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# A Half-Century of Nonclassical Organometallic Chemistry: A Personal Perspective

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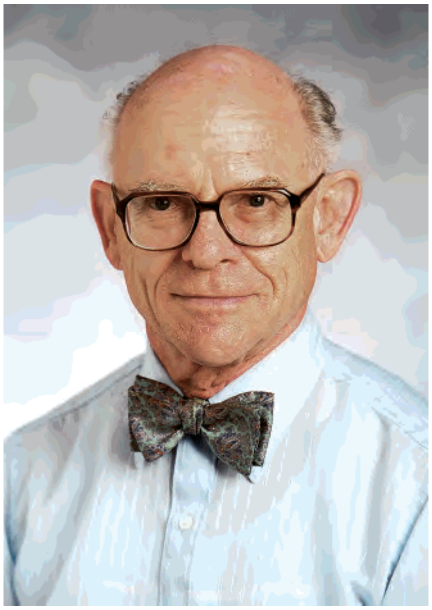
A review of some developments in transition metal (nonclassical) organometallic chemistry is presented, with emphasis on areas to which the author himself has made major and/or seminal contributions: especially fluxional organometallics, fluxional metal carbonyls, and the discovery and full explanation of agostic hydrogen atoms. An effort has been made to present these topics from the perspective of today rather than in strictly chronological order, with a sufficient number of specific examples to be concrete, but by no means encyclopedic. Particular topics covered are “ring whizzers”, concerted shifts of two or more CO ligands, twirling $M(CO)_3$ groups, and merry-go-rounds. In addition, the following topics are discussed: the unfinished business of $\mu_2,\eta^2,\eta^2$-ethene complexes and arene complexes of the lanthanides and actinides.

## Introduction

Just as chemical genetics did not exist prior to the publication of one brief note[1] in *Nature* in 1953, so too, transition metal organometallic chemistry was essentially unknown prior to the publication of another short note in *Nature* in 1951.[2] Of course, there is a significant difference between these notes. The one by Watson and Crick offered a solution to a problem; the one by Kealy and Pauson presented a problem. With that problem the era of transition metal organometallic chemistry with all its consequences for organic synthesis and for the chemical industry began. So, as it happens, did my career as a research chemist.

In the Autumn of 1951 I was a beginning graduate student, and early in the semester I had selected Geoffrey Wilkinson, a beginning assistant professor, as my Ph.D. research supervisor. In mid-December, I went home for the Christmas and New Year holidays with no unusual sense of excitement about my incipient research, which was concerned with lanthanide chemistry. When I returned in early January there had been a revolution. The issue of *Nature* containing a paper by Kealy and Pauson had arrived at the Harvard chemistry library and been read by both Wilkinson and Woodward. Both were excited by the report of an unbelievably stable transition metal dialkyl, dicyclopentadienyliron, and had already set out to investigate this substance.

To grasp the revolutionary nature of this discovery, which they both soon confirmed in the laboratory, it is necessary to know the prior history of efforts to make organo-transition metal compounds. Actually, it was not until 1955 that this



F. Albert Cotton was born in Philadelphia, PA, in 1930 and received his A.B. and Ph.D. degrees from Temple and Harvard Universities, respectively. He was on the faculty of MIT from 1955 to 1971 and has been at Texas A&M since 1972. He has been recognized by both ACS awards in inorganic chemistry, the ACS Priestley Medal, the AIC Gold Medal, the Robert A. Welch Prize, the King Faisal Prize, the Paracelsus Prize, the Wolf Prize, the Lavoisier Medal, and the National Medal of Science. His interests have been in inorganic, organometallic, and structural chemistry. He discovered the existence of quadruple bonds, as well as related triple, double, and single bonds in a similar structural context, and has explored their chemistry extensively. (Photo by Jean Wulfson. Copyright 2000 Texas A&M University.)

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(1) Watson, J. A.; Crick, F. H. C. *Nature* **1953**, *4356*, 737.

(2) Kealy, T. J.; Pauson, P. L. *Nature (London)* **1951**, *168*, 1039.

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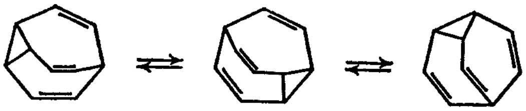

**Figure 1.** The bullvalene molecule and two of the many "degenerate" Cope rearrangements it undergoes.

history was written in a comprehensive, detailed fashion by me in an article, published in *Chemical Reviews*, entitled "Alkyls and Aryls of Transition Metals",[3] but people like Woodward and Wilkinson knew that in general such compounds were almost nonexistent.

What I made clear in my review was just how extremely barren and frustrating practically all prior efforts to make such compounds had been. In fact, the very conceptual basis of Kealy and Pauson's work was that a dialkyl or diaryl of a transition metal, such as iron, would be entirely unstable and would immediately collapse to yield the coupling product of the two alkyl or aryl radicals and the metal. Prior to the report on ferrocene, no one worked in the field of transition metal organometallic chemistry because no one believed that there was any such field to work in.

I have referred in my title to "nonclassical" organometallic chemistry. This implies that there is a "classical" organometallic chemistry. I use the term classical to refer to the organometallic chemistry of the main group metals: the alkali and alkaline earth metals, the group 12 metals (Zn, Cd, Hg), the group 13 metals (Al, Ga, In, Tl), and the group 14 metals (Sn, Pb). It is classical in that it has existed since the mid-19th century and while it encompassed a rich variety of compounds, all were based on metal to carbon $\sigma$ bonds with more or less ionic character.

In this article, which follows my award lecture but presents a great deal more detail, I shall present my recollections of the development of several important areas of transition metal organometallic chemistry to which I myself contributed. My *ca.* 330 publications in the field touch on a still greater variety of problems, but I have selected only a few areas for discussion.

## 1. Fluxional Organometallic Molecules[4]

It was in the decade of the 1960s that chemists began to think about the possibility of molecules that would undergo constant, rapid intramolecular rearrangement without ever changing their identity. The motto of such a molecule, if it spoke French, might well be *Plus que je change, plus que je suis la même chose*.

The name of this phenomenon is fluxionality, and fluxionality was in the air in the 1960s. For example, in 1963, Doering and Roth proposed (before anyone knew how to make it!) the molecule bullvalene, which undergoes the spontaneous rearrangements indicated in Figure 1. In this way all 10 of the carbon atoms become time-average equivalent; put differently, each of 10!/3 (where 3 takes account of the 3-fold axis of rotational symmetry) permutations of the 10 C−H units is accessed.[5]

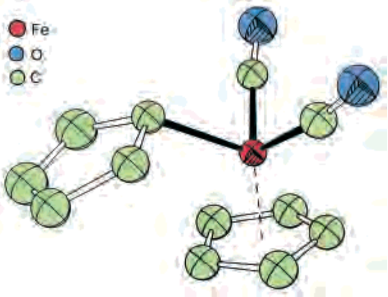

**Figure 2.** The ($\eta^5$-$C_5H_5$)Fe(CO)$_2$($\eta^1$-$C_5H_5$) molecule. This computer drawing is based on the results reported in ref 9 where no contemporary style representation was given. I thank Dr. L. M. Daniels for this drawing.

In 1965, Earl Muetterties[6] drew attention to the widespread occurrence of the phenomenon he called polytopal shifts. Polytopes are different shapes for the same $AB_n$ molecule in each of which the B atoms surrounding a central A atom define a different polyhedron. Much earlier, an example of fast polytopal shifts had been provided by $Fe(CO)_5$. Regardless of whether it had a trigonal bipyramidal or a square pyramidal structure, which was still an open question in 1957, it was expected to show two signals in its $^{13}C$ NMR spectrum, and the intensity ratio would be indicative of which structure was correct. So I proposed this experiment to my colleague John Waugh.

Actually, no $^{13}C$ NMR spectrum of a metal carbonyl had yet been published at that time (1957), and with the CW spectrometers then in use and the low natural abundance of $^{13}C$ this experiment was not a walk around the block. However, because $Fe(CO)_5$ is a liquid and because John Waugh was a master of all the tricks of the trade, we got a spectrum. To our consternation, however, it consisted of only one line. We published this result,[7] along with several tentative (but incorrect) explanations, but our work owes its real importance to Steve Berry, who wrote us (generously offering co-authorship) with the correct explanation: the now widely known Berry pseudorotation. We declined to share credit for his idea (thus sparing the future literature the cumbrous term Berry−Cotton−Waugh rearrangement; posterity should therefore thank us for being so ethical), and Berry published his idea shortly after.[8] I believe Steve Berry should be credited with the first explicit suggestion of a polytopal rearrangement although Earl Muetterties later generalized the concept.

Organometallic molecules came on the fluxionality scene in the following way. In 1956, Piper and Wilkinson[9] reported preparing the molecule shown in Figure 2. They attempted to verify the expected presence of one $\eta^5$- and one $\eta^1$-cyclopentadienyl ring (to satisfy the 18-electron rule) by the then very new technique of $^1H$ NMR spectroscopy. However, they found only two singlets, of equal intensity, one a bit broader than the other. I was there at the time, and I well remember how nonplused everyone was by this result. To reconcile this result with the expected structure, they made the following proposal:

> "An . . . explanation is to postulate that the metal atom is executing a 1,2-rearrangement at a rate greater than the expected chemical shift of 200−300 cycles per second."

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(3) Cotton, F. A. *Chem. Rev.* **1955**, *55*, 551.

(4) For more detailed reviews, published about the time the work was done, see: (a) Cotton, F. A. *Acc. Chem. Res.* **1968**, *1*, 257. (b) Cotton, F. A. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 377.

(5) For a capsule summary of the bullvalene story, see: Ault, A. *J. Chem. Educ.* **2001**, *78*, 724.

(6) Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 769.

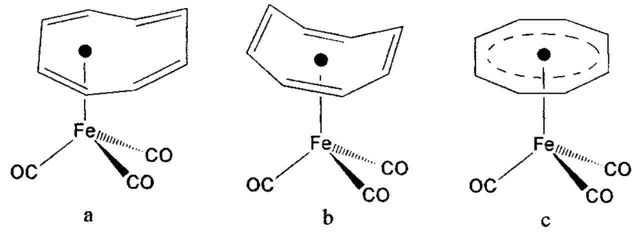

**Figure 3.** Three possible structures for $C_8H_8Fe(CO)_3$. (a) The actual structure. (b) Another structure consistent with the 18-electron rule. (c) A structure consistent with the room-temperature $^1$H NMR spectrum but inconsistent with the 18-electron rule.

Half a decade later synthesis of the $C_8H_8Fe(CO)_3$ molecule was reported by several laboratories, and it posed a problem similar to that just discussed. If the 18-electron rule were to be respected, only one of two structures, Figure 3a or 3b, could be proposed for it. For neither of these was a one-line $^1$H NMR spectrum to be expected, but that is what was found. In 1962 Dickens and Lipscomb[10] confirmed by X-ray crystallography that the structure in the solid state was that in Figure 3a. To reconcile this work with the one-line NMR spectrum Dickens and Lipscomb proposed a rapid hopping of the cyclooctatetraene ring so that all eight equivalent structures were sampled rapidly on the NMR time scale.

Essentially nothing more was known about fluxional molecules in general or organometallic ones in particular up to 1965, at which time Alan Davison and I decided to make a careful study of Piper and Wilkinson's compound. This work[11] was the first of many investigations[12-45] that I carried out over the next decade to elucidate the behavior of fluxional organometallic compounds. Only some of the highlights will be discussed here.

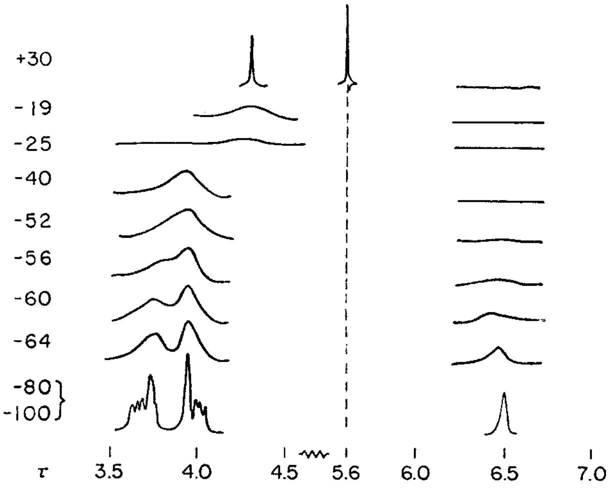

**Figure 4.** The $^1$H NMR spectra of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ at lower temperatures. The line at 5.6$\tau$, due to the $\eta^5$-$C_5H_5$ protons, does not change.

Davison and I decided to attack the problem in two ways, one of which was to make sure that in the crystal the structure was as assumed. As shown in Figure 2, it is. The other way was to investigate the $^1$H NMR spectrum at lower temperature to see if the movement could be slowed down enough to confirm Piper and Wilkinson's hypothesis. The NMR experiment was both more difficult and more rewarding than anticipated. The running of NMR spectra at temperatures as low as $-100$ °C was, to say the least, not routine in 1965, but it was done, with the results shown in Figure 4.

The most obvious conclusion to be drawn from these spectra is that when the motion is slowed enough that it ceases to affect the $^1$H NMR spectrum ($-80$ to $-100$ °C) the spectrum is perfectly consistent with the expected 18-electron structure. But equally important is the information about how the rearrangement occurs, which is contained in the spectra between $-25$ and $-80$ °C. Clearly one part of the spectrum between 3.5$\tau$ and 4.5$\tau$ is collapsing faster than the other. (The $\tau$ notation in use in the 1960s but now abandoned referred all chemical shifts to a point 10 ppm downfield from TMS.) This means that the rearrangement pathway must be such as to cause both olefinic protons of one type to undergo site exchange at every step while only one of the two of the other type changed each time. Any

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(7) Cotton, F. A.; Danti, A.; Waugh, J. S.; Fessenden, R. W. *J. Chem. Phys.* **1958**, *29*, 1427.
(8) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.
(9) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.
(10) Dickens, B.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 2084.
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(15) Bratton, W. K.; Cotton, F. A.; Davison, A.; Musco, A.; Faller, J. W. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *58*, 1324.
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(34) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 7523.
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(42) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.
(43) Cotton, F. A.; Hunter, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 1413.
(44) Bailey, W. I., Jr.; Cotton, F. A.; Jamerson, J. D.; Kolb, J. R. *J. Organomet. Chem.* **1976**, *121*, C23.
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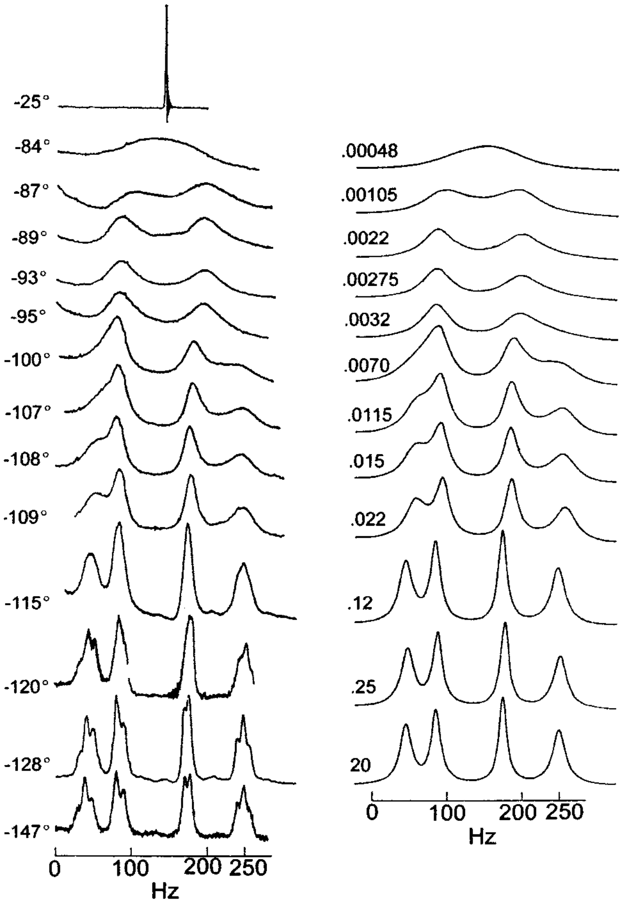

**Figure 5.** Measured and matching calculated $^1H$ NMR spectra for $(C_8H_8)Ru(CO)_3$. Temperatures in °C; mean residence times in seconds.

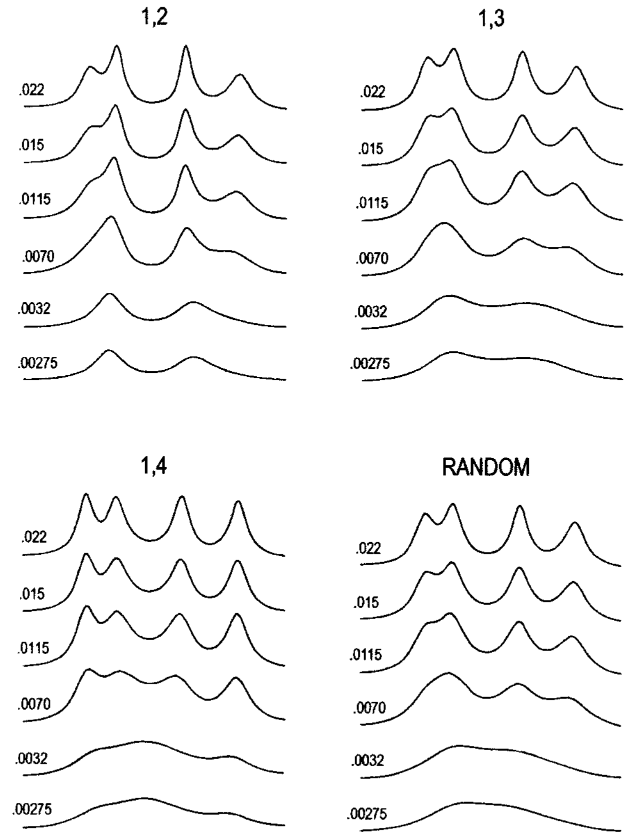

**Figure 6.** The patterns of collapse of the $C_8H_8Ru(CO)_3$ $^1H$ NMR spectrum calculated for four different rearrangement pathways over the intermediate range of mean residence times.

process leading to random exchange was ruled out, and only 1,2 or 1,3 shifts were acceptable. It was only later[34,41] that the assignment was made with certainty, which led to the conclusion that, just as Piper and Wilkinson had intuited, it is 1,2 shifts that occur. The important broad implication of this work was that not only can it be shown that fluxional behavior occurs, but the actual pathway of the rearrangement can be extracted from NMR line shape changes.

I would like to emphasize that, so far as I know, our analysis of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ spectra over a temperature range was the first time a line shape analysis had been used to determine the mechanism of a fluxional process, although several years earlier Saunders had shown that selective line broadening in the bullvalene spectrum supported the presumed mechanism.[46]

At this point, we turned immediately to the $(C_8H_8)Fe(CO)_3$ case, but found that the rearrangement here proceeds with such a low barrier that we could not get to low enough temperatures to learn very much.[13] I had a hunch that the ruthenium homologue might be slower, and this proved to be true.[15,31,32] As shown in Figure 5, we were able to reach a limiting slow-exchange spectrum and observe all the line shape changes in between. This figure well illustrates the *modus operandi* that was characteristic of many of our subsequent studies.

By using a computer program to calculate spectra over a suitable range of exchange lifetimes, beginning with one just short enough to begin affecting line shapes, a library of spectra at progressively shorter lifetimes was computed. This was done for all possible shift patterns, which in this case are 1,2; 1,3; 1,4; and random. These calculated spectra are shown in Figure 6.[32] It was found that only one set of calculated spectra could qualitatively match those observed, and thus the rearrangement pathway was unambiguously found to be 1,2 shifts. In addition, from the library for this pattern, spectra closely matching each of the observed ones were selected, as shown in Figure 5. From the resulting match of lifetimes and their associated temperatures, the activation energy of the process was also determined.

We used several approaches to bringing the limiting spectrum, from which the instantaneous structure could be determined, as well as the set of spectra where the informative line shape changes were occurring, into measurable range. In some cases the problem was to have solvents that remained liquid and nonviscous to as low a temperature as possible. With mixtures of fluorocarbons we were able to get to as low as −160 °C. Another strategy was to modify the hydrocarbon ligands so as to slow the rearrangement.

An interesting example of ligand modification was the use of 1,3,5,7-tetramethylcyclooctatetraene (TMCOT) in place of COT in the series (TMCOT)M(CO)$_3$, M = Cr, Mo, W,[12,19,20] the structure of which is shown in Figure 7. With these molecules, the concept of successive stages of fluxional activity arose for the first time. In the instantaneous structure, all four ring protons and all four methyl groups are in different environments, and this was clearly seen in an $^1H$ NMR spectrum at −23 °C (Figure 8). Clearly, there is a

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(46) Saunders, M. *Tetrahedron Lett.* **1963**, 1699.

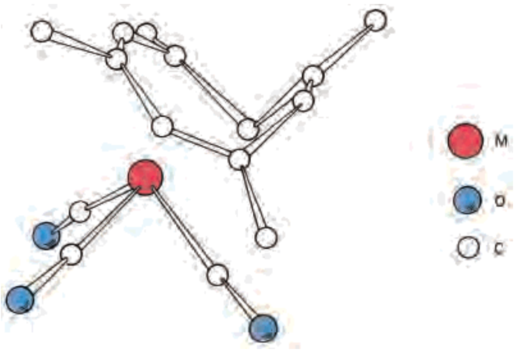

**Figure 7.** The structure of an $(C_8H_4Me_4)M(CO)_3$ molecule (M = Cr) as reported in 1968.

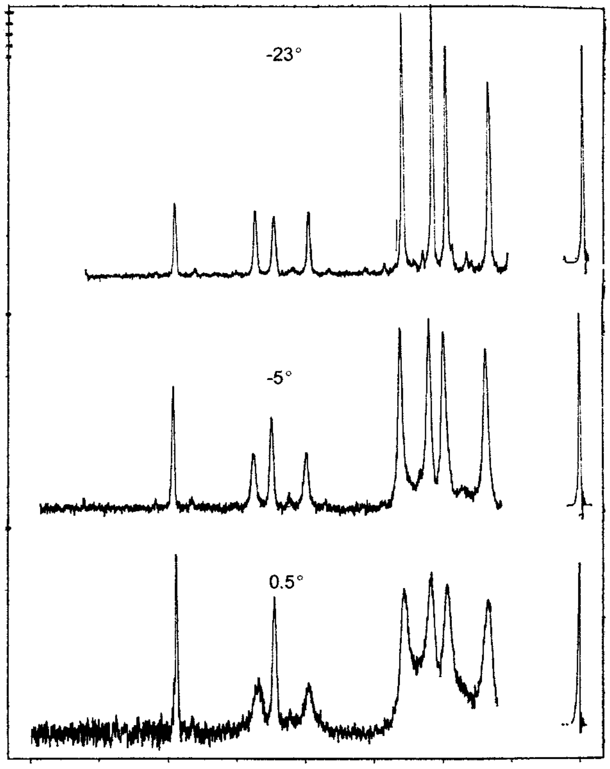

**Figure 8.** The $^1H$ NMR spectra of $(C_8H_4Me_4)Cr(CO)_3$ in the lowest temperature range.

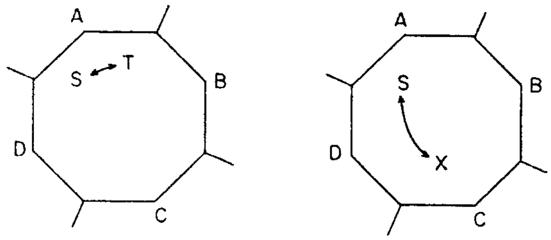

**Figure 9.** The two rearrangement paths that could explain the spectral changes in Figure 8. The correct choice depends on how the spectrum is assigned.

first stage of signal averaging in which two of the ring hydrogen signals remain unchanged. We pointed out that either of two short motions, as shown in Figure 9, could explain this; the question of which it was depended on the assignments of the resonances. We assumed that the 1,2 shift was the correct choice, but however that might be, spectra at higher temperatures showed many more changes leading, finally, to total averaging. Therefore, at least one, and probably two, more extensive shifts, with higher activation energy, had to be occurring. Further details need not be reviewed here. The point to be made is that this work first showed that fluxional molecules need not show spectral collapse that occurred, like the demise of the wonderful one-horse shay of Oliver Wendell Holmes, "all at once and nothing first", but could exhibit two or more successive stages, having progressively higher activation energies. Numerous other multistage cases have been observed since, but this was the first one.

If all the results pertaining to cyclic polyolefins attached to metal atoms are taken together, it is clear that by far the most common mode of rearrangement is by a succession of 1,2 shifts. There are, however, a few interesting exceptions. The first to be found[47] was with $(\eta^6\text{-}C_8H_8)M(CO)_3$ molecules where M = Cr, Mo, W. All of these move too fast to allow a determination of the rearrangement path by $^1H$ NMR spectroscopy, but later, with $^{13}C$ NMR spectroscopy, we obtained useful and somewhat surprising results. All four of the $^{13}C$ signals in the limiting low-temperature spectrum broadened at the same rate. This rules out all but two possibilities, 1,3 shifts and random exchanges, most likely by way of a transition state with the $M(CO)_3$ unit over the center of the ring (as in Figure 3c). Since the idea that a 1,3 shift could occur without a stop at the intermediate 1,2 shift is hard to accept, the symmetrical transition state is to be preferred.

A few years later another example, again with an $\eta^6\text{-}C_8H_8M$ unit (in $(\eta^6\text{-}C_8H_8)Ru(norbornadiene)$) turned up.[48] It seems that while an $(\eta^4\text{-}C_8H_8)M$ moiety cannot access the symmetrical transition state (which would bring four more ring electrons close to the metal atom), an $(\eta^6\text{-}C_8H_8)M$ moiety can do so.

As our work on fluxional metal polyolefin compounds proceeded, it became evident to me that clear discussion of the bonding and structures of these molecules was often hampered by the lack of a systematic notation to differentiate one mode of attachment of the olefin from another. I therefore devised a system, which, after extensive checking with others more steeped in problems of nomenclature, I presented formally in 1968.[49] It rapidly caught on and was soon adopted by IUPAC, with only the cosmetic change of replacing my use of italic h (for hapto) to the Greek letter $\eta$. In a certain sense, this hapto notation has permeated organometallic chemistry more than anything else I have done.

I was prompted to make that digression about notation because the next topic I want to mention concerns the invention and properties of what was called informally in my lab the "three-ring circus". Upon seeing Bruce King's preparation[50] of a molecule which could be designated (according to King) as $(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Mo(NO)CH_3$ (in the new notation), it occurred to me that if we replaced the methyl group by an $\eta^1\text{-}C_5H_5$ group, we would have a molecule with three different kinds of cyclopentadienyl groups attached to the same metal atom. If fluxionality also occurred, we would have three rings, all going around in circles: hence the nickname.

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(47) Cotton, F. A.; Hunter, D. L.; Lahuerta, P. *J. Am. Chem. Soc.* **1974**, *96*, 4723.
(48) Cotton, F. A.; Kolb, J. R. *J. Organomet. Chem.* **1976**, *107*, 113.
(49) Cotton, F. A. *J. Am. Chem. Soc.* **1968**, *90*, 6230.
(50) King, R. B. *Inorg. Chem.* **1968**, *7*, 90.

It should be stressed that we, and King before us, had decided on the $\eta^5,\eta^3$ assignment based on the usual, but somewhat naive rationale that (1) the total number of electrons donated by two $C_5H_5$ rings to an Mo(NO)R fragment had to be 8, so as to satisfy the 18-electron rule, and (2) a $C_5H_5$ ring that was neither $\eta^5$ nor $\eta^1$ would have to be, at least formally, $\eta^3$.

Peter Legzdins, a Ph.D. student, quickly accomplished the preparation of the putative $\eta^5,\eta^3,\eta^1$ compound and then showed that it displays two-phase fluxional behavior.[26] At −110 °C the $^1H$ NMR spectrum showed that there is a structure in which there are three different kinds of rings, one of which is certainly an $\eta^1$-$C_5H_5$ ring in an environment in which free rotation about the Mo−C bond is restricted, so that the two edges are not equivalent. In addition to the signals assigned to the $\eta^1$ ring, there were two singlets, separated by about 1.1 ppm (66 Hz), which could be assigned to each of the two other rings. We had to presume that, even at −110 °C, the $\eta^3$ ring was still “whizzing” fast enough to average out the resonances of its five protons.

In the temperature range −110 to −50 °C the two edges of the $\eta^1$-$C_5H_5$ ring become equivalent and, simultaneously, the two singlets for the other rings collapse and coalesce. Our interpretation was that the $\eta^5$ and $\eta^3$ rings were interconverting, which would necessarily cause the two edges of the $\eta^1$ ring to become equivalent. In the range −50 to +15 °C all resonances collapse and coalesce into one. Thus, we have complete, rapid interconversion of all the rings.

As to how the presumed $\eta^5$ and $\eta^3$ rings became NMR equivalent we saw two possibilities. (1) The NO group participates. It temporarily becomes a bent NO which is a one-electron donor, thus causing the $\eta^3$ ring to become an $\eta^5$ ring to keep the total electron count at 18. When the NO group goes back to being a linear three-electron donor, either of the $\eta^5$ rings has the same probability of resuming $\eta^3$ status and thus $\eta^5/\eta^3$ scrambling is accomplished. (2) The NO group remains unchanged and the $\eta^5$ and $\eta^3$ rings both move so that both adopt the same kind of irregular relationship, neither $\eta^5$ nor $\eta^3$ but something in between, to the Mo atom. From this transition state (or possibly an intermediate) the resumption of the (presumably) more stable $\eta^5,\eta^3$ status quo ante could take place in two equally probable ways.

The idea very naturally occurred to me that before considering this project complete it would be nice to determine the crystal structure of the molecule and actually verify the assumed $\eta^5,\eta^3,\eta^1$ nature of the molecule. In fact, the structure we determined[29] was a complete surprise! It *falsified* the assumed $\eta^5,\eta^3,\eta^1$ structure. There is an $\eta^1$ ring, exactly as expected, but the other two rings have, within experimental error, exactly the same relationship to the metal atom; this is shown in Figure 10. This was certainly the first time and (as far as I know, to this day) the last that a crystal structure did not appear to jibe with the implications of the low-temperature limiting NMR spectrum. This was very disconcerting.

We considered the possibility that perhaps, as a strange coincidental result of packing forces, the second transitional structure mentioned above had been trapped and stabilized in the crystal. If this were so, then surely a different compound, having different intermolecular forces, could not possibly show the same structure. We therefore determined the structure[51] of the purported ($\eta^5$-$C_5H_5$)($\eta^3$-$C_5H_5$)Mo(NO)-$CH_3$. It showed exactly the same virtual equivalence of the two rings, each in a relationship less close than $\eta^5$ but closer than $\eta^3$ to the metal atom. The nature and implications of this curious relation have been discussed.[52] In no way could the two $(C_5H_5)_2$Mo(NO)R molecules be said to be 20-electron molecules, but it is equally true that they cannot be described as having one $\eta^5$ and one $\eta^3$ ring.

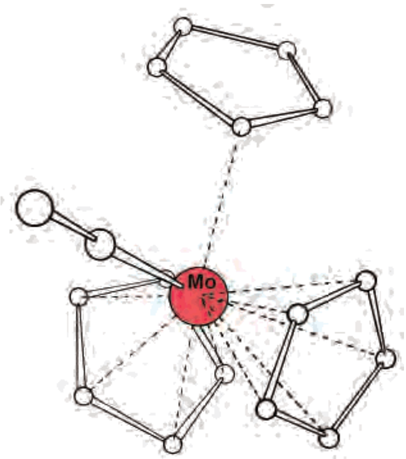

**Figure 10.** The structure of the $(C_5H_5)_3$MoNO molecule.

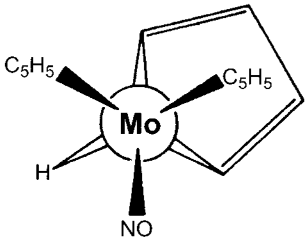

**Figure 11.** A schematic view of the $(C_5H_5)_3$MoNO molecule.

After a little thought, I realized that it was possible to reconcile the seemingly incompatible NMR and crystallographic results. If we look at the $(C_5H_5)_3$MoNO molecule from the point of view shown in Figure 11, we can see how. Two of the $C_5H_5$ rings differ because of their different relationships to the $\eta^1$-$C_5H_5$ ring, not because they are $\eta^5$ and $\eta^3$, or in any other way different in their relationship to the metal atom. At low-temperature, rotation about the Mo−C bond is so slow that these two $C_5H_5$ rings, while rotating individually fast enough to give only one signal each, have different chemical shifts; at the same time the two sides of the $\eta^1$-$C_5H_5$ ring are nonequivalent. All that is required to eliminate both of these nonequivalences simultaneously (as observed) is for rotation about the Mo−C bond to be rapid. It is also clear, from this viewpoint, why the $(C_5H_5)_2$-Mo(NO)$CH_3$ and $(C_5H_5)_2$Mo(NO)I molecules *never* show inequivalence of the $C_5H_5$ rings.[38] The final, and most important, result of all of our work on this “three-ring circus” was that the idea of an $\eta^3$-$C_5H_5$ ring, at least in this and related molecules, is a myth.

A few years earlier we studied[35,36] the $(C_5H_5)_4$Ti molecule. We first showed with certainty by X-ray crystallography that it has two $\eta^5$ and two $\eta^1$ rings. Between −27 and 60 °C, there is interconversion of the two ring types. Note that this is in contrast to the behavior of ($\eta^5$-$C_5H_5$)Fe$(CO)_2$($\eta^1$-$C_5H_5$) where no hint of ring interconversion was seen. It is entirely

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(51) Cotton, F. A.; Rusholme, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 402.
(52) Cotton, F. A. *Discuss. Faraday Soc.* **1969**, *47*, 79.

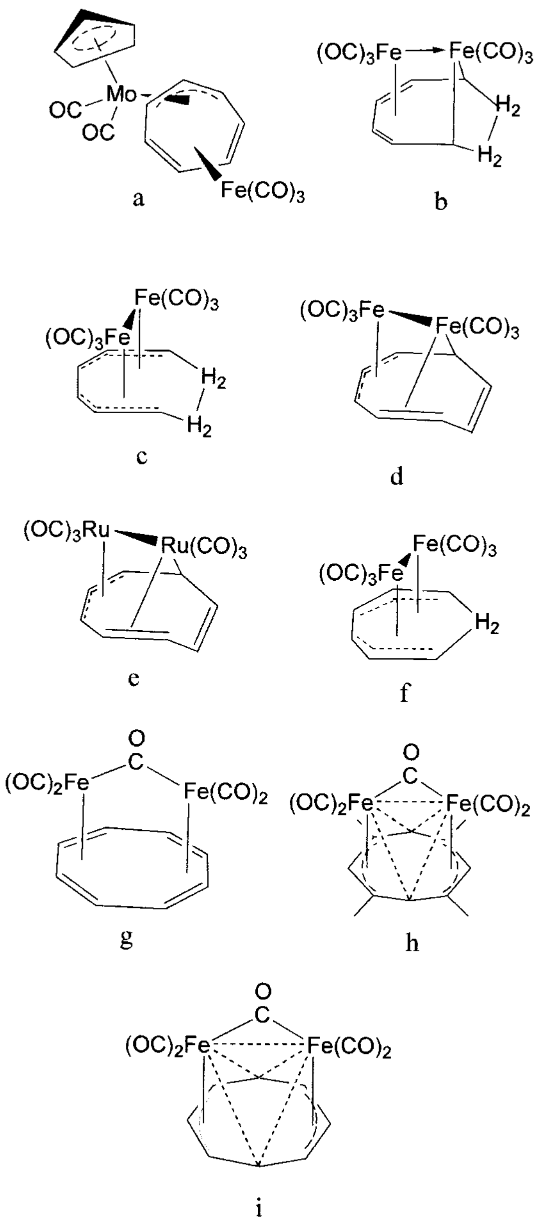

**Figure 12.** Some fluxional organometallic molecules with two or more metal atoms.

plausible that there is a transition state for such a ring interchange available in the 16-electron molecule $(\eta^5\text{-}C_5H_5)_2$-$(\eta^1\text{-}C_5H_5)_2Ti$, but not in the 18-electron iron compound. Quite possibly this transition state has two rings that have simultaneously adopted some intermediate relationship to the titanium atom, reminiscent of that seen in the $(C_5H_5)_2$Mo-(NO)R compounds just discussed.

In addition to the few examples that have been discussed in detail, many other fluxional organometallic molecules were studied. While space does not permit discussing them here, references are provided.[14,16−18,25] I would, however, like to conclude by briefly discussing some molecules that contain two metal atoms attached to the same cyclic polyolefin. These are all shown schematically in Figure 12.

**A Molecular Bicycle Chain.** The molecule shown in Figure 12a has an $(\eta^5\text{-}C_5H_5)Mo(CO)_2$ group attached on one side of a $C_7H_7$ ring to a local allyl group and an $Fe(CO)_3$ group attached on the other side *via* a local butadiene unit.[39] The $^1$H NMR spectrum matches this structure only below −50 °C; at room temperature and above, only a single sharp resonance is seen for all seven hydrogen atoms.[27] Our interpretation is that the $C_7H_7$ ring is moving around relative to the two metal atoms much as a bicycle chain moves between the sprocket and the back wheel of a bicycle.

**Molecular Windshield Wipers.** A series of compounds in which $M_2(CO)_5$ or $M_2(CO)_6$ units, M = Fe, Ru, are attached to seven- or eight-membered rings were studied by ourselves and also by Rowland Pettit. In each case, there was more than one way that the dimetal unit could be bonded to the ring, and depending on that, one or another type of fluxional behavior could occur. For example, in the $C_8H_{10}$-$Fe_2(CO)_6$ compound two structures, 12b and 12c, had been proposed for it. Structure 12c was said[53] to be supported by the Mossbauer spectrum, and both of these structures were consistent with the room-temperature $^1$H NMR spectrum, which, while complex, clearly implied that the molecule had a plane of symmetry.

We looked into this problem by low-temperature NMR spectroscopy[33] and concluded that neither of these structures is correct. Instead the structure is 12d and the molecule is fluxional, with the $(OC)_3FeFe(CO)_3$ unit flicking back and forth like a windshield wiper to give the appearance of higher symmetry at room temperature. We also showed that $C_8H_8$-$Ru_2(CO)_6$ has a similar crooked positioning of the $Ru_2(CO)_6$ unit, 12e, and again there is a rapid flicking back and forth.[23] Much later it was found that the $C_{10}H_{12}Fe_2(CO)_6$ molecule, where $C_{10}H_{12}$ is a bicyclic 6,0,2 triolefin, behaves in the same way.[42] It is interesting that for an analogous molecule with a $C_7H_8$ ring[37] rather than a $C_8H_{10}$ ring, the structure is 12f, which is analogous to the incorrect structure 12c.

**Molecular Mixer Blades.** As early as 1965 Pettit had reported the compound $C_8H_8Fe_2(CO)_5$, which had a single resonance in the $^1$H NMR spectrum; he proposed structure 12g for it, and proposed that it is fluxional.[54] Various other possible structures were dismissed without good reason, and also, this one does not satisfy the 18-electron rule. We later made the 1,3,5,7-tetramethylcyclooctatetraene analogue and found that it too is fluxional, showing only one methyl resonance and one C−H resonance.[21] A crystal structure determination[22] showed that the actual structure is 12h, which suggests that the structure of Pettit's molecule is 12i. For the observed signal averaging to occur, the $(OC)_2Fe(\mu\text{-}CO)$-$Fe(CO)_2$ unit would have to sweep completely around the ring much like the blade of a kitchen mixer.

I would like to conclude this section on fluxional organometallic molecules with one purely personal recollection. Rowland (Rollie) Pettit, who made several early contributions to the development of the subject, introduced the fanciful term "ring whizzers". Although he never used it in print (as far as I know), it became common parlance. During the period 1959−1963 I had a graduate student at MIT named Terry Haas, who then joined the faculty at nearby Tufts University. Once Rollie's term became well-known I tried to persuade Terry to work on just one fluxional molecule with a polyolefinic macrocycle in it so we could publish a paper on "the wonderful whizzer of Haas." To my everlasting disappointment, he wouldn't do it.

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(53) Emerson, G. F.; Mahler, J. E.; Pettit, R.; Collins, R. *J. Am Chem. Soc.* **1964**, *86*, 3590.

(54) Keller, C. E.; Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 1388.

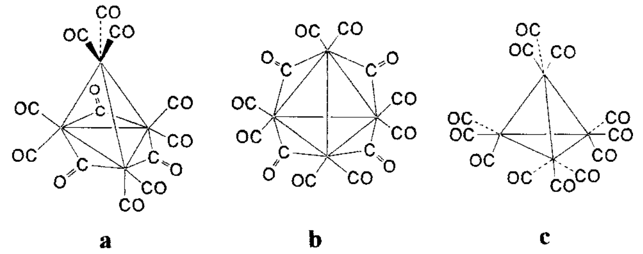

**Figure 13.** Three possible structures, all equally reasonable, a priori, for a tetrahedral $M_4(CO)_{12}$ molecule.

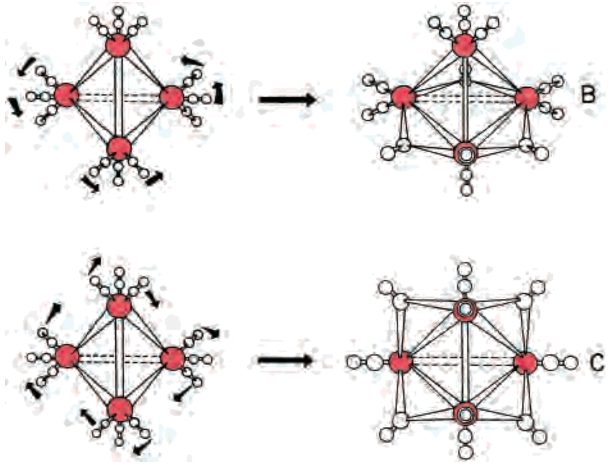

**Figure 14.** Structural rearrangements which I proposed in 1966 for a $M_4(CO)_{12}$ molecule.

## 2. Fluxional Metal Carbonyls[55]

My interest in fluxional metal carbonyls, apart from the study of $Fe(CO)_5$ mentioned earlier, actually began when I addressed the question of the structure of the $Co_4(CO)_{12}$ molecule. The initial problem was to understand how the three possible structures shown in Figure 13 might interconvert. What I proposed in 1966 was the idea that concerted shifts of CO groups from bridging to terminal positions (and, of course, vice versa) could provide a low-energy pathway for interconverting such structures. The importance of *concertedness* is that all metal atoms at all times retained their preferred complement (usually 18) of electrons. In the specific case of an $M_4(CO)_{12}$ molecule, my proposal was that shown in Figure 14, which is reproduced from the 1966 paper.[56]

In that paper I noted that if the processes shown were to occur "sufficiently fast all CO groups will appear NMR equivalent even though they are not in either of structures B or C", and that "should such a process actually occur it would constitute a case of [fluxional behavior] quite as remarkable in its scale as that provided by bullvalene." It was not until several years later that I was able to verify this prediction by studying the $^{13}$C NMR spectrum of $Rh_4(CO)_{12}$, which, by then, Dahl had shown to have the type a structure in Figure 13a. For this structure there are 12!/3 permutamers (12 × 11 times greater than for bullvalene). At that time $^{13}$C NMR spectrometers were rare; even MIT did not have one. Finally, in 1972, through the good offices of my Texas A&M colleague Barry Shapiro, I was able to have spectra run at Varian, with the results shown in Figure 15.[57] The beautiful quintet observed in the fast exchange limit shows not only that all CO groups have become time-average equivalent but that all of them are equally coupled to all four rhodium nuclei, exactly as my proposed mechanism predicted. A little later, in Jack Lewis's laboratory in Cambridge a limiting low-temperature spectrum was obtained[4d,58] at $-65$ °C which showed that the molecule in solution has structure **a** in Figure 13. Dahl had shown that $Ir_4(CO)_{12}$ has structure **c**, but no example of **b** has ever been found.

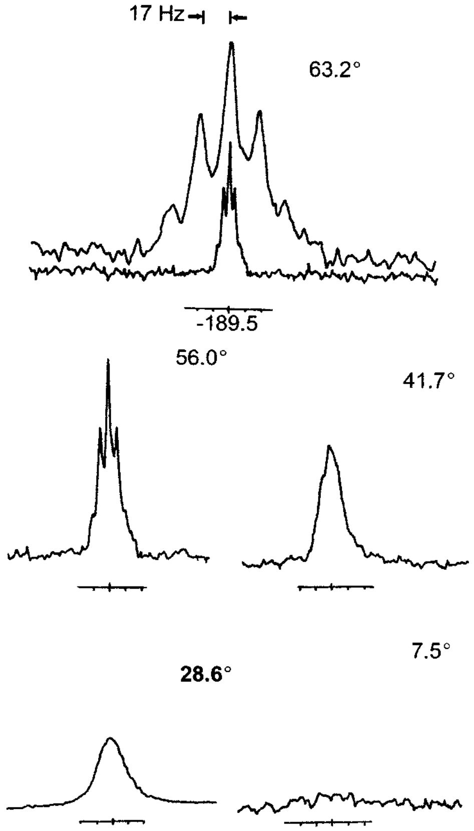

**Figure 15.** $^{13}$C NMR spectra of $Rh_4(CO)_{12}$ in the fast exchange region.

Beautiful as the $M_4(CO)_{12}$ case may be, there are other types of rapid, concerted CO shifts that have proved to be of wider occurrence and hence of more general interest; the one shown in Figure 16 is of greatest importance. When Rick Adams joined my group, in 1970, we started an extensive investigation of these. The centerpiece of this work, and the only molecule I shall discuss here, was $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. There are three isomeric forms of this molecule, as shown in Figure 17. It should be noted that the unbridged form has one trans and two enantiomeric gauche rotamers.

Both the cis and trans bridged isomers had been isolated and characterized in crystalline form. In solution both are present (in about equal amounts in nonpolar solvents)

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(55) For more detailed reviews, published about the time the work was done, see: (a) Cotton, F. A. *Bull. Soc. Chim. Fr.* **1973**, *9−10*, 2587. (b) Adams, R. D.; Cotton, F. A. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 489. (c) Cotton, F. A.; Hanson, B. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, p 379.

(56) Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1083.

(57) Cotton, F. A.; Kruczynski, L.; Shapiro, B. L.; Johnson, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 6191.

(58) Evans, J.; Johnson, B. F. G.; Lewis, J.; Norton, J. R.; Cotton, F. A. *J. Chem. Soc., Chem. Commun.* **1973**, 807.

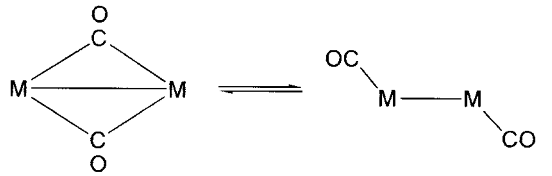

**Figure 16.** The pairwise interconversion of terminal and bridging CO ligands.

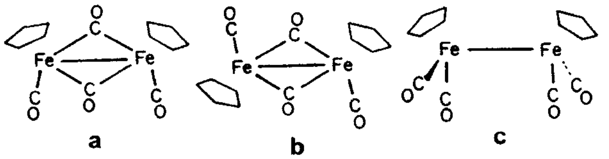

**Figure 17.** The three isomeric structures of ($\eta^5$-$C_5H_5$)$_2$$Fe_2$(CO)$_4$.

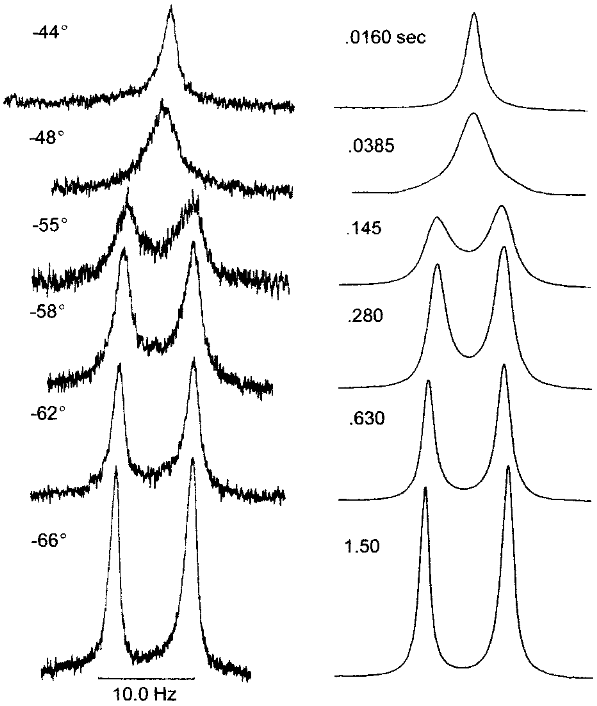

**Figure 18.** $^1$H NMR spectra of ($\eta^5$-$C_5H_5$)$_2$$Fe_2$(CO)$_4$, with the matching computed spectra.

together with a few percent of the unbridged form. We showed in 1972, by observing the cyclopentadienyl proton resonances, that the cis and trans forms interconnect rapidly at room temperature and only one resonance for both is seen. However, as shown in Figure 18, at temperatures from −30 to −70 °C this resonance collapses and separate signals are seen for the two isomers.[59]

On the basis of these data we considered that we had proof that the pair of CO bridges could open, rotation could occur about the Fe−Fe bond, and the other isomer could then form by reclosing the bridges. I believe this was the first proven example of such behavior, unless one is willing to believe that interconversion can somehow occur without opening the bridges. However, with only the proton spectra, much of importance about the interconversion process was missed. For example, as the isomers interconvert by the above process, the bridge and terminal CO groups must also exchange, but without $^{13}$C NMR spectroscopy we could not test that prediction.

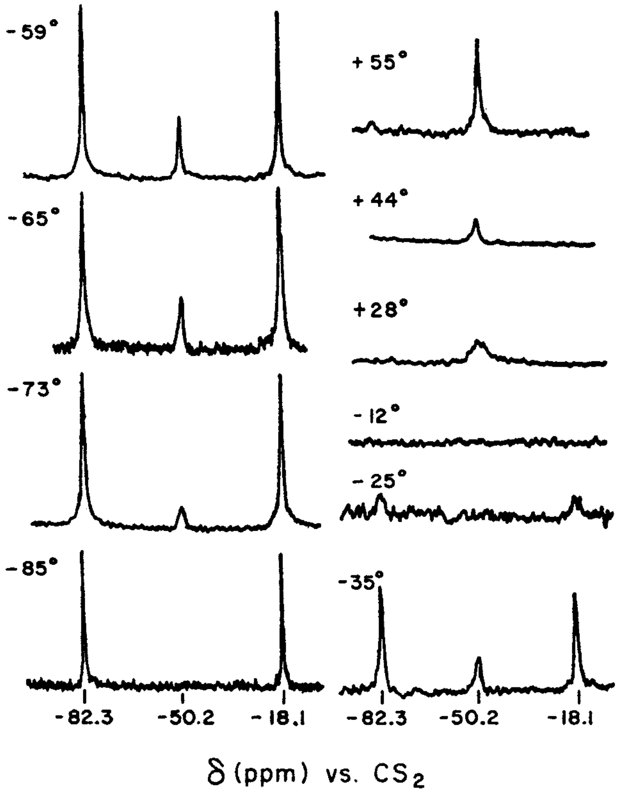

**Figure 19.** The $^{13}$C NMR spectra of ($\eta^5$-$C_5H_5$)$_2$$Fe_2$(CO)$_4$, at various temperatures. Reprinted with permission from ref 60. Copyright 1972 American Chemical Society.

In early 1972 Otto Gansow, one of the very few people then set up to do the necessary $^{13}$C NMR measurements, reported the $^{13}$C spectra[60] at temperatures from −85 to +55 °C; his results are shown in Figure 19. These spectra confirmed that bridge/terminal CO exchange occurs, but also gave a great deal of additional information that Gansow et al. did not discuss concerning stereospecificities in the process.

In the meantime, to circumvent my continued lack of a $^{13}$C NMR facility, I had had Rick Adams make and study a series of ($\eta^5$-$C_5H_5$)$_2$$Fe_2$(CO)$_n$(CNR)$_{4-n}$ compounds. In early 1973 we were able to propose a comprehensive explanation for the entire range of behavior of all these compounds.[61] As shown in Figure 20, the rearrangement pathways open to the ($\eta^5$-$C_5H_5$)$_2$$Fe_2$(CO)$_4$ isomers, with allowance for CO exchanges, form a rather complex pattern. The key feature here is the fact that in the unbridged forms there is a barrier to internal rotation. Because of this, bridge/terminal exchange can occur rather easily in the cis isomer, but only in concert with isomer interconversion for the trans isomer. The rate of both of the latter processes is governed by the barrier to internal rotation, whereas bridge/terminal exchange in the cis isomer is much faster because it is restricted only by the rather low barriers in going from the bridged form to one of the two enantiomeric nonbridged forms. The essence of this situation is captured in the potential energy diagram in Figure 21.[62]

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[59] Bullitt, J. G.; Cotton, F. A.; Marks, T. J. *Inorg. Chem.* **1972**, *11*, 671.

[60] Gansow, O. A.; Burke, A. R.; Vernon, W. D. *J. Am. Chem. Soc.* **1972**, *94*, 2550.

[61] Adams, R. D.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6589.

[62] Adams, R. D.; Cotton, F. A. *Inorg. Chim. Acta* **1973**, *7*, 153.

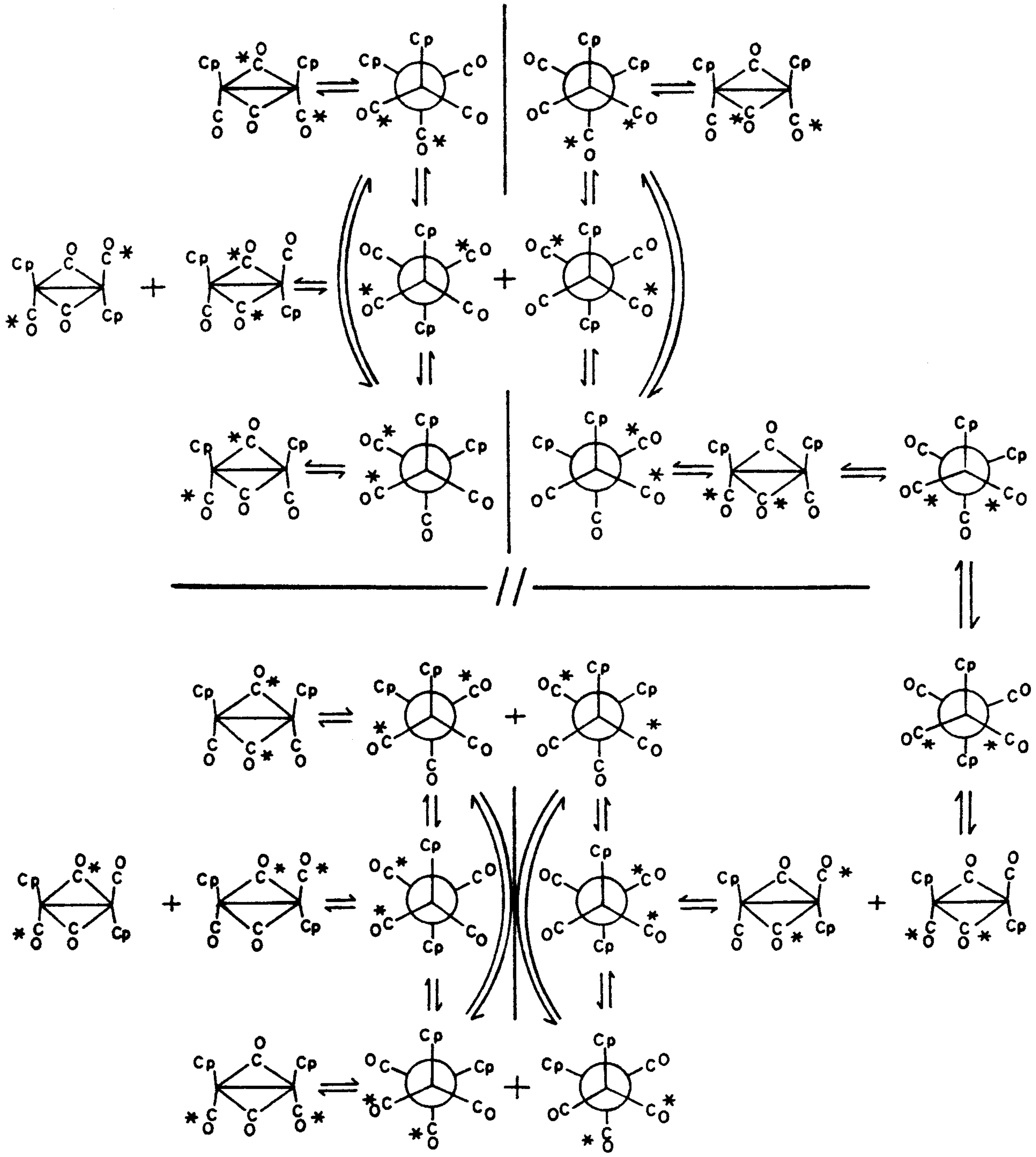

Figure 20. A scheme covering all the rearrangements of all the isotopomers of the cis and trans $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ molecules.

It is interesting that, because of the decreasing stability of a pair of bridging CO groups relative to a pair of terminal CO groups as metal atoms become larger, for $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$ the nonbridged isomers become about as stable as the bridged ones, and the barriers to interconversion are so low that all isomers are rapidly interconverting even at −100 °C.[63]

It was also shown at about the same time[64] that CO groups in $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ (where all CO groups are terminal) are scrambled over all six positions (a total of 6!/4 permutamers) by the intermediacy of pairs of bridging CO ligands. The interconversion of gauche and trans rotomers was also studied for this molecule.

**Twirling M(CO)$_3$ Groups.** When an M(CO)$_3$ group is bound to an olefin moiety, the low symmetry of the latter makes one CO different from the other two, or even all three different. At room temperature, the $^{13}C$ NMR spectrum of such a group nearly always consists of one sharp line, but at lower temperatures (usually much lower) one sees two or three lines. The first example of this, I believe, was reported as early as 1973[65] in $C_7H_8Mo(CO)_3$ and the second in 1974 in the closely related case of $C_8H_8Mo(CO)_3$.[66] The pertinent

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(63) Bullitt, J. G.; Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 2155.

(64) Adams, R. D.; Brice, M.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6594.

(65) Kreiter, C. G.; Lang, M. *J. Organomet. Chem.* **1973**, *55*, 627.

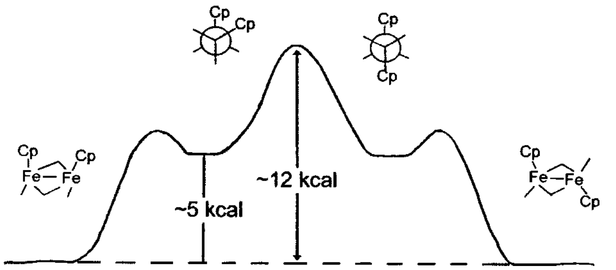

**Figure 21.** A potential energy diagram showing the importance played by the barrier to internal rotation in the dynamic behavior of the ($\eta^5$-$C_5H_5$)$_2$-$Fe_2(CO)_4$ molecule. Redrawn from ref 62. The negligible differences in the energies of the cis and trans isomers as well as the trans and gauche unbridged intermediates shown here would apply only for a nonpolar solvent.

averaging processes were proposed to be twirling of the Mo$(CO)_3$ groups around their local quasi-3-fold axes.

Shortly thereafter, compounds with two $Mo(CO)_3$ or two $W(CO)_3$ groups attached to an azulene or substituted azulene molecule, one to the seven-membered ring and one to the five-membered ring with an M−M bond between them, were studied.[67,68] We found that while the CO groups do not pass from one metal atom to the other, the $^{13}C$ NMR spectra of the $M(CO)_3$ groups are temperature dependent because of local twirling. Of special interest was the fact that the two rates were vastly different. Coalescence was seen at about −30 °C for the one attached to the seven-membered ring while it is seen at about −100 °C for the one on the five-membered ring. This means that the two activation energies must differ by 4−5 kcal mol$^{-1}$.

There are many cases of $Fe(CO)_3$ twirling. I will not consider any of them individually here, but note that I listed a great many in a paper in 1977.[69] The activation energies range from 6 to 16 kcal mol$^{-1}$. This same paper has a collection of results for other $M(CO)_3$ groups.

**Merry-Go-Rounds.** With the discovery and characterization of $Fe_2(CO)_7$(dppm) another new aspect of metal carbonyl fluxionality was first encountered.[70] In this molecule, whose structure is shown in Figure 22a, all seven CO groups are in more or less different environments, and in agreement with this, there are seven CO stretching bands in the infrared spectrum. In the $^{13}C$ NMR spectrum at 25 °C, however, there is only one signal, and it is a 1:2:1 triplet with a chemical shift in the range for terminal carbonyl groups. These data strongly imply that there is a site exchange process (or perhaps several) going on that (a) makes all CO groups time-average equivalent, but (b) also causes all CO groups to spend equal time on both iron atoms (assuming that the dppm ligand is not jumping around). Unfortunately, no line shape change occurred, even at the lowest temperature that could be reached, so no certain information could be obtained directly for this compound.

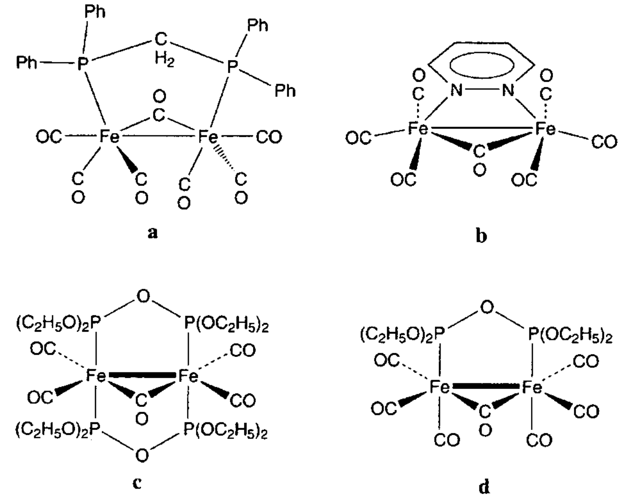

**Figure 22.** Some molecules displaying merry-go-round fluxionality: (a) $Fe_2(CO)_7[(Ph_2P)_2CH_2]$, (b) (1,2-diazine)$Fe_2(CO)_7$, (c) $Fe_2(CO)_5[(Et_2O)_2POP(OEt_2]_2$, and (d) $Fe_2(CO)_7[(EtO)_2POP(OEt)_2]$.

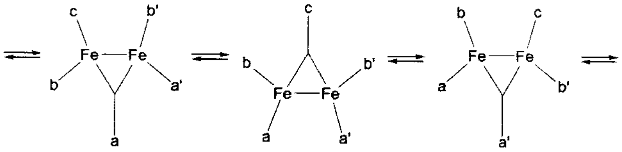

**Figure 23.** The type of merry-go-round motion (which can go in either direction) proposed for the molecules shown in Figure 22.

Later, however, several other molecules were made which did provide the necessary data on what proved to be merry-go-rounds. One of these is shown in Figure 22b.[71] A study of the $^{13}C$ NMR spectrum confirmed this structure in solution at −140 °C: there are four lines, three in the region of terminal CO groups, and one in the bridging region, of relative intensities 2:2:2:1. On raising the temperature, two of the first three and the last one broaden, and by −100 °C, they have coalesced to a single line of relative intensity 5 at the correct weighted average position. Above about −60 °C this and the remaining original peak begin to collapse, and from about −30 °C on up there is a single peak, which by room temperature is very sharp. It seems clear that in the first stage (−140 to −60 °C) the exchange process that is responsible for the line shape changes is a merry-go-round of the five CO groups in the central plane, as shown in Figure 23. After that is going quite fast, the two $Fe(CO)_3$ groups start to twirl rapidly.

In the case of the molecule shown in Figure 22c we devised an arrangement that is perfect for studying the merry-go-round.[72] All the interesting behavior is in a measurable temperature range, and couplings to the phosphorus nuclei help keep track of what is going on. At −158 °C there are a bridging CO resonance that is a quintet and two terminal CO resonances each of which is a quartet. These all broaden, collapse, and coalesce into a single signal at the correct average position; at −40 °C and above this signal is a sharp quintet. Thus we have a textbook case of the kind of merry-go-round shown in Figure 23.

Finally, in the molecule shown in Figure 22d we have a close relative to the one with which this section began, Figure 22a, where $(EtO)_2POP(OEt_2)$ replaces $Ph_2PCH_2PPh_2$. Here, however, the whole two-stage scrambling process was observed.[71] Beginning with a limiting low-temperature

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(66) Cotton, F. A.; Hunter, D. L.; Lahuerta, P. *J. Am. Chem. Soc.* **1974**, *96*, 4723.

(67) Cotton, F. A.; Hunter, D. L.; Lahuerta, P. *J. Organomet. Chem.* **1975**, *87*, C42.

(68) Cotton, F. A.; Lahuerta, P.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 1866.

(69) Cotton, F. A.; Hanson, B. E. *Isr. J. Chem.* **1977**, *15*, 165.

(70) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4422.

(71) Cotton, F. A.; Hanson, B. E.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1977**, *99*, 3293.

(72) Cotton, F. A.; Haines, R. J.; Hanson, B. E.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 2010.

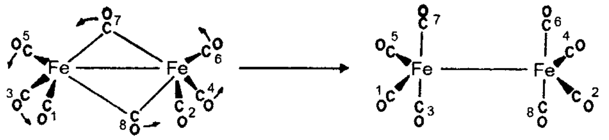

**Figure 24.** A diagram showing how the CO ligands associated with the bridged edge of the $Fe_3(CO)_{12}$ molecule would move as the bridges are opened in a concerted manner.

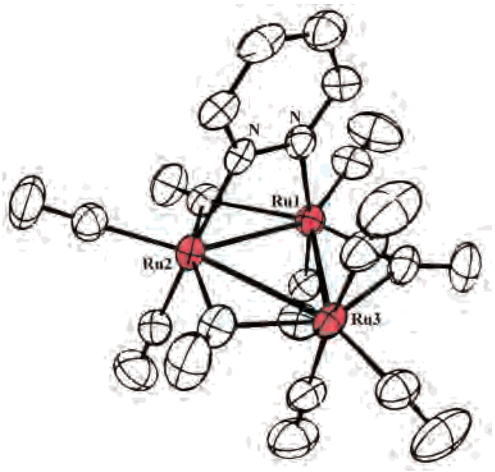

**Figure 25.** The structure of $Ru_3(CO)_{10}$(1,2-diazine).

spectrum at −149 °C, which confirmed the expected structure, there is an averaging of all the six terminal CO resonances into one triplet, followed by averaging of this with the signal for the bridging CO so that by 0 °C there is one resonance with sharply resolved triplet structure. Twirling of the two $Fe(CO)_3$ groups followed by a merry-go-round process accounts for the observations.

Merry-go-round processes have also been found in metal carbonyls of nuclearity greater than two. As I noted at the beginning of this section, such processes go on in a three-dimensional way in $Rh_4(CO)_{12}$. They probably also occur in $Co_4(CO)_{12}$ and $Ir_4(CO)_{12}$, but experiments to detect them would be far more difficult and have not been done.

We first observed merry-go-round behavior in trinuclear compounds in the mid-1970s. Already in 1972 Gansow[60] had reported that for $Fe_3(CO)_{12}$ the $^{13}C$ NMR spectrum consisted of only a single line down to −10 °C, where low solubility prohibited going further. In view of the structure of $Fe_3(CO)_{12}$ in the solid, which evidently persisted, at least partly, in solution according to the infrared spectrum, I proposed in 1974 the process shown in Figure 24 to explain how all CO groups in the molecule could achieve time-average equivalence.[73] However, a new possibility was suggested by the structure shown in Figure 25.[74] While $Ru_3(CO)_{12}$ has all CO groups in terminal positions, the structure of $Ru_3(CO)_{10}$(1,2-diazine) has a central planar arrangement with three terminal and three bridging CO ligands. Thus, the possibility of a cycling process of the type shown in Figure 26 is suggested for an $M_3(CO)_{12}$ molecule. Of course, this could not by itself average all CO resonances, but it could participate.

The $Ru_3(CO)_{10}$(1,2-diazine) molecule is soluble enough that its $^{13}C$ NMR spectra could be observed down to −150 °C, where a spectrum completely in accord with the crystal structure was seen.[75] Between −156 and −86 °C we observed exactly the changes that would be expected by the merry-go-round process in Figure 26. In addition, two other exchange processes which were not uniquely determined take place in this molecule so that by 75 °C all 10 CO groups contribute to only one sharp resonance.

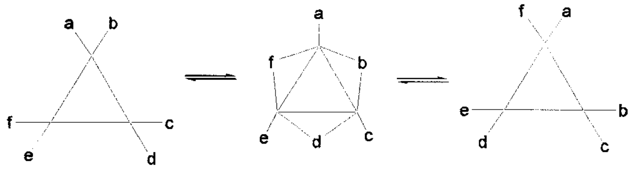

**Figure 26.** A merry-go-round process for the in-plane CO groups in an $M_3(CO)_{12}$ molecule.

It is very interesting that the osmium analogue[76] of $Ru_3(CO)_{10}$(1,2-diazine) has a structure that differs in only one key respect: it has only terminal CO groups. This was not entirely unexpected since bridging is frequently seen to be less favored for compounds in the third transition series compared to the second. Again, however, the same merry-go-round process was indicated by the $^{13}C$ NMR line shape changes, as well as other processes leading finally (54 °C) to a one-line spectrum. Merry-go-round cycling is about 4 kcal/mol easier in the Ru compound than in the Os compound, due to the relatively lower stability of bridges in the latter.

Still other examples of merry-go-rounds in triangular trinuclear carbonyls were discovered in this time period,[77] but they will not be discussed here. Clearly, merry-go-rounds were in vogue.

## 3. The Discovery of Agostic Interactions

Toward the end of 1970 Jerry Trofimenko reported that he had made a number of compounds that had a *noninert-gas configuration*. For one of these compounds he proposed structure **a** in Figure 27, although noting that the 18-electron structures **b** and **c** might also be considered.[78] I think his preference for **a** was based on the fact that he had made analogues in which only allyl groups were present, and in these compounds structures similar to b and c would be impossible. I was skeptical of the idea of 16-electron compounds of this type, and so we undertook an X-ray crystal structure determination on this compound.[79] As a result, we showed that the actual structure was *none of the above*, but instead the one shown in Figure 28. The data set was a very good one, and the structure behaved so well that all 46 hydrogen atoms in both enantiomorphs were refined isotropically and independently.

The structure does show an $\eta^3$-$C_7H_7$ ring, as proposed by Trofimenko, but there is not a 16-electron configuration. It can be seen that the conformation of the pyrazolylborate has an unprecedented severely puckered boat configuration. This

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(73) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155.

(74) Cotton, F. A.; Jamerson, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 5396.

(75) Cotton, F. A.; Hanson, B. E.; Jamerson, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 6588.

(76) Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1977**, *16*, 2820.

(77) (a) Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1977**, *16*, 3369. (b) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 144. (c) Tachikawa, M.; Richter, S. I.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *1258*, C9. (d) Johnson, B. F. G.; Lewis, J.; Reichert. B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403.

(78) Trofimenko, S. *Inorg. Chem.* **1970**, *9*, 2493.

(79) (a) Cotton, F. A.; Calderon, J.; Jeremic, M.; Shaver, A. *J. Chem. Soc., Chem. Commun.* **1972**, 777. (b) Cotton, F. A.; Jeremic, M.; Shaver, A. *Inorg. Chim. Acta* **1972**, *6*, 543.

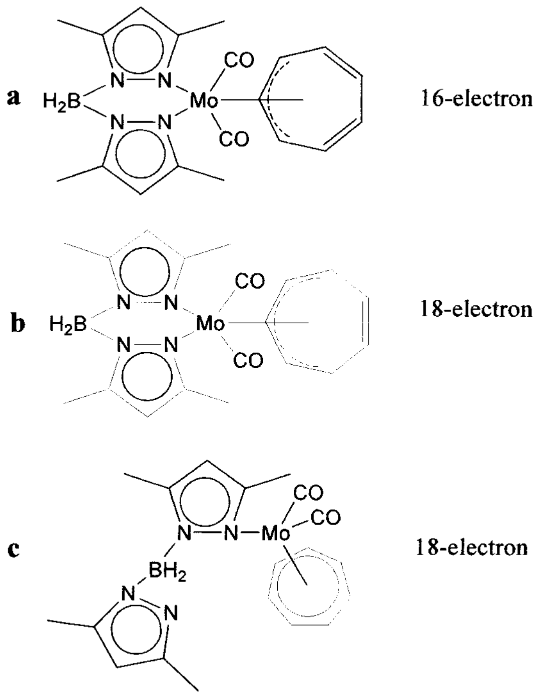

**Figure 27.** The three structures initially suggested for a $(H_2Bpz_2)Mo(CO)_2C_7H_7$ molecule.

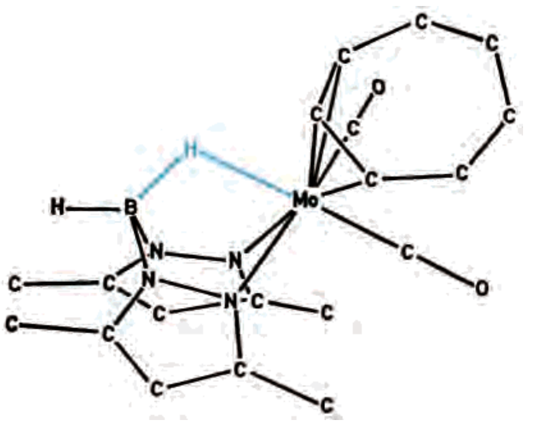

**Figure 28.** The actual structure found for the $(H_2Bpz_2)Mo(CO)_2C_7H_7$ compound.

is what I said about this structure. The reason for this “puckering is that one of the hydrogen atoms on the boron atom approach[es] the molybdenum atom closely, forming a B−H−Mo 3-center, 2-electron bond. . . . the molybdenum atom can be considered to achieve an effective 18-electron configuration when the two electrons in the bonding orbital that extends over the B−H−Mo group are counted.” And later in the paper, “the central Mo atom achieves an effective 18-electron configuration by virtue of its share in the electron pair occupying the bonding orbital spread over the three-centered system B−H−Mo.” In our discussion of this compound we were therefore proposing *in detail*, for the first time, a B−H•••M interaction that was a precedent and a model for what was later designated an *agostic* interaction when there is a C−H bond instead of a B−H bond.

With the “agostic” B−H case to contemplate, I was led to wonder what would be the result of substituting for the $BH_2$ group in the pyrazolyl ligand a $BR_2$ group, while also having a simple allyl group which could not possibly be more than a 3-electron donor. I discussed this with Jerry Trofimenko, and he pointed out to me that he had already reported[78] just the compound that I needed and noted that it had unusual NMR features. He was kind enough to send me a sample. In the Spring of 1973 we determined the structure. The result was the first fully documented and fully explained example of an *agostic* C−H bond, as shown in Figure 29.[80] In our paper, we pointed out that “there is an interaction between an aliphatic C−H bond and a metal atom” and described this interaction as “a three-center, two-electron bond encompassing the C•••H•••Mo atoms.”

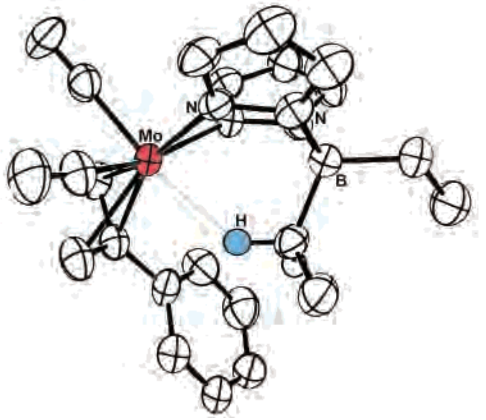

**Figure 29.** The structure of $(Et_2Bpz_2)Mo(CO)_2(2\text{-}C_6H_5allyl)$.

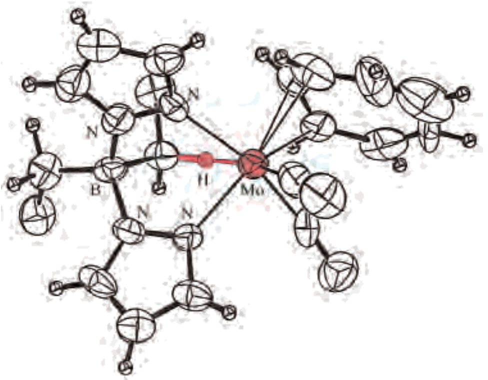

**Figure 30.** The structure of $(Et_2Bpz_2)Mo(CO)_2C_7H_7$.

Almost immediately after that we showed that such an interaction is a strong one.[81] This was done by using NMR spectroscopy to measure the activation energies for the alternation of the two α-hydrogen atoms on the endo $CH_2$ group in the bonding position as well as several other fluxional processes in the molecule. These results were used to estimate that “17−20 kcal $mol^{-1}$ . . . probably approximates to the strength of the C−H•••Mo interaction.”

Finally, the structure of the (diethyldi-1-pyrazolylborato)-$Mo(CO)_2C_7H_7$ molecule was examined[82] to answer the following question: “Can a CH-to-metal interaction of the type found in [the analogous compound with a 2-phenylallyl group] . . . be strong enough to compete with the far better established process of more extended interaction of a metal atom with a cyclic polyolefinic ligand?” The answer, which may be seen in Figure 30, is “that the $C_7H_7$ ring is a three-electron donor . . . there is a C−H−Mo interaction . . . [and]

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(80) Cotton, F. A.; LaCour, T.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 754.

(81) Cotton, F. A.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 5074.

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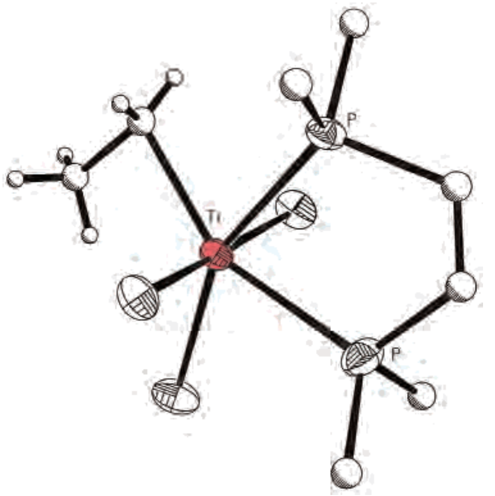

**Figure 31.** The $TiCl_3(dmpe)C_2H_5$ molecule.

such a C−H−Mo . . . interaction is structurally and thermodynamically competitive with olefin−metal bonding."

It was not until several years later that other examples of C−H···M bonding began to appear in the literature. The first one was in $\{Fe[P(OMe)_3]_3(\eta^3\text{-}C_8H_{13})\}(BF_4)$, which was obtainable in the form of large enough crystals to permit collection of neutron diffraction data.[83] This revealed a situation identical in two essential ways to the one I had described six years earlier: (1) a metal atom that would have a 16-electron configuration without the C−H···M interaction; (2) significant distortion of the ligand owing to the strength of the C−H···M interaction. There was a small difference in the sense that the C−H···Fe interaction was somewhat more toward the side-on type and the C−H···Mo more toward the linear type. Many other genuine examples (as well as chimerical ones, such as $TiCl_3CH_3$) have since been found, and in a review in 1983 the term agostic[84] was proposed for this interesting and important phenomenon which I am proud to have discovered.

There is one recent piece of work done in my laboratory that I would like to mention because it shows that the very common practice of inferring a reaction mechanism from a feature seen in a crystal structure can be unreliable. In 1986 the molecule shown in Figure 31 was reported.[85] This molecule provides an excellent example of an agostic interaction; the ethyl group is highly distorted ($\angle$Ti−C−C = 84°) so that a $\beta$-hydrogen atom can approach the titanium atom closely. The posture of the ethyl group seems to suggest that, as the authors themselves put it, it "models a stage about halfway along the reaction coordinate for a $\beta$-elimination reaction to form the titanium−ethylene−hydride complex $[TiH(dmpe)(\eta\text{-}C_2H_4)Cl_3]$." As they also pointed out, the latter compound would certainly be unstable. Since the parent compound is itself thermally unstable (decomposing at *ca.* 37 °C in solution), it would seem likely that ethylene would be eliminated easily from $TiCl_3(dpme)C_2H_5$, and ultimately the dinuclear species $Cl_2(dmpe)Ti(\mu\text{-}Cl)_2TiCl_2(dmpe)$ would be formed. We did, indeed, isolate and characterize this latter species.[86] However, in spite of the suggestion that seems implicit in the structure shown in Figure 31, we found[87] that decomposition actually occurs by a Ti−C bond homolysis, giving ethyl radicals which then form $C_2H_4$, $C_2H_6$, and $C_4H_{10}$ in the expected ratio.

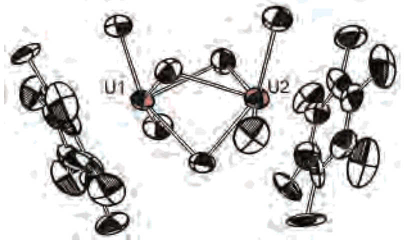

**Figure 32.** The structure of $[I(C_6Me_6)Cl_2U(\mu\text{-}Cl)_3UCl_2(C_6Me_6)]AlCl_4$.

## 4. Other Topics

I will conclude by mentioning briefly two other topics of my research that I remember with pleasure and believe to have been of particular interest in the development of nonclassical organometallic chemistry.

**Arene Complexes of Lanthanides and Actinides.** Cyclopentadienyl compounds of lanthanide and actinide elements are an old story. Wilkinson and co-workers made the first ones in the 1950s, namely, $(C_5H_5)_5UCl$[88] and an entire series of lanthanide compounds of the type $(C_5H_5)_3Ln$ (Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, and Yb).[89] Wilkinson insisted that the bonding in these compounds is highly ionic. In 1984, a theoretical study found a "very small U−Cp overlap population" in the uranium compound.[90] Despite the large amount of work done by Marks, Evans, and others on $C_5H_5$ and $C_5Me_5$ compounds where ionic bonding is possible, and *could*, perhaps, be the whole story, prospects for $(C_6H_nR_{6-n})_xM$ compounds of lanthanides and actinides, where ionic bridging is not possible, were considered poor. Until 1985 only one such compound, $(C_6H_6)U(AlCl_4)_3$, had been reported.[91]

I was not convinced that the prospects for others were as dim as the conventional wisdom seemed to say. Since donor bonding rather than ionic bonding would be necessary, the best chance seemed to be with hexamethylbenzene. It was quickly shown that uranium compounds can indeed be made, and in 1985 and 1986 we published three that were fully characterized.[92] One of these is shown in Figure 32. We also showed that a compound, shown in Figure 33, can be made with samarium.[93] It seems to me that our success provides a clear indication that there is more chemistry to be discovered here, and I hope someone will pursue it, perhaps in China, where the lanthanide elements occur abundantly in Nature and much research on other classes of lanthanide compounds is now vigorously carried out.

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(91) Cesari, M.; Pedretti, U.; Zazzetta, A.; Lugli, G.; Marconi, W. *Inorg. Chim. Acta* **1971**, *5*, 439.
(92) (a) Cotton, F. A.; Schwotzer, W. *Organometallics* **1985**, *4*, 942. (b) Campbell, G. C.; Cotton, F. A.; Haw, J. F.; Schwotzer, W. *Organometallics* **1986**, *5*, 274. (c) Cotton, F. A.; Schwotzer, W.; Simpson, C. Q., II. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 637.
(93) Cotton, F. A.; Schwotzer, W. *J. Am. Chem. Soc.* **1986**, *108*, 4657.

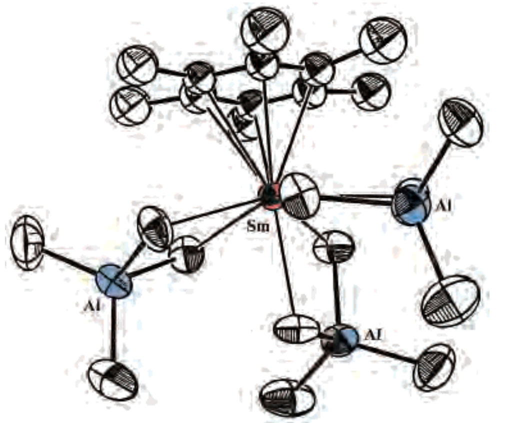


**Figure 33.** The structure of Sm($\eta^6$-$C_6Me_6$)($AlCl_4$)$_3$.

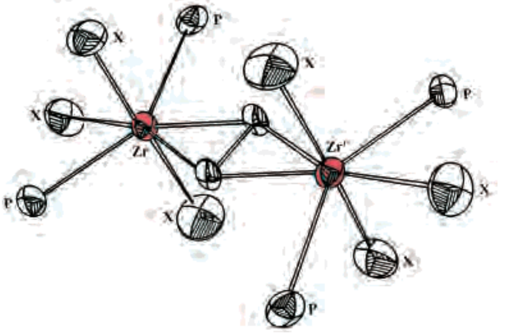
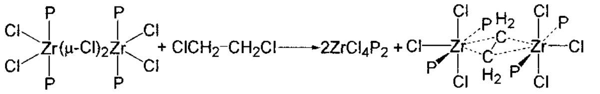


**Figure 34.** The structure of the $[ZrX_3(PEt_3)_2]_2(C_2H_4)$ molecules (X = Cl, Br) with ethyl groups and hydrogen atoms omitted.

***$\mu_2,\eta^2,\eta^2$-$C_2H_4$*.** It is remarkable, considering the enormous volume of work that has been done on metal−olefin complexes (the first $C_2H_4$ complex, Zeise's salt, having been made as early as 1827), that it was not until 1987 that the first examples of a $\mu_2,\eta^2,\eta^2$-$C_2H_4$ compound were knowingly reported. I use the word "knowingly" deliberately, for a reason that will be made clear later.

The first $\mu_2,\eta^2,\eta^2$ compound[94] to be recognized as such by X-ray crystallography is shown in Figure 34. It was made by the indirect reaction (1). The bromo analogue was also reported. In a paper submitted only a month later another $\mu_2,\eta^2,\eta^2$ compound[95] was reported by a more direct method, i.e., by joining another metal center to an already formed $\eta^2$-$C_2H_4$ compound, eq 2. Subsequently, other examples have been reported,[96] and there is also an $N_2$ bridged compound, $[(C_5Me_5)_2Sm]_2N_2$, that seems to be similar.[97]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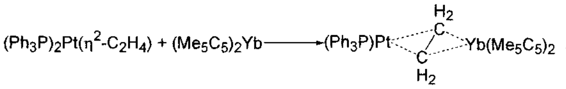
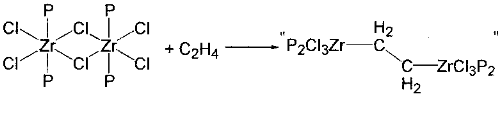

(2)


(3)


(4)

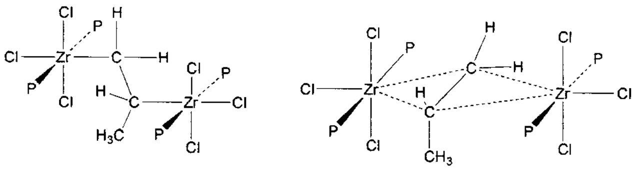


**Figure 35.** Two possible structures for $[ZrCl_3(PEt_3)_2]_2CH_2CHCH_3$.

In a full paper[98] that followed our original report, we showed that hafnium analogues of the zirconium compounds could be made. In addition, MO calculations were made that showed clearly how the bonding occurs, at least in the molecules that we made, and probably in the others. It is interesting, however, that all attempts to make analogues with substituted ethenes, such as propene, failed. It was concluded that this was due to steric hindrance.

The most recent example of $\mu_2,\eta^2,\eta^2$-$C_2H_4$ is the infinite polymer $[Rh_2(O_2CCF_3)_4C_2H_4]_\infty$, which again was made by indirect reaction of $Rh_2(O_2CCF_3)_4$ with $ICH_2CH_2I$.[99]

I conclude this section by noting that in 1981, the reaction shown in eq 3 was reported.[100] Of course, the product is not as indicated, which is simply what the authors assumed it would be, but it is the $\mu_2,\eta^2,\eta^2$ compound that we later obtained by a different route and correctly characterized by X-ray crystallography. However, these authors also reported that, *by their route*, they could make the propene homologue, which we failed to obtain. The real kicker in this story is that, apparently, the propene compound may really have the 1,2-$[ZrCl_3(PEt_3)_2]CH_2CHCH_3$ structure, at least according to the NMR spectrum reported for it, as I shall now explain.

Consider the two structures, as shown in Figure 35. For the 1,2 structure, assuming free rotation about the Zr−C bonds, there are two equivalent P atoms on each end of the $-CH_2-CH(CH_3)-$ bridge. Assuming further that coupling of the two on one end with the two on the other end is negligible, one would expect to see two $^{31}P$ singlets of equal intensity. On the other hand, for the $\mu_2,\eta^2,\eta^2$ structure, the two ends of the molecule should be equivalent, while the two P atoms on one Zr atom would not be equivalent but would be strongly coupled to each other, as always occurs for nonequivalent, trans phosphines. The spectrum should therefore be a doublet of doublets. The reported spectrum is two singlets, and this is consistent only with the 1,2-ethane structure. Perhaps this should be checked.

If this is true, the question arises as to whether equilibria of the type shown in eq 4 may occur. It is also pertinent to note that several structures have been reported in which the bond angles and distances are between the extremes represented by the $\mu_2,\eta^2,\eta^2$ and 1,2-ethane models. Thus, we have the two situations shown in Figure 36.[101,102] The entire

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(94) Cotton, F. A.; Kibala, P. A. *Polyhedron* **1987**, *6*, 645.

(95) Burns, C. J.; Anderson, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 915.

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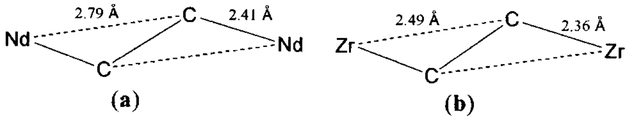

**Figure 36.** Two intermediate structures. For **a** see ref 101; for **b** see ref 102.

question of the nature of olefin-bridged binuclear compounds may actually be complex. It may also have some additional importance because this may play a role in the action of certain olefin polymerization catalysts. Evans has proposed[103] that there may be a $(C_5Me_5)_2Sm(\mu_2,\eta^2,\eta^2\text{-}C_2H_4)Sm(C_5Me_5)_2$ intermediate in the catalysis of ethylene polymerization by $(C_5Me_5)_2Sm$.

## Postfactory Remarks

I have found nonclassical organometallic chemistry to be great fun for just about the entire half-century it has existed, and it seems to me that the fun is far from over. Apart from the fun, of course, this field has had a huge—multibillion dollar—impact on the chemical industry, and there is no doubt that that is going to continue for a long time to come.

I am, of course, greatly indebted to many co-workers, most of whose names are mentioned in the references, for their vital contributions to all that has been accomplished in my laboratories over the years. Support by the National Science Foundation, the Robert A. Welch Foundation, and Texas A&M University (through the Laboratory for Molecular Structure and Bonding) have been indispensable.

I am very pleased that my work has been recognized by the ACS Award in Organometallic Chemistry for 2001.[104]

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(104) This is my final word. Harry S. Truman (my favorite president in my lifetime) once said “no two people ever see the same thing in quite the same way, and when they tell it the way they saw it, they aren’t necessarily lying if it’s different.” I think I am entitled to my opinion when it’s just a matter of opinion, but if I got some facts wrong in this account of things that happened years ago, I should be very glad to hear from anyone who can point out a factual error. If this happens, I shall ask the editor to publish an erratum—or, if necessary, errata.