pentacarbonyls to the 15- and 17-electron square pyramidal pentacarbonyls.

Recently Turner and coworkers<sup>1</sup> have reported infrared spectroscopic evidence for  $\text{Cr}(\text{CO})_5$  formed in the 228.8-nm matrix photolysis of  $\text{Cr}(\text{CO})_6/\text{Ar}$  mixtures at 15°K. Apart from the intense carbonyl absorption belonging to  $\text{Cr}(\text{CO})_6$ , three new CO stretching modes were observed at 2093.4 (vw), 1965.4 (s), and 1936.1 (m)  $\text{cm}^{-1}$  and were assigned to a  $C_{4v}$  square pyramidal form of  $\text{Cr}(\text{CO})_5$ . These deductions were based in part on the number, frequencies, and relative intensities of the observed CO stretching modes and by comparison with the results of Sheline and coworkers<sup>2</sup> for  $\text{Cr}(\text{CO})_5$  formed by photolysis of  $\text{Cr}(\text{CO})_6$  in frozen hydrocarbon glasses at 77°K.

(1) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971).

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

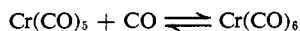
Further investigations by Turner and coworkers<sup>3</sup> led them to suggest that the primary photolysis products of  $\text{Cr}(\text{CO})_6$  in weakly interacting matrices such as methane, or argon matrices doped with nitrogen, were  $\text{Cr}(\text{CO})_5\text{S}$ , where  $\text{S} = \text{CH}_4$  or  $\text{N}_2$ . As expected, the  $\text{Cr}(\text{CO})_5\text{S}$  complexes so formed had very similar infrared spectra to the proposed  $C_{4v}$   $\text{Cr}(\text{CO})_5$  in Ar. On the basis of these results and the solution photolysis experiments of others,<sup>4</sup> it was proposed<sup>1,3</sup> that the primary photolysis product of  $\text{Cr}(\text{CO})_6$  in solution at room temperature was  $\text{Cr}(\text{CO})_5\text{S}$ , where  $\text{S} = \text{solvent}$ .

An intuitively disconcerting aspect of Turner's results

(3) M. A. Graham, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J. Organometal. Chem.*, **C34**, 34 (1972).

(4) M. A. El-Sayed, *J. Phys. Chem.*, **68**, 433 (1964); G. R. Dobson, *ibid.*, **69**, 678 (1965); J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organometal. Chem.*, **29**, 269 (1971).

was the high activation energy barrier for the *thermal* reverse reaction, which was proposed to explain the reluctance of  $\text{Cr}(\text{CO})_5$  to react with CO at 35–40°K to form  $\text{Cr}(\text{CO})_6$ , at which temperatures it is known that CO diffuses quite rapidly in argon.<sup>5</sup> Nevertheless, the facile 440 nm reverse *photolytic* reaction



was ascribed to a local annealing effect of the matrix, induced by electronic excitation of  $\text{Cr}(\text{CO})_5$  to  $\text{Cr}(\text{CO})_5^*$  followed by a nonradiative decay process of  $\text{Cr}(\text{CO})_5^*$  to its ground state in the Ar lattice.

Recent work performed in our laboratories, involving the cocondensation of Cr atoms with CO at 4.2–10°K, has led us to believe that the trigonal bipyramidal form of  $\text{Cr}(\text{CO})_5$  is capable of an independent existence and may in fact be the thermodynamically stable form of the pentacarbonyl. In this paper we report such data.

### Experimental Section

Chromium is commercially available in powder form with 99.99% purity (A. D. Mackay, N. Y.) and was vaporized from a directly heated tantalum Knudsen cell. The wall thickness was generally 0.38 mm with an orifice size of 0.5 mm. The furnace used for the evaporation of the metals has been described previously.<sup>6</sup> The rate of chromium deposition was continuously monitored using a quartz crystal microbalance<sup>7</sup> set behind a second 0.5-mm orifice in the Knudsen cell. Research grade  $^{12}\text{C}^{16}\text{O}$  (99.99%) and Ar (99.99%) were supplied by Matheson of Canada and  $^{13}\text{C}^{16}\text{O}$  (50–55%) by Prochem, N. J. Gas mixtures were prepared by conventional vacuum-line techniques. Matrix gas flows, controlled by a calibrated micrometer needle valve and an Upton-Braden helicoid gauge, were usually in the range 2–8 mmol/hr. In the infrared experiments matrices were deposited onto a CsI window cooled to 4.2–10°K by means of an Air Products liquid helium transfer or closed cycle Displex helium refrigerators. Spectra were recorded on a Perkin-Elmer 180 infrared spectrophotometer.

### Results and Discussion

When Cr atoms were cocondensed with pure  $^{12}\text{C}^{16}\text{O}$  at 4.2–10°K, the major product of the reaction is seen to be  $\text{Cr}(\text{CO})_6$  (referred to as 6 in Figure 1). However, *two* other intense carbonyl absorptions at 1962 and 1933  $\text{cm}^{-1}$  and a third very weak absorption at 2020  $\text{cm}^{-1}$  always accompanied the hexacarbonyl. These three new lines appeared with the *same* relative intensities in a number of different runs in which the Cr:CO ratio was varied by as much as a factor of 100 and are ascribed to a species A. The 1962- and 1933- $\text{cm}^{-1}$  carbonyl absorptions have very similar frequencies and relative intensities (*ca.* 3:1) to those of Turner's pentacarbonyl.<sup>1</sup> Furthermore, annealing of the CO matrix at 40–45°K had essentially *no* effect on the spectrum, a result which parallels the annealing behavior of Turner's pentacarbonyl in Ar/CO matrices.<sup>1</sup>

If A is indeed a coordinatively unsaturated square pyramidal pentacarbonyl, we feel that its reluctance to react with CO is most disquieting, especially in a "pure" CO matrix, and leads us to believe that the vacant coordination site in the  $\text{C}_{4v}$   $\text{Cr}(\text{CO})_5$  fragment is blocked to give one of the complexes shown below containing an isocarbonyl (I) or sideways-bonded  $\pi$ -type carbonyl (II) ligand, respectively.<sup>8</sup>

(5) G. C. Pimentel in "Formation and Trapping of Free Radicals," A. M. Bass and H. P. Broida, Ed., Academic Press, New York, N. Y., 1960, p 77.

(6) H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Spectrosc.*, **14**, 137 (1972).

(7) M. Moskovits and G. A. Ozin, *J. Appl. Spectrosc.*, **26**, 481, 1972.

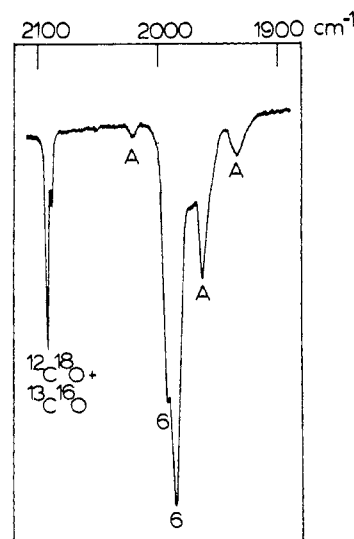
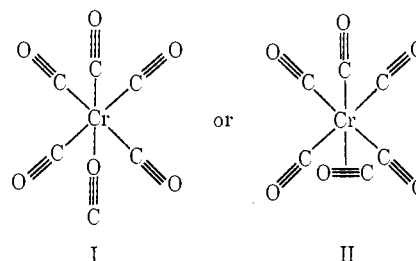
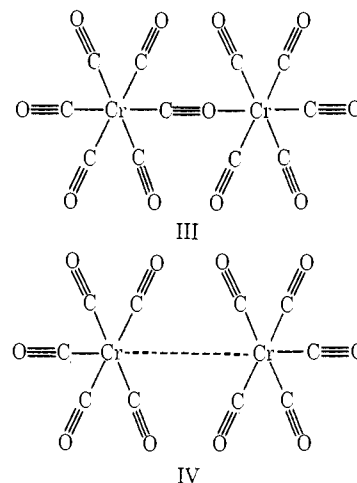


Figure 1. The matrix infrared spectrum of the products of the cocondensation reaction of Cr atoms and pure  $^{12}\text{C}^{16}\text{O}$  at 4.2°K (see text for notation).



That this set of circumstances does not favor the most stable configuration of a truly pentacoordinate  $\text{Cr}(\text{CO})_5$  species stems from our results in dilute CO/Ar matrices, which yield evidence for *all* of the species  $\text{Cr}(\text{CO})_n$  (where  $n = 1-5$ ). Full details of this work will be reported in a forthcoming publication.<sup>10</sup> When

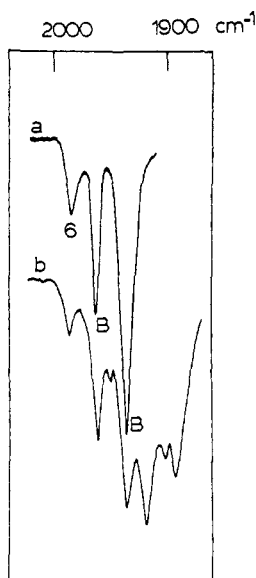
(8) (a) Although impossible to check by mixed isotope experiments, it is conceivable that the weak absorption at 2020  $\text{cm}^{-1}$  is the stretching mode of the isocarbonyl (I) or sideways-bonded carbonyl (II) ligand. It is worth noting that the data do not preclude the formation of a bridged complex (III) or a weakly interacting dimer (IV) of the types shown below



which are both acceptable formulations for A in pure CO. (b) We note that similar suggestions to our isocarbonyl and side-on-bonded carbonyl have previously been made by Gray, *et al.*, in an emission study of some tungsten carbonyl complexes.<sup>9</sup>

(9) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 4336 (1971).

(10) E. P. Kündig and G. A. Ozin, to be submitted for publication.



**Figure 2.** The matrix infrared spectrum of the products of the cocondensation reaction of Cr atoms with (a)  $^{12}\text{C}^{16}\text{O}:\text{Ar} \approx 1:20$  after warm-up to 30–35°K and (b) with  $^{12}\text{C}^{16}\text{O}:^{13}\text{C}^{16}\text{O}:\text{Ar} \approx 1:1:40$  after warm-up to 30–35°K. (See text for notation.)

Cr atoms are cocondensed with  $^{12}\text{C}^{16}\text{O}:\text{Ar} = 1:20-1:100$  mixtures at 4.2–10°K and then annealed at 30–35°K, a single species is produced having *two* CO stretching modes at 1964 and 1937  $\text{cm}^{-1}$  with relative intensities approximately equal to 2:3 (referred to as **B** in Figure 2a), quite different from species A and from Turner's pentacarbonyl (both *ca.* 3:1).

The results of the corresponding mixed isotope experiment,  $^{12}\text{C}^{16}\text{O}:^{13}\text{C}^{16}\text{O}:\text{Ar} = 1:1:40$ , yield a definitive isotope pattern (Figure 2b) for a  $D_{3h}$  trigonal bipyramidal pentacarbonyl  $\text{Cr}(^{12}\text{C}^{16}\text{O})_n(^{13}\text{C}^{16}\text{O})_{5-n}$  and therefore specify the original 1964- and 1937- $\text{cm}^{-1}$  carbonyl absorptions as the  $A_2''$  (axial) and  $E'$  (equatorial) asymmetric CO stretching modes, in agreement with their observed relative intensities of 2:3.

For the purposes of this brief discussion, the isotope pattern expected for the trigonal bipyramidal molecules  $\text{Cr}(^{12}\text{C}^{16}\text{O})_n(^{13}\text{C}^{16}\text{O})_{5-n}$  (where  $n = 0-5$ ) is most easily understood by visualizing the pentacarbonyl as being composed of a triangular planar  $\text{Cr}(^{12}\text{C}^{16}\text{O})_p(^{13}\text{C}^{16}\text{O})_{3-p}$  (where  $p = 0-3$ ) equatorial residue and a linear  $\text{Cr}(^{12}\text{C}^{16}\text{O})_q(^{13}\text{C}^{16}\text{O})_{2-q}$  (where  $q = 0-2$ ) axial residue. This model assumes that the coupling between the axial and equatorial CO stretching modes is small and that we can therefore approximate the spectrum of  $\text{Cr}(^{12}\text{C}^{16}\text{O})_n(^{13}\text{C}^{16}\text{O})_{5-n}$  to a superposition of the  $D_{3h}$   $\text{Cr}(^{12}\text{C}^{16}\text{O})_p(^{13}\text{C}^{16}\text{O})_{3-p}$  and  $D_{\infty h}$   $\text{Cr}(^{12}\text{C}^{16}\text{O})_q(^{13}\text{C}^{16}\text{O})_{2-q}$  isotope patterns.

For all isotopic species of the  $D_{3h}$  residue there are eight ir active modes of which one mode of  $\text{Cr}(^{12}\text{C}^{16}\text{O})(^{13}\text{C}^{16}\text{O})_2$  is degenerate with the  $E'$  mode of  $\text{Cr}(^{13}\text{C}^{16}\text{O})_3$  and one mode of  $\text{Cr}(^{12}\text{C}^{16}\text{O})_2(^{13}\text{C}^{16}\text{O})$  is degenerate with the  $E'$  mode of  $\text{Cr}(^{12}\text{C}^{16}\text{O})_3$ , leaving six modes to be accounted for. Of these, two in-phase, high-frequency  $^{12}\text{C}^{16}\text{O}$  stretching modes can reasonably be expected to be weak (see, for example,  $M(^{12}\text{C}^{16}\text{O})_p(^{13}\text{C}^{16}\text{O})_{3-p}$ <sup>11,12</sup> where  $M = \text{Ni}, \text{Pd}, \text{or Pt}$ ,  $p = 0-3$ )

(11) E. P. Kündig, D. McIntosh, M. Moskovits, and G. A. Ozin, *J. Amer. Chem. Soc.*, **95**, 7234 (1973).

(12) J. H. Darling and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 2496, 1972, 1097 (1973).

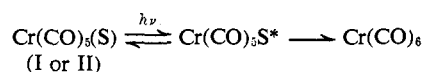
and may overlap with the very strong absorptions of *free*  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$  which are always present in the matrix.<sup>11,12</sup> One can therefore reasonably expect to observe 4 ir modes for this residue.

For all isotopic species of the linear  $\text{Cr}(^{12}\text{C}^{16}\text{O})_q(^{13}\text{C}^{16}\text{O})_{2-q}$  residue, four modes are ir active. However, the in-phase, high-frequency  $^{12}\text{C}^{16}\text{O}$  stretching mode can be expected to be weak (see, for example,  $M(^{12}\text{C}^{16}\text{O})_q(^{13}\text{C}^{16}\text{O})_{2-q}$ <sup>11,12</sup>) and/or could be masked by the  $T_2$   $^{12}\text{C}^{16}\text{O}$  stretching mode of small concentrations of free  $\text{Cr}(\text{CO})_6$ . One can then expect to observe three ir modes for this residue. Because of the anomalously high intensity of the  $A_2''$   $\text{Cr}(^{13}\text{C}^{16}\text{O})_5$  line at 1921  $\text{cm}^{-1}$ , a single accidental coincidence is postulated. Hence, excluding the  $A_2''$  and  $E'$   $^{12}\text{C}^{16}\text{O}$  stretching modes of  $\text{Cr}(^{12}\text{C}^{16}\text{O})_5$ , *four* new lines are predicted and *four* are observed (1953, 1921, 1902, and 1892  $\text{cm}^{-1}$ ) below 1964  $\text{cm}^{-1}$ . The observed isotope pattern is quite distinct from that predicted for a square pyramidal pentacarbonyl.

The low-frequency region was examined carefully for absorptions which could be assigned to Cr–C or Cr–O stretching modes. However, as is often found to be the case in low concentration matrix studies of carbonyl complexes, only very weak absorptions were observed in the region 460–430  $\text{cm}^{-1}$  and, apart from the  $\text{Cr}(\text{CO})_6$  band at 448  $\text{cm}^{-1}$ , were impossible to assign with any degree of certainty.

Under these conditions, where the pentacarbonyl (**B**) is essentially *free* from the effects of "matrix cage CO interactions," thermal annealing at 40–45°K causes the trigonal bipyramidal pentacarbonyl to react with CO to give  $\text{Cr}(\text{CO})_6$ .<sup>13</sup> Particularly noteworthy during this annealing process is the concomitant *reversal* in the absorption intensities of the 1964- and 1937- $\text{cm}^{-1}$  lines, tending finally toward the situation described for  $\text{Cr}(\text{CO})_5\text{S}$ .

We can conclude by stating that the results of this study authenticate the existence of a trigonal bipyramidal form (**B**) of  $\text{Cr}(\text{CO})_5$  in argon matrices. The warm-up data prove that of the "truly" pentacoordinate species the trigonal bipyramidal form is the thermodynamically most stable. However, the trigonal bipyramidal pentacarbonyl (**B**) *does* react further with CO in Ar to give  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5\text{S}$  (**A**  $\equiv$  I or II). This process necessitates a molecular rearrangement of the pentacarbonyl skeleton which results in a kinetically slow process at the low temperatures employed. These results imply therefore that Turner's pentacarbonyl is not a true pentacarbonyl but is a  $\text{Cr}(\text{CO})_5\text{S}$  species where S represents the photo-detached CO ligand, interacting with the  $C_{4v}$  pentacarbonyl fragment in either configuration I or II, within the matrix cage. One can then envisage a simple mechanism for Turner's reverse photolysis as follows



which involves absorption of light by the "caged"  $\text{Cr}(\text{CO})_5\text{S}$  complex, followed by molecular rearrangement

(13) It is worth noting that the frequency difference between  $\text{Cr}(\text{CO})_6$  in pure CO and in dilute CO/Ar (1:10  $\rightarrow$  1:500) matrices is quite small; i.e.,  $\text{Cr}(\text{CO})_6$  in CO shows a doublet (matrix splitting<sup>1</sup>) at 1992.0/1986.8  $\text{cm}^{-1}$  while  $\text{Cr}(\text{CO})_6$  in Ar shows a single line at 1988  $\text{cm}^{-1}$ .

of the isocarbonyl or sideways-bonded carbonyl to yield  $\text{Cr}(\text{CO})_6$ .

### Structure and Bonding of Transition Metal Pentacarbonyls and Pentacarbonyl Anions

Using matrix synthetic techniques, a number of new pentacarbonyl species have become accessible to study by spectroscopic methods of analysis. The infrared spectra of these species have been most informative, establishing the molecular structures shown in Table I.

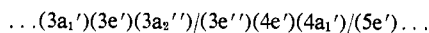
**Table I.** Molecular Structures and Electronic Configurations of Some Pentacarbonyl Species

Penta-carbonyl	Stereo-chemistry <sup>b</sup>	No. of valence shell electrons	Ref
$\text{V}(\text{CO})_5$	SP ( $C_{4v}$ )	15	10
$\text{Cr}(\text{CO})_5$	TB ( $D_{3h}$ )	16	This study
$\text{MeMn}(\text{CO})_4^a$	TB ( $C_{3v}$ )	16	c
$\text{HMn}(\text{CO})_4^a$	TB ( $C_{3v}$ )	16	c
$\text{Mn}(\text{CO})_5$	SP ( $C_{4v}$ )	17	d
$\text{Cr}(\text{CO})_5^-$	SP ( $C_{4v}$ )	17	e
$\text{Fe}(\text{CO})_5$	TB ( $D_{3h}$ )	18	f
$\text{Mn}(\text{CO})_5^-$	TB ( $D_{3h}$ )	18	g

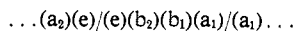
<sup>a</sup> Although these are not formally pentacarbonyls, they are included for the purposes of comparison, being trigonal bipyramidal pentacoordinate carbonyl species isoelectronic with  $\text{Cr}(\text{CO})_5$ .

<sup>b</sup> SP = square pyramidal; TB = trigonal bipyramidal. <sup>c</sup> A. J. Rest and J. J. Turner, *Chem. Commun.*, 375 (1969). <sup>d</sup> H. Huber, E. P. Kündig, G. A. Ozin, and A. J. Poë, *Can. J. Chem.*, in press. <sup>e</sup> P. A. Breeze and J. J. Turner, *J. Organometal. Chem.*, **C7**, 44 (1972). <sup>f</sup> R. V. G. Evans and M. W. Lister, *Trans. Faraday Soc.*, **72**, 1107 (1950). <sup>g</sup> W. F. Edgell, J. Huff, J. Thomas, H. Lehman, L. Angell, and G. Asato, *J. Amer. Chem. Soc.*, **82**, 1254 (1960); B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, **11**, 1109 (1972).

Isoelectronic species are grouped together according to whether they contain 15, 16, 17, or 18 electrons in their outer valence shells and it can be seen that isoelectronic species (presumably in their most stable configurations) are also isostructural. Secondly, *even* (16 or 18) electron valence shell species have trigonal bipyramidal stereochemistries while *odd* (15 or 17) electron valence shell species have square pyramidal stereochemistries. These stereochemical changes are clearly electronic in origin and can be rationalized most easily in terms of the generally accepted MO sequences for transition metal trigonal bipyramidal and square pyramidal complexes<sup>14</sup>



and

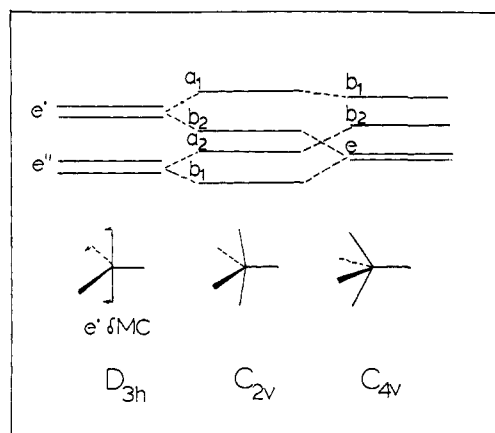


respectively, where the d orbital manifolds are enclosed in parentheses.

Assuming that the low-spin configuration is adopted by the  $\text{M}(\text{CO})_5$  species, which is not unreasonable in the light of, for example, low-spin  $\text{Cr}(\text{CO})_6$ , then it is seen that the  $e''$  ( $d_{xy}, d_{zz}$ ) levels are filled and the  $e'$  ( $d_{xz}, d_{yz}$ ) levels partially filled for the 15- and 17-electron pentacarbonyls. These molecules will both be subject to first order Jahn–Teller<sup>15</sup> distortions from a  $D_{3h}$  trigonal bipyramidal towards a  $C_{4v}$  square pyra-

(14) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 1252, 4947 (1969).

(15) H. A. Jahn and E. Teller, *Proc. Roy. Soc., Ser. A*, **161**, 220 (1937).



**Figure 3.** Molecular orbital correlation diagram and types of Jahn–Teller distortions for a trigonal bipyramidal  $\text{M}(\text{CO})_5$  species with a partially filled  $e'$  level (note that only the  $e''$  and  $e'$  states of the  $D_{3h}$  molecule are considered and that the  $x$  and  $z$  axes have been interchanged to facilitate a straightforward correlation from  $D_{3h}$  to  $C_{4v}$ ).

midal structure.<sup>16</sup> The latter itself is not unstable with respect to first-order Jahn–Teller distortions but the 17-electron  $C_{4v}$  system is predicted to be unstable with respect to a  $B_1$  vibration toward a  $C_{2v}$  structure (Figure 3) through a second-order Jahn–Teller effect.<sup>14</sup> Whether this instability is of a kinetic type (*i.e.*, a finite but low activation barrier) leading to facile interconversion of  $C_{2v}$  and  $C_{4v}$  forms or whether it is thermodynamic so that there is effectively no barrier to the  $C_{4v} \rightarrow C_{2v}$  distortion, the latter form, being more stable, appears to depend on the energy gap between the highest filled and lowest empty molecular orbital.<sup>14</sup>

The 16- and 18-electron, low-spin pentacarbonyls are stable toward first-order Jahn–Teller distortions in either the  $D_{3h}$  or  $C_{4v}$  forms. The 18-electron system is predicted to be unstable toward interconversion by a second-order Jahn–Teller effect, provided the energy gap is small enough. This instability is evidently not sufficient to make the intermediate  $C_{2v}$  form the most stable, but interconversion of apical and equatorial carbonyl ligands is evidently very easy, presumably *via* the  $D_{3h} \leftrightarrow C_{4v}$  mechanism.<sup>17</sup>

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(16) There is considerable debate over the ordering of the  $e$  and  $b_2$  levels in  $C_{4v}$   $\text{M}(\text{CO})_5$  species. The ordering of levels has been shown to be quite sensitive to the angle  $\text{CO}_{ax}\text{-M-CO}_{eq}$ : Guenzburger, *et al.*, *Chem. Phys. Lett.*, **14**, 239 (1972). Thus, if the  $e$  level lies higher than the  $b_2$ , the 15-electron  $C_{4v}$   $\text{V}(\text{CO})_5$  species will be susceptible to a first-order Jahn–Teller distortion.

(17) Support for this idea stems from Basolo and Keeton's recent photochemical substitution reactions<sup>18</sup> of  $\text{Mn}(\text{CO})_5(\text{NO})$  with  $\text{P}(\text{C}_6\text{H}_5)_3$ . To explain the  $\text{S}_{\text{N}}2$  pathway for this reaction, they proposed a mechanism for pentacoordinate molecules in which an electron was excited from the 18-electron valence shell of the metal and isolated on the NO group, thereby stabilizing a  $C_{4v}$  tetragonal pyramid structure for  $\text{Mn}(\text{CO})_5(\text{NO})$  in its first excited state. The nucleophile can then react with this stabilized  $C_{4v}$  structure to form a six-coordinate intermediate which then goes on to product.

(18) D. P. Keeton and F. Basolo, *Inorg. Chim. Acta*, **6**, 33 (1972).