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(22) Reference 6, p 238.
(23) (a) Cf. P. Meakin, E. L. Muetterties, and J. P. Jesson, J. Amer. Chem. Soc., 95, 75 (1973). (b) It should be noted that an alternative rationale of the line-shape changes is in quadrupolar relaxation effects.
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(28) Plausible structural alternatives are a "bidentate" allyl ligand bridging two equatorial sites or an equatorial and an axial site in an idealized trigonal bipyramid, provided there is fast rotation of the allyl group in the C_3 plane, and bridging an apical and basal site (free allyl group rotation) or two basal sites of an idealized square pyramid. In the last case, there would be the possibility of two diastereomers unless allyl group rotation

in the C_3 plane is fast. Geometric distinctions among all alternatives are small. A crystallographic study of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ is planned.
(29) An alternative based on trigonal bipyramidal or square pyramidal structural forms[27] comprises some type, e.g., a Berry process, of five-coordinate rearrangement. In these alternative idealized structural forms, rotation of the allyl ligand about some CoP_3 axis will not lead to environmental equivalence of phosphorus atoms. Assuming solution state structure emulates closely the solid state structure, the planned[27] crystallographic study may resolve this point if the solid state structure is very close to either of these two[27] idealized structures.
(30) The $\eta^3 \rightleftharpoons \eta^1$ conversion is postulated as a first step in the catalytic function of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ in aromatic hydrocarbon hydrogenations, E. L. Muetterties and F. J. Hirsekorn, J. Amer. Chem. Soc., 96, 4063 (1974).
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Carbon-13 Nuclear Magnetic Resonance Study of the Fluxional Behavior of Cyclooctatetraenetricarbonylchromium, -molybdenum, and -tungsten and Tetramethylcyclooctatetraenetricarbonylchromium

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Abstract: The fluxional behavior of 1,3,5,7-tetramethylcyclooctatetraenetricarbonylchromium, (TMCOT)Cr(CO)$_3$, previously shown by ^{1}H nmr to be based on a single, reversible type of 1,2-shift has been reexamined with ^{13}C nmr. The previous conclusions are confirmed. For the cyclooctatetraenetricarbonyl metal compounds, (COT)M(CO)$_3$, M = Cr, Mo, or W, for which no pathway had previously been established, ^{13}C nmr shows conclusively that 1,2-shifts are not the pathway and that only 1,3-shifts or a process resulting in random shifts are admissible. While 1,3-shifts cannot be ruled out rigorously, it is argued that a process in which the metal atom moves to a position over the midpoint of a virtually flat octagonal ring whence it can pass with equal probability to any of the eight equilibrium positions is more likely. On this basis the qualitatively different behavior of the (TMCOT)M(CO)$_3$ and (COT)M(CO)$_3$ compounds can be understood as arising from the different energies required to flatten the rings.

For almost a decade now there has been much interest in stereochemically nonrigid molecules. Conjugated cyclopolyenemetal compounds such as (COT)M(CO)$_3$, where COT = cyclooctatetraene and M = (Fe, Ru, Os), 1, and (Cr, Mo, and W), 2, have been studied in much detail.[1-8] The bonding of the group VIII and group VI metals to the cyclooctatetraene ring differs[1,9] making a direct comparison of the spectra and dynamical behavior of the two groups inappropriate. Earlier work has been reviewed[2,10] previously in detail. The rearrangement process for the group VIII metals has been shown directly from the fitting of simulated spectra to have an omnidirectional 1,2-shift mechanism. Because of the extensive spin-spin coupling, the spectra of the group VI metals were too complex for a dynamical analysis. The mechanism was thus inferred after a study[11] of the isostructural[9,12] (TMCOT)M(CO)$_3$, where TMCOT = 1,3,5,7-tetramethylcyclooctatetraene and M = Cr, Mo, and W, which indicated that a 1,2-shift was operative as the low energy process in the substituted complexes.

Little if anything more could be done to elucidate the mechanism of the site exchange in compounds of type 2 until Fourier transform carbon-13 spectrometers became available. Carbon-13 offers several advantages over proton nmr for the study of fluxional molecules.[13] Of particular relevance here is the fact that the low natural abundance of

carbon-13 eliminates complications due to spin-spin coupling when broad-band proton decoupling is employed. Thus in the present case, compounds 2 should have simple spectra consisting of four discrete lines in the slow exchange limit. As the temperature is raised, the mode of collapse of these peaks, i.e., uniform or selective, can easily be discerned.

The 1,2-shift originally discovered for (COT)Ru(CO)$_3$[4] has been confirmed via carbon-13 for (COT)Fe(CO)$_3$.[14] In a preliminary communication[15] we have reported that (COT)Mo(CO)$_3$ does not undergo a 1,2-shift as the four ring signals broaden uniformly. We have now completed a carbon-13 nmr study of the compounds 2 as well as (TMCOT)Cr(CO)$_3$ and report the results in detail here.

Experimental Section

The compounds were all prepared by methods described previously.[6,11,16-18] All samples were handled under nitrogen. Solvents were dried over Na-K benzophenone and distilled just prior to use.

Instrumental Measurements. The proton nmr spectra were measured on a Varian Associates HA-100 spectrometer. Temperature calibrations for the variable temperature spectra were obtained from either methanol or ethylene glycol standards and are expected to be accurate to ±3°.

Carbon-13 nmr spectra were recorded on a Jeol PFT-100/Nicolet 1080 Fourier transform spectrometer at 25.035 MHz. The

Table I. Chemical Shift of Ring Carbon Atoms in the Cyclooctatetraene Complexes

Metal	Solvent	Chemical shift (ppm)				Temp, °C	Dec, °C
Cr	Toluene[a]	131.9	106.5	102.7	93.1	−25	
	Toluene[a]		108.2			+40	<80
	Acetone-d_6	131.9	106.5	104.4	94.9	−25	
Mo	Toluene[a]	131.7	105.0	101.4	88.5	−20	
	Toluene		106.7			+95	>95
	CDCl$_3$–toluene	131.8	105.0	101.8	88.6	−20	
W	Tetrachloro-ethane[a]	133.2	101.3	98.6	82.1	0	<85

[a] External lock used.

Table II. Carbonyl Chemical Shift Data

	Shift, ppm		Temp, °C
(COT)Cr(CO)$_3$	244.4	225.8	−64
		231.2	+80
(COT)Mo(CO)$_3$	228.2	213.5	−60
		218.2	+41
(COT)W(CO)$_3$[a]		207	+44

[a] A high boiling solvent, tetrachloroethane, was used for the W complex in an attempt to observe the fast exchange process in the ring. As a result temperatures could not be lowered enough to see the slow exchange spectrum of the carbonyls.

samples were dissolved in freeze–thaw degassed solvents and transferred to a 10-mm diameter serum stoppered tube using inert atmosphere techniques. The temperatures were measured with a copper–constantan thermocouple inserted into an nmr tube and read on a Leeds and Northrup Model 913 digital thermometer. The temperature was set by placing the thermocouple in the probe and was again checked after each run and found to be invariant within ±2°. Chemical shifts were measured relative to TMS (±0.1 ppm) and 40 mg of Cr(acac)$_3$ were added to aid in relaxation of the carbonyls.[19]

Results

The variable temperature carbon-13 nmr spectra have been recorded for the (COT)M(CO)$_3$ compounds over a temperature range extending from the slow exchange to the intermediate exchange region in a variety of solvents. Protio- rather than deuteriotoluene was used since the broad multiplet arising from the C–D coupling obscured the downfield ring signal. It was therefore necessary to use an external lock, but no extraneous peak broadening or other peculiarities were noted when compared to the results that were obtained using 20% CDCl$_3$ for internal locking.

Table I gives the chemical shifts for the ring carbon atoms in the different solvents. For each of the three compounds **2**, the four peaks representing the four carbon environments in the ring all broadened at the same rate.

A definite assignment of all the ring peaks cannot be made based on the data collected. Previous results[20,21] suggest that complexing a polyolefin results in an upfield shift with the terminal coordinated carbon atoms being shifted farthest upfield. The central carbon atoms of the polyolefin are shifted less far upfield. Free cyclooctatetraene gives one peak at room temperature at 132.6 ppm. Thus we can be fairly certain in assigning the downfield signals at 133–130 ppm to the carbon atoms containing the free olefin.

We have not attempted to collect a set of data suitable for a complete, quantitative line-shape analysis that would provide activation parameters, since we have no need for such quantities at this time. From a comparison of the spectra with one another, useful conclusions as to relative rates and activation energies can be obtained.

The slow exchange spectrum appeared at −25, −20, and

Table III. Chemical Shift Data for (TMCOT)Cr(CO)$_3$[a]

	C-CH$_3$	C-H	−CH$_3$
(TMCOT)Cr(CO)$_3$[b]	139.8	126.3	31.6
	114.2	106.7	29.5
	112.9	104.7	26.7
	112.0	89.5	23.2
TMCOT	138.5	128.6	23.8
J_{CH} (Hz)	0.0	150.5	25.7

[a] ±0.1 ppm in tetrachloroethane with 20% CDCl$_3$ for internal locking. [b] Spectrum recorded in the slow exchange region at −24°.
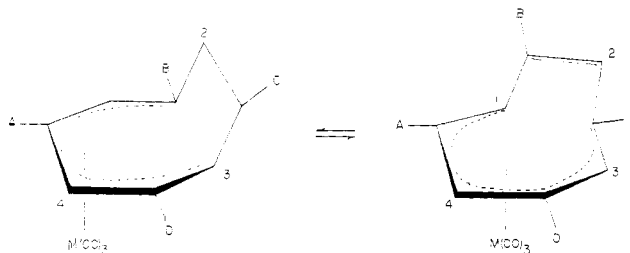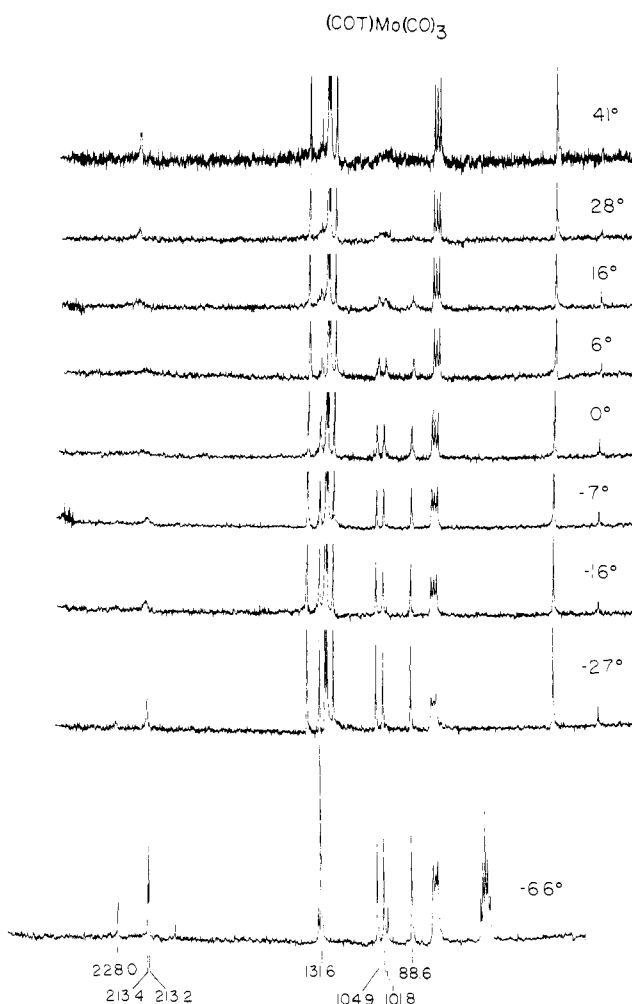
Figure 1. The low energy 1,2-shift for (TMCOT)M(CO)$_3$.

Figure 2. Spectra of C$_8$H$_8$Mo(CO)$_3$ at various temperatures. The four ring carbon resonances are those upfield with numerical values of the chemical shifts marked. The carbonyl carbon resonances are those downfield with their chemical shifts marked. The lower (−66°) spectrum was recorded in CDCl$_3$–CD$_2$Cl$_2$ while the others were run in CDCl$_3$–toluene. Lines not due to the sample in the 41° spectrum are due to toluene ring carbons (*ca.* 130 ppm), CDCl$_3$ (*ca.* 77 ppm) and TMS (0 ppm). A weak line due to free C$_8$H$_8$ can be seen at *ca.* 133 ppm in the −66 and 41° spectra.

0° for Cr, Mo, and W, respectively. The coalescence temperatures, each ±5°, occurred at 22, 28, and 63°, respectively. At 80° for Cr and 95° for Mo, the fast exchange spectrum was just beginning to appear when noticeable decomposition terminated the experiment. These results indicate that the activation energies for rearrangement decrease in the order W > Mo > Cr, assuming that frequency factors are substantially identical.

Table II gives the chemical shifts of the carbonyl carbon atoms of 2. The temperatures at which the ring and the carbonyl rearrangements take place differ markedly; the limiting spectrum for the carbonyls is in each case about 30° below that for the ring.

The temperature-dependent spectra of (TMCOT)-Cr(CO)₃ were recorded and the chemical shift data are given in Table III. Again complete assignments cannot be made, but the signal farthest downfield for each type of ring carbon can be assigned to the free olefin carbon atoms. The difference between the $C-H$ and $C-H_3$ carbon atoms is readily detected by the difference in intensity resulting from the nuclear Overhauser effect for the $C-H$ carbon atoms. When the temperature is raised from −24 to +16°, an averaging of carbon atoms 1 and 3 is observed, while carbon atoms 2 and 4 do not interchange. The process representing the low energy rearrangement is depicted in Figure 1.

The variable temperature proton nmr spectra were recorded for (COT)M(CO)₃ where M = Cr and Mo. The results were the same as previous ones[6,22] confirming that we were studying the desired molecules and that proton data do not yield mechanistic information.

Discussion

There are several mechanisms that are to be considered in explaining the site exchange in the (COT)M(CO)₃ compounds. Random shifts as well as the several 1,n- shifts, where n = 2, 3, 4, and 5, should be considered. The mechanism that was previously inferred[11] from the low energy process of the isostructural TMCOT molecules consisted of 1,2-shifts. Only carbon-13 data can test this assumption, and symmetrical collapse of the four peaks in the COT molecules as shown in Figure 2 is inconsistent with this pathway.

In order to be sure that 1,2-shifts could be completely ruled out, we recorded the temperature-dependent spectra of (TMCOT)Cr(CO)₃ in the region of the low energy process, previously studied by proton nmr. This allowed us to confirm that our instrument is fully sensitive to the selective collapse that results from the 1,2-shift process. The spectra in Figure 3 from −24 to +45° demonstrate conclusively that the selective collapse resulting from a 1,2-shift process can be observed. It also confirms that the low energy process in TMCOT compounds is indeed a reversible 1,2-shift where the metal does not "cross" a methyl substituted carbon atom. All of the qualitative conclusions previously discussed[11] for the proton spectra as to the relations between observed line-shape variations and the different rearrangement processes can be applied, mutatis mutandis, to the ³C spectra and that analysis need not be reiterated here.

For the (COT)M(CO)₃ compounds the 1,4- and 1,5-, as well as the 1,2-shifts, can be ruled out since, for each one, two of the lines should have initial rates of broadening that are twice as great as for the other two. Only 1,3-shifts and random shifts remain as possible pathways since each of these would cause uniform (i.e., nonselective) collapse of the four resonances.

There are two factors that caused us to rule out the 1,3-mechanism. First of all there are no known molecules where

Scheme I

etc.
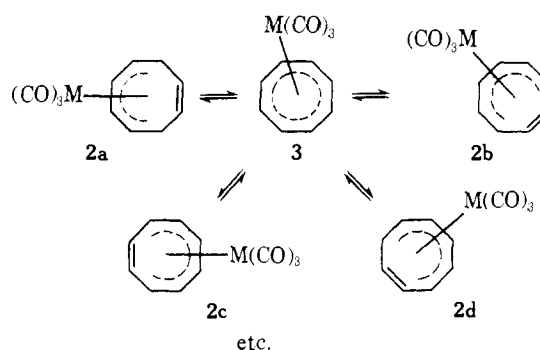
a cyclic polyolefin undergoes a 1,3-shift.[10] This in itself does not merit dismissing the 1,3-shifts but there are molecules[10,23,24] known that would be fluxional if they could undergo a 1,3-shift. Secondly it does not seem credible that the relative motion of the ring to the metal atom required for a 1,3-shift could occur without passage through an intermediate configuration so close to the immediately adjacent minimum-energy configurations as to cause the system to drop into that configuration—i.e., to execute a 1,2-shift. Thus, we are left with only random shifts as a rearrangement pathway for the (COT)M(CO)₃ molecules where M is a group VI metal. We propose that the intimate mechanism is likely to involve a transition state in which the ring has become essentially flat and octagonal (that is, adopted nearly D_{8h}, or at least C_{8v}, symmetry) and the M(CO)₃ group lies over the midpoint, at an equal distance from each ring carbon atom. It can proceed then, with equal probability, to any of the eight ground-state binding positions. This is illustrated in Scheme I.

In this "piano stool" intermediate, where the C₈H₈ ring is the seat and the CO groups the legs, the metal atom can interact with all but two of the ring π-electrons. The two electrons which must be omitted from the ring-to-metal bonding scheme because of the lack of an additional valence orbital on the metal atom would occupy the symmetrical (A_1) π orbital of the ring. In this orbital they have very low energy and such an orbital, being a very large diameter torus, cannot overlap well with any A type orbital $(d_{z^2}, \delta,$ or $p_z)$ of the metal anyway. Thus they are nonbonding electrons with respect to ring-to-metal interaction. With the C₈M₈M(CO)₃ molecules where M is from group VIII, a piano stool intermediate would be strongly destabilized by the presence of yet another pair of electrons which must occupy some sort of E orbital that cannot help but be substantially antibonding. That, we suggest, is why the 1,2-shift path pertains for C₈H₈Ru(CO)₃ but can be, and is, replaced by the path involving the piano stool intermediate in molecules 2.

In the argument rejecting 1,3-shifts because they would structurally lead to 1,2-shifts, we are not unmindful of symmetry arguments. We recognize, of course, that it is the essence of symmetry-based "selection rules," such as the ones propounded by Woodward and Hoffmann[25] and others, that in properly defined cases the proper matching of orbital symmetries can be the determining factor and can cause long jumps to occur in preference to short (i.e., least-action) ones. This has been shown experimentally for a host of
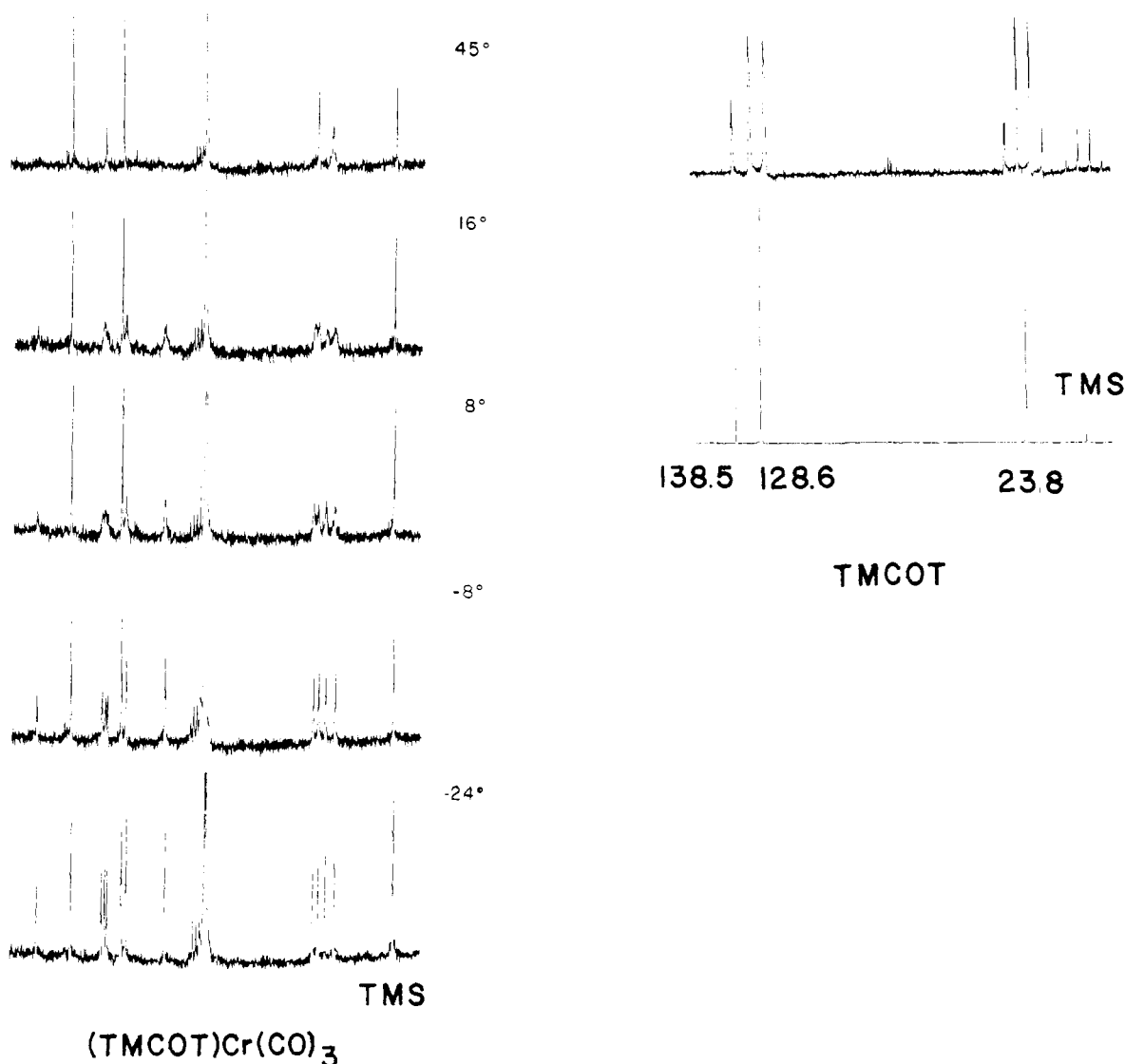
Scheme II
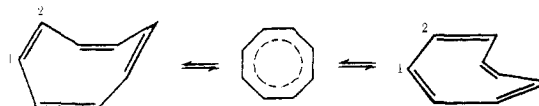
Figure 3. The spectra of (TMCOT)Cr(CO)₃ in the temperature range where the low energy process occurs. The coupled (upper) and broadband proton-decoupled (lower) spectra of TMCOT are shown to the right. The splitting in the coupled spectrum allows a definite assignment to be made which is given in Table III. The 12 different carbons that result when TMCOT is complexed can be seen in the −24° spectrum. Of the eight downfield ring carbons, the four less intense peaks are C-CH_3; the more intense are C-H. The solvent (CDCl₃-tetrachloroethane) signals are the next upfield (*ca.* 75 ppm). The four methyl carbons and their TMS are the upfield signals.

organic molecules and also in the case of $C_7H_7Sn(C_6H_5)_3$.[26] However, in cases such as those we are dealing with, where transition metals are involved, the presence of five d orbitals in the valence shell of the metal means that there are orbitals available to meet any symmetry requirement likely to arise. Thus other factors will become determinative of mechanism since symmetry requirements can be satisfied for all otherwise reasonable mechanistic possibilities.

In view of the discussion so far, one naturally arrives at the question of why a 1,2-shift applies in (TMCOT)M(CO)₃ and not in (COT)M(CO)₃. The answer appears to be in the steric effect of the four methyl groups. This effect is already established semiquantitatively by studies of bond shift in cyclooctatetraene[27] and 1,3,5,7-tetramethylcyclooctatetraene.[28] The bond shifts are believed to require passage through planar transition states, as shown in Scheme II. For C_8H_8 the E_a is <13.7 kcal mol⁻¹ whereas in 1,3,5,7-(CH₃)C₈H₄ it is 21.5 ± 2.0 kcal mol⁻¹. Thus the replacement of four hydrogen atoms by four methyl groups has enough of a steric effect to appreciably destabilize the transition state of the planar molecule.

Applying this to the complexed molecules, it is easy to understand that while (COT)M(CO)₃ could undergo a rearrangement process involving a planar ring, the additional 8 kcal mol⁻¹ required for (TMCOT)M(CO)₃ to achieve a planar ring could make this intermediate inaccessible in competition with the observed twitching 1,2-shift, thus making the latter their low energy process.

It is also noteworthy that the piano stool intermediate is credible in terms of its accessibility from the ground state. In the ground state[9] the metal atom already lies rather close to the central point that will arise as the ring becomes flat, and only the two carbon atoms which form the "uncoordinated" double bond need move very much as the other six are already essentially coplanar.

Carbonyl Scrambling. It should be noted that the scrambling of carbonyl groups among themselves occurs independently of the rearrangement just discussed. Temperatures below −50° had to be employed before the slow exchange spectrum could be obtained. The fact that this process occurs at a lower temperature than that of the ring could, by itself, be attributed to the smaller chemical shift difference involved. However, the actual rates at 10° for the Cr com-

pound are such that the carbonyl rearrangement process is 20 times faster than the ring process. This indicates that even though the motion of the ring can itself average the carbonyls, there is an independent mechanism which does so. This type of independence has been observed before in $C_8H_8Fe(CO)_3$,[14] $C_7H_8Fe_2(CO)_6$,[29] and $C_7H_8M(CO)_3$ where M = Mo and Cr.[30]

Extension to Other Cases. The explanation proposed above for the behavior of the molecules **2** suggests where to look for other cases of random exchange *via* a symmetrical, "piano stool" type intermediate configuration. The principle involved implies that in any case where the metal is attached to a relatively large ring (seven-, eight-, or nine-membered, but probably not six-membered) so as to employ all but one pair of π-electrons, the random shift process may be more facile than the 1,2-shift process. Specific examples which we have commenced to investigate are those containing C_7H_7 rings, such as $C_7H_7Fe(CO)_3{}^+$,[31] and the recently reported C_8H_8Fe (norbornadiene).[32] Compounds with C_7H_7 rings are of special interest because it can easily be shown that for this case all of the 1,n-shift processes, namely, 1,2, 1,3, and 1,4, there will be selective line broadening. Should a uniform pattern of broadening be observed, the occurrence of random shifts will be indicated in a completely unequivocal way, without need for any argument such as the one used in the present case to reject 1,3-shifts.

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Photoelectron Spectra of Some Cyclic Di- and Polyamines. Lone Pair–Lone Pair Interaction in 1,3- and 1,4-Diamines

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Abstract: Nitrogen "lone pair" ionization potentials measured by photoelectron spectroscopy are reported for four bicyclic and four monocyclic 1,3- and 1,4-diamines and for examples of bridgehead di-, tri-, and tetraazaadamantanes. Assignments of the ionizations to symmetric and antisymmetric lone pair orbital combinations based on extended Hückel calculations are consistent with observed vibrational structure in the few cases where such structure was observed. The magnitude of through-space and through-bond contributions to the observed splittings and the possible utility of photoelectron spectroscopy for conformational analysis of 1,3- and 1,4-diamines (not very promising due to a lack of large enough splitting differences between lone pair axial-equatorial and equatorial-equatorial conformers in six-ring systems, causing drastic overlapping of the spectra) are discussed.

Hoffmann has discussed the general importance of through-space and through-bond orbital interactions[1] and several applications of these concepts. One of the nicest examples of such interactions occurs in 1,4-diazabicyclo[2.2.2]octane (Dabco, **1**). The nitrogen lone pair orbitals

have a through space interaction which tends to place n_- higher in energy than n_+. Through bond interaction of n_+ with other orbitals (most importantly the symmetrical σ_{CC} orbital depicted as σ_+ which can be perfectly aligned for maximum lone pair–σ_{CC} overlap) preferentially raises the energy of the (now mixed but still principally) n_+ orbital. Extended Hückel calculations[2] predicted that n_+ would actually be 1.57 eV higher in energy than n_- (MINDO/2 calculations gave a 1.36-eV splitting).[3] This prediction was