pates in the redox reaction can be explained by the occurrence of the reaction

$$R^{3+} + R^0 \longrightarrow R^+ + {}^3(R^{2+})^* \qquad (3)$$

followed immediately by (2) forming additional excited triplet. Similarly, when R^- is the reactant, the reaction

$$R^{3+} + R^- \longrightarrow R^0 + {}^3(R^{2+})^* \qquad (4)$$

occurs first, followed by (3) and (2). For the RRDE electrode, where the flux of R^{3+} at the ring is greatly in excess of the flux at the disk for this same electrode process the occurrence of this sequence of reaction, when either R^+, R^0, or R^-, is generated at the disk, can explain the 1:2:3 ratio of emission intensities observed (Figure 6). This explanation requires that the efficiency of excited state formation is the same for all three redox processes 2–4 and that quenching of the triplet by the electrogenerated intermediates is probably negligible. An alternate explanation is that only a single redox step (2), (3), or (4) occurs but that the efficiency of formation of the excited state increases as the free energy of the redox step increases; the observed 1:2:3 ratio would then have to be coincidental. The observed ratios for single electrode ecl would be explained in a similar manner; theoretical simulation of a case such as this has not yet been accomplished.

Previous spectroscopic studies[4,5] have suggested that the observed emission for $Ru(bipy)_3{}^{2+}$ at 607 nm is derived from an excited triplet state. The photoexcited emissions in solution at room temperature, obtained by Lytle and Hercules[18] and the present work, differ from the spectra taken in rigid glass in that they only exhibit the shortest wavelength emission. In their paper, Klassen and Crosby[21] assign this emission band to 0–0 transition derived from the (d–π*) transition. The longer wavelength emissions are assumed to be 0–1, 0–2, and 0–3 transitions from the same excited triplet state. However, the shoulder at 630 nm, noted in the ecl of $Ru(bipy)_3{}^{2+}$, does not appear in the solution phosphorescence. It appears unlikely that this shoulder represents a transition from triplet $Ru(bipy)_3{}^{2+}$; it perhaps is caused by a different conformation of the complex or by a species such as a dimer, formed during the redox reaction but not during photoexcitation.

Acknowledgment. The support of this research by the Army Research Office, Durham, and the National Science Foundation (NSF GP-31414X) is gratefully acknowledged. We thank Professor K. DeArmond for helpful comments on this work.

On the Pathway of Bridge–Terminal Ligand Exchange in Some Binuclear Metal Carbonyls. Bis(*pentahapto*cyclopentadienyldicarbonyliron) and Its Di(methyl isocyanide) Derivative and Bis(*pentahapto*cyclopentadienylcarbonylnitrosylmanganese)

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Abstract: The previously reported proton (Bullitt, Cotton, and Marks) and carbon (Gansow, Burke, and Vernon) nmr data for $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and new data reported here for $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$ are discussed in terms of possible pathways by which bridge and terminal ligands (CO and/or CH_3NC) can be interchanged. It is shown how all of the data can be understood using two assumptions: (1) bridges open and close only in pairs; (2) rotational barriers in unbridged tautomers contribute critically to activation energies when such rotations are necessary. It is further shown that simple one-for-one bridge–terminal interchanges are not only unnecessary to account for any of the observations but that their occurrence is incompatible with the data for $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$. The published results for rearrangements of $(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_2(NO)_2$ (Marks and Kristoff) are also analyzed using the proposed mechanism.

In 1966 the idea was first proposed[1] that in a polynuclear metal carbonyl, the carbonyl ligands might be able to migrate from bridging to terminal positions and *vice versa*. At that time, the question of rate was not explicitly discussed since it was not relevant to the problem then under consideration.[2] In 1970 bridge–terminal site exchange was again proposed, with the explicit suggestion that it can be rapid and thus afford the basis for fluxional or other stereochemically nonrigid behavior in polynuclear metal carbonyls.[3-6] Specifically, it was shown that the cis

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[1] F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966).

[2] It has recently been shown that the most important one of the particular isomerization processes discussed in 1966 is indeed rapid, thus making $Rh_4(CO)_{12}$ a molecule with fluxional character as remarkable as that of bullvalene: *cf.* F. A. Cotton, L. Krucynski, B. L. Shapiro, and L. F. Johnson, *J. Amer. Chem. Soc.*, **94**, 6191 (1972).

[3] J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 3155 (1970); *Inorg. Chem.*, **11**, 671 (1972).

[4] Although it was observed independently by two groups[5,6] that the ^{59}Co nmr spectrum of $Co_2(CO)_8$ in solution shows only a single signal, despite the fact that infrared studies[7] had shown that both bridged, $(CO_3)Co(\mu\text{-}CO)_2Co(CO)_3$, and nonbridged, $(CO)_4CoCo(CO)_4$, isomers are present, in neither case was the rapid interconversion of the two

and trans isomers of bis(*pentahapto*cyclopentadienyl-μ-carbonyliron), $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, **1** and **2**, rapidly interconvert at room temperature. It was proposed that this interconversion proceeds by (1) pairwise opening of the CO bridges to give a nonbridged tautomer, (2) suitable rotation about the Fe–Fe single bond, and (3) pairwise reclosing of bridges to complete the transformation.

More recently the dynamic properties of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ were revealed in considerably more detail by the work of Gansow, Burke, and Vernon[8] employing ^{13}C nmr spectra at various temperatures. Their data confirmed directly that bridge–terminal site exchanges of the CO groups do occur, as would have been expected from the pathway proposed by Bullitt, Cotton, and Marks for the interconversion of isomers. In addition, Gansow and coworkers observed that bridge–terminal exchange in one of the isomers (which they identified as the trans isomer) is already rapid at low temperatures where neither isomer interconversion nor bridge terminal interchange in the other (cis) isomer is yet rapid enough to influence line shapes. Finally, they found that at about −35° the signals from the cis and the trans isomers begin to broaden simultaneously and they inferred from this that "the cis form may begin intramolecular conversion or may simply begin to participate in the cis–trans equilibration which dominates the cmr and pmr spectra at temperatures above −25°."[9]

We believe it is important to understand from a mechanistic viewpoint why these remarkably specific, separate stages of carbonyl interchange occur. No such explanation has heretofore been presented. We are addressing ourselves to the following questions.

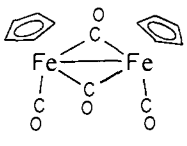
(1) Why is the trans isomer capable of rapidly interchanging its bridge and terminal CO groups at −80 to −40°, while the cis isomer cannot?

(2) How is the trans isomer able to interchange bridge and terminal CO groups rapidly without simultaneously being able to equilibrate rapidly with the cis isomer?

(3) Why is it that cis–trans isomerization and bridge terminal interchange in the cis isomer become rapid enough to cause line broadening at the same temperature?

In this paper we shall first propose a simple scheme which answers these questions fully and neatly. We shall then report for the new compound $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$, in which two CO groups are replaced by methyl isocyanide groups, experimental results which are again highly stereospecific and which can only be satisfactorily interpreted using the same basic scheme. We shall then show that data already reported and partially analyzed for $(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_2(NO)_2$ by Marks and Kristoff[10] are also fully consistent with the proposed scheme. Finally, we shall mention several other conceivable schemes and show that they cannot account for the observations.

Proposed Pathway of Rearrangement. The essential steps are these. (1) For a species which has a pair of bridging groups, *e.g.*, two μ-CO groups or one μ-CO and one μ-CNR, the two bridges open simultaneously, each moving to a terminal position on a different metal atom. Step 1 is accompanied by whatever minimal degree of twist or deformation is necessary to pass into the most directly accessible *staggered* rotational conformation of the unbridged isomer. This is a key requirement of the mechanism. It means, explicitly that when a cis isomer, **3**, opens bridges, it must go to one of the rotamers **4** or **5**; it may not spend any finite length of time in the eclipsed configuration **6** or **7**. This assumption is crucial in accounting for the stereospecificity of the rearrangements (*vide infra*). For a trans isomer, **8**, bridge opening to give the closest accessible staggered configuration would lead to direct formation of **9** or **10**.



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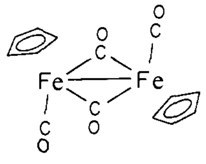

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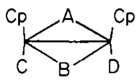

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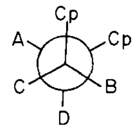

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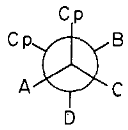

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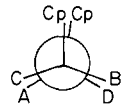

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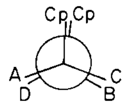

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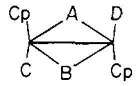

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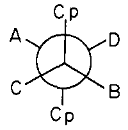

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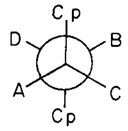

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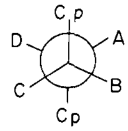

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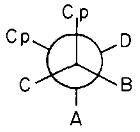

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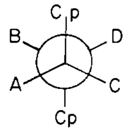

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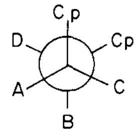

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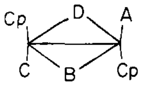

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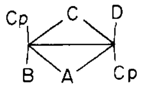

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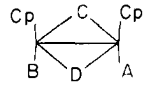

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(2) Rotations by $\pm 2\pi n/3$ (n = 1, 2) may occur con-

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isomers proposed as an explanation. Both groups reported that the signal was extremely broad and, because of complications which could arise from the large quadrupole moment of ^{59}Co, refrained from proposing any definite explanation.

(5) H. Haas and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **29**, 693 (1967).

(6) E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc. A*, 148 (1967).

(7) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963); G. Bor, *ibid.*, **19**, 2065 (1963).

(8) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, **94**, 2550 (1972).

(9) By intramolecular conversion we understand them to mean bridge–terminal interchange.

(10) T. J. Marks and J. S. Kristoff, *J. Organometal. Chem.*, **42**, 277 (1972).

verting, for example, **4** to **11** or **12**, or **5** to **13** or **14**. Such rotations are assumed to be hindered by barriers of the order of magnitude of 5 kcal/mol so that they contribute significantly to the activation energy of any processes in which they must occur.

(3) Any nonbridged rotamer may reclose two bridges simultaneously. Here it is important to respect the principle of microsopic reversibility. Structure **3** can go directly only to **4** or **5** (but not to **11** or **12**) and **3** is also the only bridged isomer which can be recovered from **4** or **5**. Rotamer **11** will generate **15** or **16** and rotamer **12** will generate **17**, none of which are identical with **3**.

We shall now apply these general postulates to the three specific systems for which experimental data are available. Each of these is a special case, less complex than the general case, since the four ligands, A, B, C, and D, are not all different.

$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. For this special case in which the ligands A, B, C, and D are all of the same chemical identity, our mechanistic postulates lead to the scheme shown in Figure 1. It is not our purpose here, nor is it necessary, to consider all of the permutamers and their connexities. It will be obvious that not all of the bridged structures shown are distinguishable unless the two metal atoms (or two cyclopentadienyl rings) are differently labeled.

The only features of this scheme of importance now are the following three. (1) For the trans isomer (see upper part of scheme), in order to move CO groups from bridging to terminal positions, it is only necessary to open the bridges, thus generating a rotamer of C_{2h} symmetry in which all CO groups are now equivalent. Then, *without any internal rotation* bridges may be re-formed using the CO groups which were previously in terminal positions. (2) For the cis isomer (see lower part of scheme) the nonbridged rotamers obtainable directly can only reclose a pair of bridges using the *same* CO's that were initially in bridging positions. *Only after internal rotation* can a cis molecule be re-formed in which bridge–terminal interchange has occurred. (3) The only way any trans isomer can become a cis isomer, or *vice versa*, is if internal rotation occurs in the nonbridged intermediate.

If our second postulate, namely, that there is a significant barrier to internal rotations in the nonbridged species is correct, then the observations of Gansow, *et al.*, can be very neatly accounted for. Bridge–terminal interchange in the trans isomer has a relatively low activation energy because no rotational barrier need be surmounted. Both the process of bridge–terminal interchange in the cis isomer *and* the process of cis–trans interconversion necessitate the same or very similar high-energy internal rotation steps; this causes them both to have equal or nearly equal activation energies which are significantly higher than that for bridge–terminal interchange in the trans isomer.

It should be pointed out, especially in preparation for the use of Figure 1 in subsequent sections of this paper, that the species in the upper and lower parts of the scheme constitute nonoverlapping sets. No species is common to both. The only way that a species in one set can be transformed into some species in the other set is *via* a nonbridged intermediate in which both CO* ligands are simultaneously located on the same metal atom, a so-called unsymmetrical intermediate. One such path connecting species in the upper and lower parts of the scheme is explicitly shown at the right side of the figure. Obviously, when all four ligands are chemically the same the labels (asterisks) have no physical reality and, in $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ for example, all permutamers are accessible to any given molecule. For cases in which there are two ligands of one type and two of another, unsymmetrical intermediates may be too unstable to play a role in the rearrangements. Then, not all species will be accessible from all others. The next two examples will illustrate this possibility amply.

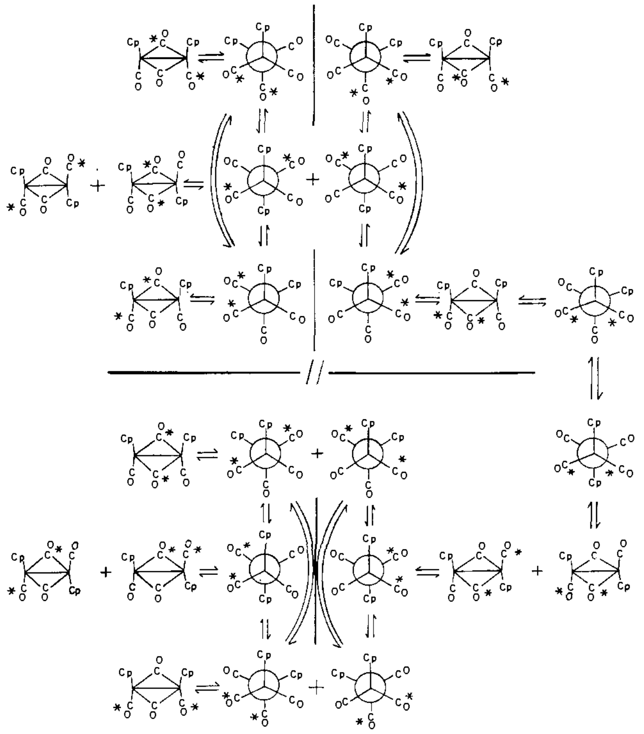

Figure 1. A scheme showing how the various isomers, and isotopomers of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ can interconvert according to the postulates explained in the text (Cp = $\eta^5\text{-}C_5H_5$). Several of the structures shown are identical unless labeling of the iron and/or Cp's is assumed.

$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$. A complete report on the preparation and characterization of this substance will be presented later when our studies of the entire series, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_n(CNCH_3)_{4-n}$, n = 1–3, are published.

The infrared spectrum, recorded using a solution in cyclohexane, consists of the following CO and CN stretching bands (cm^{-1}): 2134(m), terminal CN; 1993(s), 1965(s), 1947(s), terminal CO; 1785(s), bridge CO; 1723(s, broad), bridge CN.

Six bridged isomers must be considered for this substance, as shown in Figure 2. Those two which have two different bridging groups exist as enantiomers.

The presence of the band at 1993 cm^{-1} indicates that a cis isomer having two terminal carbonyl groups must be present. Isomer 1, Figure 2, is the only one which meets this requirement. One of the other two terminal CO bands and the band at 1723 cm^{-1} due to bridging $CNCH_3$ must also be attributed to

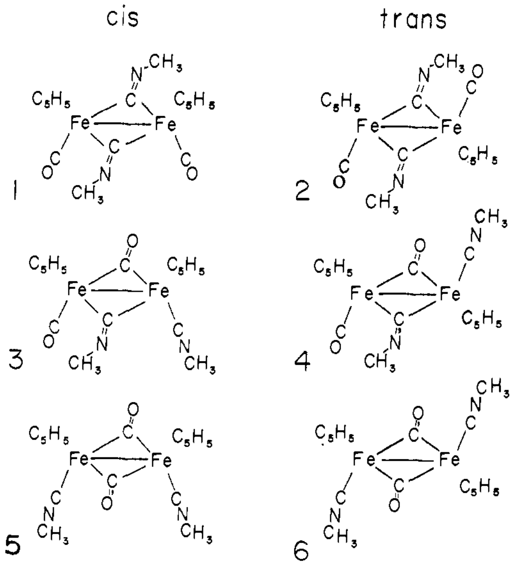

Figure 2. The six positional and geometric bridged isomers of (η^5-$C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$. Isomers 3 and 4 lack any element of symmetry and exist in enantiomers. The orientations shown for the methyl groups in bridging $CNCH_3$ ligands are arbitrary.

this isomer. The remaining ir bands can be assigned to an isomer with one terminal CO group, one bridging CO group,one terminal $CNCH_3$ group, and one bridging $CNCH_3$ group, the latter giving rise to a portion of the band at 1723 cm^{-1}. This second isomer could be either 3 or 4 on the ir evidence alone, but it will be seen presently that it must be 4.

The proton nmr spectrum (Figure 3) in the slow exchange limit confirms these assignments. The signals at τ 5.33 and 6.37, with a 5:3 intensity ratio can be assigned to the cyclopentadienyl and methyl protons of isomer 1. The signals at τ 5.38, 5.47, 6.23, and 7.48, with relative intensities of 5:5:3:3 can be assigned to cyclopentadienyl, cyclopentadienyl, bridging $CNCH_3$, and terminal $CNCH_3$ groups, respectively, of either 3 or 4.

As the temperature is raised the nmr lines broaden and, eventually, at *ca.* 100° there is only one fairly narrow cyclopentadienyl resonance, while the methyl resonances are roughly at their coalescence temperature and no signal is observed. Clearly, the two isomers eventually interconvert rapidly on the nmr time scale. Of particular interest and importance, however, is the fact that prior to isomer interconversion, there is interconversion of the two cyclopentadienyl rings and, simultaneously, bridge–terminal exchange of the $CNCH_3$ groups in the isomer which has one bridging and one terminal $CNCH_3$ ligand.

Exchange rates have been determined by line shape calculations using the computer program EXCHSYS written by Professor G. M. Whitesides of the Massachusetts Institute of Technology.[11] For the lower energy process the line widths of the cyclopentadienyl resonances were used to evaluate residence times, while for the higher energy process the broadening of the methyl resonance of isomer 1 was used. The rates so evaluated were then used to compute the line shapes for the cyclopentadienyl signals throughout the temperature range. These are shown at the left in Figure 3; it can be seen that they match quite well. The rates at various temperatures were then used to evaluate the kinetic activation parameters for each process. These results are given in Table I.

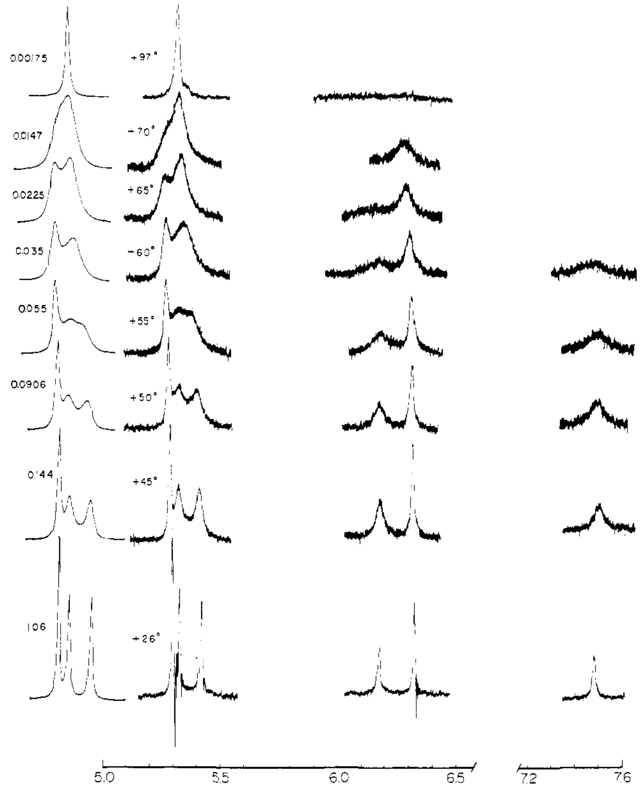

Figure 3. The proton nmr spectra of (η^5-$C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$ at various temperatures, using *o*-dichlorobenzene as solvent. At left are computer simulated spectra for various residence times (sec) based on the exchange processes described in the text.

Now let us consider how the six structures shown in Figure 2 can be interconverted according to the mechanistic postulates presented above and see if predictions consistent with all of the experimental data can be obtained.

Let us ask first, "What are the isomers accessible from isomer 1?" The lower part of Figure 1 supplies the answer if we read $CNCH_3$ for CO*. Isomer 1 can be converted to either enantiomer of isomer 4 and to isomer 5. These three structural isomers form a closed set. Similarly isomer 2 can only be transformed into the enantiomers of 3 and into 6. These latter three form another closed set. The upper part of Figure 1 illustrates this. Thus, the scheme which results from our postulates is fully consistent with the very singular experimental observations. Given that isomer 1 is present, the other isomer present must be 4. Evidently isomer 5 is just not stable enough thermodynamically to exist in equilibrium with 1 and 4 at a detectable concentration. Also, once again, we see that the lower activation energy (by *ca.* 3 kcal/mol) for bridge–terminal ligand exchange in isomer 4 as compared to the activation energy for isomer interconversion can be readily understood within the framework of our postulates. One important factor is that isomer interconversion requires internal rotation whereas bridge–terminal interchange accompanied by site exchange of the cyclopentadienyl groups in isomer 4 can proceed without internal rota-

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[11] For details see J. K. Krieger, Ph.D. Thesis, Massachusetts Institute of Technology, 1971.

Table I. Kinetic Activation Parameters for Rearrangements in the $(\eta^5\text{-}C_5H_5)_2(CO)_2(CNCH_3)_2$ System

Process	Solvent	E_a, kcal/mol	Log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}_{298}$, kcal/mol
Lower temp	$o\text{-}C_6H_4Cl_2$	19.8 ± 1.0	14.5 ± 1.0	19.2 ± 1.0	5.6 ± 2.5	17.5 ± 1.0
Higher temp	$o\text{-}C_6H_4Cl_2$	23.0 ± 1.0	15.8 ± 1.0	22.3 ± 1.0	11.6 ± 3.5	18.9 ± 1.0

tion. There may, of course, be other contributory factors arising from possible intrinsic differences in activation energies for the opening and closing of isonitrile bridges as compared to carbonyl bridges.

$(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_2(NO)_2$. Marks and Kristoff[10] have reported that this compound exists in solution as a mixture of cis and trans isomers, each with a structure in which there is one CO bridge and one NO bridge. From the proton nmr spectra at temperatures from −62 to 40° they concluded that each of the two isomers rearranges intramolecularly so as to make its two sets of ring protons equivalent at about room temperature. In effect, within each isomer the metal atom initially having the terminal NO ligand becomes the one with the terminal CO ligand and *vice versa.* This exchange can occur more rapidly in each isomer than the rate at which the isomers interconvert with each other.

Although Marks and Kristoff proposed an explanation for these facts that is correct as far as it goes, certain details are left obscure. We therefore analyze the results in terms of our scheme both to show that it is applicable and to make the basically correct explanation advanced by Marks and Kristoff more precise as to one detail.

Again, Figure 1 may be used. In order to do so, the CO* groups are to be regarded as NO groups. End-to-end scrambling of ligands can occur in the trans isomer without the occurrence of rotation in the nonbridged intermediate, whereas the same net result in the cis isomer can only occur if there is a rotation step. Consistent with this, scrambling occurs more easily in the trans isomer than in the cis one, although in this case the difference is small. That the difference exists is quite apparent in the spectra, but Marks and Kristoff's line shape analysis suggested that the difference in activation energies is perhaps less than 1 kcal/mol.

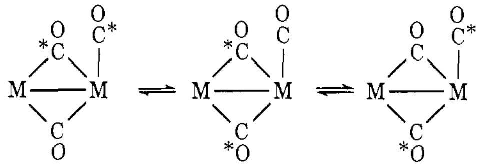
It is clear from the scheme in Figure 1 that there is no way, within the limits of our postulates, to interconvert the cis and trans isomers so long as we restrict ourselves to nonbridged intermediates in which each metal atom has one CO and one NO ligand. We are led, therefore, to the same conclusion as Marks and Kristoff, namely, that bridge opening to an unsymmetrical nonbridged structure which is less stable than the symmetrical ones can occur but is less probable. After internal rotation, such an intermediate can reclose bridges to complete the isomerization process.

Concluding Remarks

We have demonstrated that our proposed mechanism for rearrangements in certain binuclear bridged molecules which have ligands that can occupy either bridging or terminal sites can account in full detail for the remarkable stereospecificities observed in these rearrangements. We know of no other mechanism, either more simple or more complicated, which can also give a satisfactory account of all the facts. There are two other mechanisms which come readily to mind but these are inconsistent with the facts as will now be shown.

The possibility that an isomer with two bridges rearranges to an unstable intermediate with four bridges might be considered. However, this can immediately be dismissed as it would allow all conceivable isomerization and exchange processes to occur at the same rate for each of the three systems discussed.

The possibility that individual one-for-one bridge–terminal interchanges might occur has the appeal of simplicity. There may be cases in which such processes do occur, but their occurrence is inconsistent with the data for the systems discussed here. First of all, it is not clear why such a process would proceed at appreciably different rates in 1 and 2, although, admittedly, it is not impossible that this might be so.



In the case of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$, the one-for-one interchange can be rigorously rejected. It would permit isomer 3 to be obtained from 1, and 2 from 4. However, even when a solution containing 1 and 4 has been heated to *ca.* 100°, and then cooled to room temperature, no additional peaks appear in the proton nmr spectrum. There can be no doubt that 1 and 2, as well as 3 and 4, are of similar thermodynamic stability, just as are the cis and trans isomers of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. If there were a kinetically suitable pathway to convert 1 to 2 and 4 to 3, such conversions would doubtless occur.

The concerted pairwise opening and closing of bridges we have discussed for three specific systems may also form the basis for rearrangements in systems other than those with doubly bridged ground-state structures. We call attention to the following specific situations.

(1) Molecules in which the ground-state structure has no bridges. Ligands may pass from one metal atom to another through a bridged intermediate. A particular example of this is reported by us in the following paper.[12]

(2) A molecule in which there are three bridges might open two of them and then be able to restore them using ligands previously in terminal positions. $Fe_2(CO)_9$ is the only obvious example but is a rather intractable subject for study owing to its insolubility. This situation may thus be of little or no practical importance.

(3) A molecule with only a single bridge might be able to swing two terminal ligands into bridging positions and then, on returning to the singly bridged

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[12] R. D. Adams, M. Brice, and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6594 (1973).

structure, the ligand initially in the bridging position could become a terminal ligand. A real example of this might be provided by $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$, which has actually been shown to undergo rapid bridge–terminal exchange.[13]

(4) In binuclear systems where bridged and nonbridged structures have about equal stability and are thus both present in detectable amounts, there will probably be only extremely low activation energies for isomer interconversion and site exchange, since the activation energy to open or close bridges and that for internal rotation would act separately rather than wholly or in part additively. This expectation is consistent with the observation[3] that isomer interconversion for $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$, in which all three isomers, cis bridged, trans bridged, and nonbridged, are present in comparable quantities, is too rapid to broaden the single observed cyclopentadienyl signal even at −100°. It would also appear that the basic reason why only one ^{59}CO signal was observed[5,6] for $Co_2(CO)_8$ is because the isomer interconversion is rapid.

Finally, we want to state very clearly that we do *not* contend that our proposed rearrangement pathway (concerted double opening and reclosing of bridges or *vice versa*, often with internal rotation in between) is universal. There may be cases in which a different pathway is followed. It does appear likely, however, that for a great many important systems, and certainly in the three very representative ones discussed in detail here, our pathway is the correct one.

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Intramolecular Ligand Scrambling *via* Bridged Transition States or Intermediates in Di(*pentahapto*cyclopentadienyl)-(methyl isocyanide)(pentacarbonyl)dimolybdenum

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Abstract: It is shown that in solution $(\eta^5\text{-}C_5H_5)(CO)_3MoMo(CO)_2(CNCH_3)(\eta^5\text{-}C_5H_5)$ exists as a mixture of nonbridged isomers and permutamers and that at room temperature all of these are rapidly interconverted by unimolecular processes. It is especially notable that the isocyanide ligand passes rapidly from one metal atom to the other at room temperature and above. It is further proposed that important transition states, and/or intermediates, in this complex pattern of interconversions are the doubly bridged species $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\mu\text{-}CO)_2Mo(CO)(CNCH_3)(\eta^5\text{-}C_5H_5)$ and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\mu\text{-}CO)(\mu\text{-}CNCH_3)Mo(CO)_2(\eta^5\text{-}C_5H_5)$. The compound forms crystals consisting exclusively of the trans rotamer of *trans*-$(\eta^5\text{-}C_5H_5)(CO_2)(CNCH_3)MoMo(CO)_3(\eta^5\text{-}C_5H_5)$. The dark maroon crystals are tetragonal, space group $C^4_{4h}\text{-}P4_2/n$ with $a = 21.085$ (3) Å, $c = 8.223$ (3) Å, and $Z = 8$. Anisotropic refinement of 1874 reflections with intensities at least three times greater than their esd's converged at $R_1 = 0.046$ and $R_2 = 0.060$. The Mo–Mo bond distance is 3.230 (1) Å, which closely resembles that (3.222 Å) in the unsubstituted prototype, $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$, as do all other features of the structure.

It has been shown that carbonyl scrambling reactions in polynuclear metal carbonyls, and such isomerizations as are naturally associated with them, occur quite commonly and are often fast enough to influence nmr line shapes at temperatures of interest, thus making the molecules stereochemically nonrigid, or fluxional.[1–6] In the preceding paper[7] we showed that a common and important rearrangement pathway for some of these systems involves the opening of an existing pair of ligand bridges, some degree of rearrangement of the nonbridged intermediate, and then reclosing of a pair of bridges. We also pointed out that an obvious corollary to this concept is that a molecule which does not have bridges in its stable structure might undergo ligand scrambling reactions *via* intermediates or transition states in which a pair of bridges is formed. It is the purpose of this report to present detailed evidence for such phenomena in a representative system. A very brief, partial preliminary account of some of our observations has been published.[4]

Experimental Section

All preparations were carried out in atmosphere of nitrogen. Solvents were dried over sodium benzophenone and distilled under nitrogen just prior to use. Methyl isocyanide[8] and $(\eta^5\text{-}C_5H_5)$Mo-

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