Journal of Organometallic Chemistry, 100 (1975) 29—41

FLUXIONALITY IN ORGANOMETALLICS AND METAL CARBONYLS

F.A. COTTON
Department of Chemistry, Texas A & M University, College Station, Texas 77843 (U.S.A.)

I have recently reviewed the field of fluxional, and other stereochemically nonrigid, organometallic molecules, as well as the contiguous, if not in fact overlapping, field of nonrigidity of metal carbonyls and their derivatives, in considerable technical detail in two rather lengthy articles [1,2]. It is indicative of the importance of these fields and the level of activity in them that both articles, especially the latter, which cover the literature to about the middle of 1973, are already in serious need of updating. However, this is not the occasion on which to do that. This article has a different purpose. I shall give here my personal recollections of the main developments and how they have led to the present state of knowledge. It is my good fortune to have been personally close to, and often an active participant in, nearly every major development. I hope therefore that this retrospective and anecdotal account may convey some of the special flavor of the events as seen from a personal and inside vantage point.

The earliest developments

Genesis. Since the only general method of detecting fluxionality has been NMR spectroscopy, it is not surprising that recognition and study of the phenomenon, widespread and important though it is, awaited the availability of commercial NMR spectrometers. The first observation was made, however, very soon after the Varian spectrometer went on sale, and it was in the field of organometallic compounds*.

In 1955 Wilkinson, who was then at Harvard, was carrying out an extensive program to prepare and characterize cyclopentadienyl compounds of the transition elements. The main thrust was towards compounds containing "sandwich-bonded" (or, as now described, *pentahapto*) rings. In the course of this program, one of his more productive students, the late T.S. Piper, prepared the four compounds $C_5H_5CuPEt_3$, $(C_5H_5)_2Fe(CO)_2$ $(C_5H_5)_2Cr(NO)_2$ and $(C_5H_5)_2$-Hg. These along with other compounds were examined by proton NMR as well as by other physical and chemical methods. In each case experimental evidence

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* It is true that the NMR equivalence of the fluorine atoms in PF_5 was reported in 1954 (H.S. Gutowsky, D.W. McCall and C.P. Slichter, J. Chem. Phys., 21 (1953) 279), but no explicit suggestion of an intramolecular exchange or rearrangement process was made.

and/or qualitative ideas of electronic structure were believed to indicate that one σ *monohapto* C_5H_5 ring is present. However, in each case the complex spectrum expected for such a ring was absent and only a single line was observed [3].

I can well remember the consternation and cudgeling of brains that this produced in Wilkinson's energetic little research group. After the initial, obvious suspicions that the spectrometer wasn't working properly or had been ineptly operated were invalidated by careful rechecking, Wilkinson himself produced the idea that the ring was perhaps moving so that the metal-to-carbon bond switched rapidly enough from one carbon atom to the next to cause all resonances to be seen as one. He himself has later pointed out that this idea came to him as a kind of analogy with motion picture projection. Be that as it may, the idea seemed rather bizarre and I doubt if anyone in the group, the boss included, would have been prepared to bet his life insurance on it. However, no one thought of anything else which could begin to explain the facts. Following the Holmsian [4] principle ("When you have eliminated the impossible, whatever remains, however improbable, must be the truth") Wilkinson and Piper published this suggestion in 1956:

"An alternative 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; the cyclopentadienyl group may thus be regarded as rotating, and in respect to NMR measurements all of the protons thus become equivalent."

The essential idea here, namely, that rapid site exchange could lead to signal averaging, was not, of course, new. It had been known for several years [5] and had been fleshed out in considerable detail by Gutowsky [6] who showed exactly how the spectrum would vary with the rate of site exchange for an uncoupled, two-site process. To the best of my remembrance, however, none of us in Wilkinson's group were aware of this work and in any event, the rotating cyclopentadienyl group was still a bold and clever idea. It might be noted also that the specific suggestion of 1,2 shifts, which has since been proved correct, was made without explicit consideration that other pathways or intimate mechanisms (e.g., 1,3 shifts or a symmetrical transition state) could equally well explain the one available observation of a single line. Finally, it may be noted that the copper compound has since been shown to contain an η^5-C_5H_5 ring, although a tautomer with an η^1-C_5H_5 ring may be only slightly less stable and may be realized in certain solvents [7].

It can be said, however, that the iron compound and its isoelectronic chromium nitrosyl analog stand out clearly as the first recognized examples of fluxionality. Curiously, this remarkable discovery generated no direct or immediate sequel. Wilkinson had moved to England and was in the throes of revitalizing the inorganic laboratory at Imperial College. John Birmingham and Albert Fischer went into industry. Stan Piper resolutely abandoned organometallics for ligand field theory, and I was trying, as Wilkinson counseled all his students, not to "keep rewriting my Ph.D. thesis", i.e., to work in new areas. As far as outsiders were concerned, the observation appeared to have been "little noted nor long remembered."

Metal carbonyls. Metal carbonyls seemed to me to provide a tremendously open-ended field of research in 1955, when I started my independent career, despite the magnificent, pioneering efforts of Hieber [8] and others, and I decided to plunge in. While with Wilkinson I had carried out some of the first exercises in the now familiar game of employing symmetry-based selection rules to deduce from infrared spectra the structures of carbonyls and their derivatives. This seemed a good thing to expand, and the very important molecule $Fe(CO)_5$ posed a nice problem. Unfortunately the question of whether it had a trigonal bipyramidal or square pyramidal structure did not yield unambiguously to vibrational spectroscopy. Ronald Nyholm and I had, in fact, established a friendly rivalry about nailing the structure, with piquancy added by the fact that I favored the TBP and he the SP. It occurred to me that ^{13}C NMR might afford a definitive result since the two signals would have intensity ratios of 2/3 and 1/4 for the two structures. Thus it was that I approached my colleague John Waugh at MIT and the first ^{13}C NMR spectrum of a metal carbonyl was recorded [9]. This required all of John's very considerable expertise because Fourier transform spectrometry did not exist, and even for neat, liquid $Fe(CO)_5$, with ^{13}C at only the natural (1%) level, signal to noise was a severe problem. The observed spectrum was a single line. We were nonplussed, and suggested three possible explanations: (1) coalescence of the two signals due to rapid exchange under the influence of impurities, (2) an unresolvably small chemical shift difference, (3) a very large T_2 for one signal, such that it became saturated when the other was recorded.

The next development will be evident from the letter which is shown in facsimile on pages 32 and 33. Here the reader can see the "Berry pseudorotation"described long prior to the publication by R.S. Berry of his landmark paper. John Waugh and I recognized, with some reservations, the appositeness of his suggestion, and I know that I regretted not having thought more about the results before publishing. We did not feel we should accept his invitation to associate ourselves with his now celebrated pseudorotation, which Berry submitted for publication in October of the same year [10]. I replied to him (January 26, 1959) as follows:

"Thanks for your recent letter concerning the trigonal bipyramid problem. John and I were aware of Gutowsky's work on PF_5 and did feel that the iron carbonyl situation must be comparable. It might interest you to know that Lauterbur... confirms our results... Frankly, I do not see what can be done except to suggest that this rapid inversion-like motion occurs... I think you should go ahead and publish [the idea] yourself, since neither John nor I have anything significant to contribute...."

As an amusing sidelight, Nyholm (who did not know Lauterbur had confirmed our result) thought we had simply missed the weaker peak of what he expected to be a 1/4 spectrum. He therefore went to great expense and trouble to have the experiment repeated with ^{13}C-enriched $Fe(CO)_5$. Result: the same as ours, one line [11].

Organometallics again. The next development, which subsequently proved to be crucial, occurred in 1959. The compound $C_8H_8Fe(CO)_3$ was prepared in four laboratories [12-15]. While I was in England in the spring of 1959, Wilkinson and his student, Ray Burton, told me that they had prepared this compound but were perplexed by its NMR spectrum, which consisted of but one sharp line.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF MICHIGAN • ANN ARBOR, MICHIGAN

January 21, 1959

Dr. F. Albert Cotton
Department of Chemistry
Massachusetts Institute of Technology
Cambridge 39, Mass.

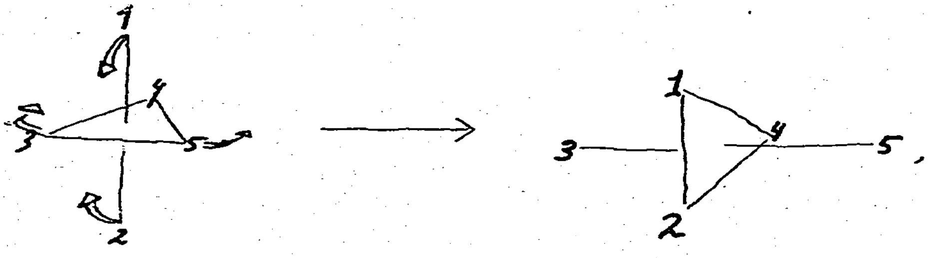
Dear Al,

The note you had in the latest JCP is quite interesting. I think I can guess what may be going on in Fe(CO)$_5$ now. As I understand it, your data indicate completely equivalent CO's in NMR but a trigonal bipyramid structure according to the infrared spectrum.

These are completely consistent. In fact Bill Moffitt had been working on the trigonal bipyramid problem before he died, and I have been concerned with apparently anomalous equivalences in NMR spectra myself, as in B$_5$H$_{11}$. Anyway, the explanation seems to run like this:

The NMR line width or observation time is long compared with the vibrational frequency. But in the trigonal bipyramid, the vibrations lead to distortions which scramble the vertices and give the equivalent of a rotation. The result is that the carbons all become equivalent even though the molecule has an instantaneous trigonal bipyramid structure. An exactly equivalent problem arises in the case of the single F^{19} NMR absorption in PF$_5$, on which Gutowsky and McCall or Gutowsky and Slichter did some work.

Thus



etc.

Dr. F. Albert Cotton
Page 2

The whole thing arises from the peculiarities of the group for a trigonal bipyramid. So there it is. If you want more details, I can write you about them. Perhaps you, John and myself could do a little note or something if you are interested.

Irrelevant personal matters deleted.

As ever,
Steve
R. Stephen Berry

RSB:ddk

Soon after, an issue of the Proceedings of the Chemical Society turned up with the report by Manuel and Stone [12] who had made the same observation. The latter proposed a symmetrical structure with a planar, octagonal ring and, on the basis of the appearance of the infrared spectrum in the C—H stretching region I also favored such a structure, and attempted to rationalize it in molecular orbital terms [16]. I now believe that the MO scheme I proposed is intrinsically unrealistic since some of the interactions I chose to regard as nonbonding would, in fact, be antibonding, thus destablizing the symmetrical structure. In due course, all speculation was supplanted by cold fact: Dickens and Lipscomb [17] showed that the structure in the crystal involved coordination of two adjacent double bonds; it was simply an analog of the very old (1930) Reihlen compound, (1,3-butadiene)$Fe(CO)_3$ [18]. To account for the single proton resonance, Lipscomb and Dickens suggested: "A dynamical effect amounting to permutation of the C atoms of the ring relative to the $Fe(CO)_3$ group..." and further commented that "A temperature dependence study of the resonance spectrum of (COT)$Fe(CO)_3$ may verify the above situation."

In making their suggestion that $(C_8H_8)Fe(CO)_3$ is a dynamical molecule, Dickens and Lipscomb made no reference to Wilkinson and Piper's suggestion, six years earlier, of the same sort of thing for $(\eta^1\text{-}C_5C_5)$M compounds. I presume that they were not aware of it; few people were. Even later when, I think, the idea that $(C_8H_8)Fe(CO)_3$ might indeed be a dynamical molecule in solution had been more or less generally accepted as plausible (though still unproved), the relationship to Wilkinson's earlier work was not generally recognized. Thus, in Philadelphia in April of 1964, at the 147th National ACS meeting there was a very successful symposium on organometallic compounds, so successful indeed, that I think it was instrumental in encouraging the establishment of the continuing biennial series of International Conferences on Organometallic Chemistry. At this meeting I remember Roland Pettit presenting a talk on polyolefin complexes of iron carbonyl groups, some of which he postulated to be dynamical, like $(C_8H_8)Fe(CO)_3$. It was here, to the best of my knowledge, that his colorful sobriquet "ring-whizzer" made its debut. I very clearly remember pointing out in the discussion following his paper, and in conversation with him later, that the Piper and Wilkinson paper had revealed the first "ring-whizzers" years before. Pettit, too, had simply not been aware of this work.

It was after April of 1964 that I began to think seriously about conducting an investigation into the nature of such species as Wilkinson's $(\eta^1\text{-}C_5H_5)M$ compounds and $C_8H_8Fe(CO)_3$. The fact that there were these two different kinds of compounds, as well as several others that Pettit had described, which all seemed likely to be "dynamical" to use Lipscomb's word, and the fact that, apparently, no one else seemed to be cognizant of the probable range of the subject made me think that this might be a field ripe for study, and that the results might have broad implications. Clearly, the main thing that had to be done was to examine the NMR spectra of such molecules at low temperatures, where their instantaneous structures would be revealed by the spectra. Martin Saunders had already pointed the way with his study of bullvalene [19]. At that time, however, I was in the thick of discovering the first quadruple bonds and was also planning to spend the first 9 months of 1965 in Buenos Aires. Hence, procrastination seemed inevitable, until fate took a hand.

Arthur Cope was then on the Scientific Advisory Board of the Robert A. Welch Foundation and had accepted the responsibility of organizing a meeting, for November of 1965, on organometallic chemistry. He asked me if I would give one of the lectures, to which I speedily agreed. As 1964 wore on I began to think that it would be very nice to report some hot results on dynamical organometallics in that lecture, but my impending absence for 9 months was a serious obstacle, and a low-temperature probe for the NMR spectrometer did not become functional until near the end of the year. Finally, just before I was to leave I broached the idea of a collaborative effort, specifically on $(C_5H_5)_2Fe(CO)_2$, to Alan Davison. He had also noted the various indications that dynamical molecules might be widespread and important, especially among organometallics, and was instantly receptive to the idea. Thus, late Saturday afternoon, December 26, 1964, the day before I left for what proved to be, *inter alia*, a glorious equestrian holiday in Argentina, we laid our plans. Several of my students would do the crystal structure to confirm absolutely the $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Fe(CO)_2$ nature of the molecule and Alan personally would try to record NMR spectra at low temperatures.

During the early part of 1965 there was some good news and some bad news. The NMR spectra were recorded as low as about —60° ; the single peak originally reported by Piper and Wilkinson was seen to collapse and disappear and a broad, new signal was seen in the olefinic region. It appeared that still lower temperatures were needed to see the limiting spectrum, but the probe was only guaranteed to about —60° and the front office of the MIT chemistry department was unwilling to take a chance on going lower. Meantime, the crystal structure had run into a technical snag. The latter problem was sorted out by the end of September by Michael Bennett, who had just arrived from Mason's Laboratory at Imperial College to take up postdoctoral work. On my return I broke the log jam regarding the NMR side of things by virtually demanding that we be allowed to go below —60°, at the same time promising to pay for any damage to the cryostat. Thus it was that just days before the Welch Conference we had proof of the structure both in the crystal at 25° and in solution at about —80° and I was able to report [20] that the dynamical nature of this molecule had been demonstrated, just about a decade after it was first postulated.

Next came what I think is the most important development in the field of fluxional molecules. John W. (Jack) Faller, who had been doing thesis research with Davison on other problems, became interested in our work and asked to participate. The first job we gave him was to rerun the NMR spectra and get a set of clean, publishable spectra at various temperatures. With these spectra it became unmistakable that something of great significance could be seen: The two portions of the *AA'BB'* multiplet in the olefinic region were collapsing at distinctly different rates as the temperature rose from about —80° to about —60°. Since these two signals are equidistant (to within 10%) from the other signal, this could only be due to a selectivity in the site exchange scheme (i.e., the mechanism or pathway). Jack Faller grasped this immediately, and promptly produced an analysis in terms of little column matrices showing the way in which 1,2 and 1,3 shift pathways would affect residence times at different sites. This analysis demonstrated that the correct pathway had to be one of these two and that we had *only* to decide on which half of the *AA'BB'* multiplet to assign to which set of olefinic protons in order to have the final answer. The assignment, however, was a nontrivial problem. Since the two chemical shifts are so similar, we considered chemical shift arguments to be untrustworthy (how right we were has since been shown) and based our assignment on coupling constants (recognizing, of course, that this is not entirely conclusive either). This led us to decide in favor of 1,2 shifts. In some dozen or more papers published since, there is satisfactory evidence to confirm this. Thus it was that by the end of February, 1966 we were able to submit an account of the first complete structural and mechanistic analysis of a fluxional molecule.

The concept that the detailed, qualitative behavior of the line shapes in suitable cases carries mechanistic information had never before been published, as far as I am aware. Previous use of NMR to study chemical exchange processes [6,19] had involved only the determination of rates as a function of temperature in cases where the mechanism was either already known, not of interest, or trivial. We were delighted to have this powerful new tool at our disposal and immediately proceeded to look for other cases to which we could apply it. The obvious possibility was $(C_8H_8)Fe(CO)_3$. Unfortunately, this has such a low activation energy that a limiting spectrum is inaccessible even at —155°. It was thanks to Earl Muetterties that we were able to make this measurement at what was then the record low temperature. The fact that no one, including ourselves, appreciated that this spectrum was nowhere near being the slow-exchange spec-

Alan Davison, J.W. Faller and F.A. Cotton examining a low-temperature NMR spectrum in 1966 at MIT.

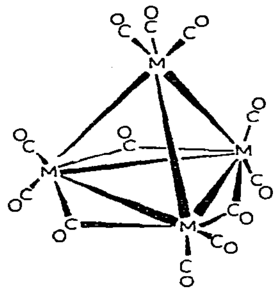
trum led to a rather tedious imbroglio involving ourselves, Pettit, Winstein and Kaesz, and Lippard, which has already been rehashed once [21] and need not be discussed again.

The difficulties with $C_8H_8Fe(CO)_3$, which could not be overcome by any direct attack on that molecule, prompted me to look for ways to outflank it. One idea was to use the symmetrically substituted derivative $[1,3,5,7\text{-}(CH_3)_4\text{-}C_8H_4]Fe(CO)_3$ and another was to try $C_8H_8Ru(CO)_3$ in the hope that a higher activation energy would bring it within range. The former approach eventually led to a number of interesting results [22], but failed in its primary objective since the iron tricarbonyl compound contains the [4.2.0] bicyclic ring system instead of the one desired [23].

However, with $C_8H_8Ru(CO)_3$ it did prove possible to obtain a definitive result [24,25,26]. The interpretation of this system was easier in one way and harder in another than $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ had been. The assignment did not present excessive difficulty, but because of complexity of the spectrum it was not possible to select (from among 1,2, 1,3 and 1,4 shifts) the correct pathway with certainty by a purely qualitative argument. However, computer programs capable of producing simulated spectra had been written (the first one, I think, by Martin Saunders) and, fortunately, a suitable one had been written and tested at MIT by George Whitesides. With the help of his program we were able then to show that only the 1,2 shift pathway gave results in satisfactory agreement with the observed spectra.

Polynuclear metal carbonyls. It is now clear that scrambling of CO ligands at least over several sites on the same metal atom and frequently from one metal atom to another is characteristic of metal carbonyls as a class of compounds. The awareness of this fundamental characteristic of this important class of compounds arose in the following way. The work on $Fe(CO)_5$ already described did not stimulate any followup study of metal carbonyls as such. It was, however, one significant component in another story developed mainly by Earl Muetterties, to which I shall refer later. The systematic investigation of CO scrambling in metal carbonyls has two points of departure, different from the $Fe(CO)_5$ work.

In early 1966 there still existed considerable uncertainty about the structure of $Co_4(CO)_{12}$, and it appeared that the structure might be I in the crystal and II in solution. At the Middle Atlantic Regional ACS Meeting in Philadelphia on February 3, 1966 I pointed out that interconversion of I and II could occur via the intermediate III and that if such "rearrangement processes... are sufficiently fast, all CO groups will appear NMR equivalent using ^{13}C or ^{17}O..." Unfortunately it was almost six years before I had access to the necessary instrumentation to test this prediction. It was a period of considerable frustration.



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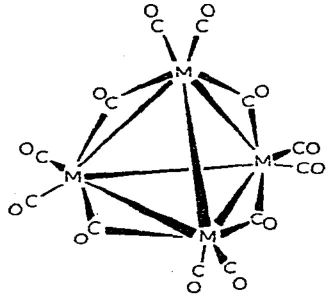

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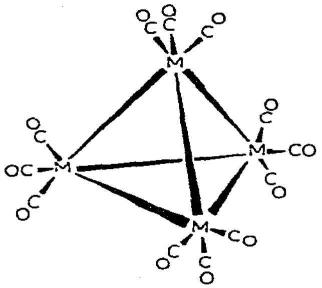
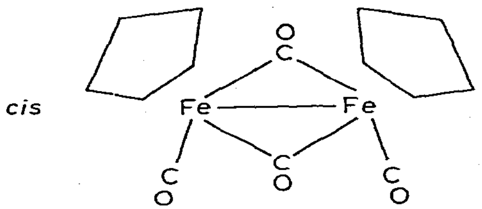


(III)

Actually, even in 1972 I still did not have the necessary instrumentation, but with the assistance of B.L. Shapiro and Leroy Johnson at Varian, the ^{13}C experiment, using $Rh_4(CO)_{12}$, was run in April 1972 and confirmed the fluxionality of $Rh_4(CO)_{12}$ fully [27]. The suggested mechanism, i.e., the intermediacy of the symmetrical intermediate, was demonstrated soon after, in collaboration with Jack Lewis and Brian Johnson, by low temperature ^{13}C spectra recorded at Cambridge [28].

The second point of departure was the observation in late 1969 that the *cis* and *trans* forms of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, IV and V, interconvert rapidly on the NMR time scale, as observed using the ^1H ring resonances [29]. It was proposed that the only sensible way to explain this was to postulate the rapid occurrence of pairwise opening and reclosing of CO bridges. The important implication of the work was clearly stated: such bridged—nonbridged interconversions



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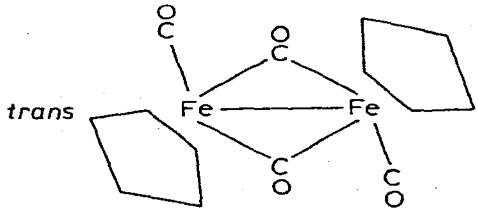


(V)

"can occur very rapidly and can therefore form the basis for an extensive and important class of stereochemically nonrigid or fluxional molecules."

Obviously, direct proof of our proposal that rapid scrambling of bridge and terminal CO groups was occurring in the iron compound could only be obtained by ^{13}C (or ^{17}O) NMR and the necessary facilities were unavailable to us. Thus it was that Otto Gansow was the one to do this experiment and supply the proof of our proposal [30]. However, Gansow's results revealed far more than just the correctness of the general idea of CO scrambling. They had features from which fairly explicit mechanistic detail could be inferred, as pointed out by Richard Adams and me [31]. We have since proceeded with many experiments designed to test the general validity of this mechanism and to determine whether there are any others which significantly compete with it; none have so far been found [2,32,33].

Fluxionality in other inorganic molecules. This article would be incomplete without some reference to the important work of Earl Muetterties, even though it is not specifically concerned with organometallics or carbonyls. His note in 1965 [34], which was concerned with molecules and complexes of the type ML_n (and which I only saw on my return from Argentina, since the journals went there by boat!), drew the attention of inorganic chemists to the concept of a "time-scale" being associated with each type of structure-sensitive physical measurement. I remember visiting Earl not long after my return from Argentina (to run the $C_8H_8Fe(CO)_3$ spectra) and finding his office almost knee-deep (slight exaggeration) in plastic models of all sorts of polyhedra. He showed me, with great enthusiasm, how many of these were interconvertible by rather easy manipulations. Out of all this, within the next few years came his papers on polytopal rearrangements. The experimental study of ML_n species was then pioneered by Muetterties and his coworkers, Peter Jesson and Paul Meakin. Muetterties' work has, in effect, generalized Berry's isolated analysis of the ML_5 case and shown the range of importance of stereochemical nonrigidity [35].

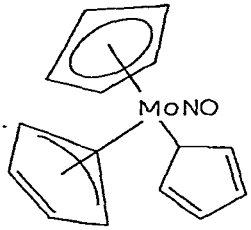
Problems of nomenclature and terminology

As the study of fluxional molecules expanded, problems of terminology arose, as often happens when new phenomena need to be named. Even by about mid-1966 there existed a profusion (or perhaps I should say a confusion) of terms, and I thought it would be desirable to establish some concensus before too many more papers, all using different terms for the same thing, accumulated in the literature. Muetterties had already introduced the terms *stereochemically nonrigid*, and *polytopal*, and Doering had described molecules such as homotropilidene and bullvalene as having *fluxional structures*. In addition the terms *valence tautomers* and *degenerate tautomers* were in use. There have been still other proposals in recent years but I shall not discuss them here, and I hope Myron Rosenblum will not mind if I pass quickly by his proposal of *teeter-tautomers*. The term *polytopal* has its own special sphere of application and has never, I believe, been controversial. However, the other terms I have just mentioned provoked definite, often strong, reactions of advocacy or opposition.

Among those with whom I corresponded about the problem during June and July, 1966 were Saul Winstein and Bill Doering. Winstein voiced an objection to "stereochemically nonrigid" which I heard quite frequently from organic chemists. He said, in part: "I've been snowed under getting ready to go to England. I am right now on a Pan Am. flight to London. I still don't like sterically (sic) nonrigid. Rigidity has come to mean something, to organic chemists at least, about flexibility." Bill Doering made a case for "fluxional" (even though, as I pointed out to him for amusement, definition (7) in the Oxford English Dictionary is "of or pertaining to movements of the bowels") and expressed his disdain for *valence tautomerism* as "an old, awkward term," a sentiment I share.

Perhaps there are no unimpeachable terms. I personally think that *stereochemical nonrigidity* is a good term for the entire range of phenomena in which fast, reversible intramolecular rearrangements are involved. *Fluxionality* can then designate that special subset of processes in which there is no net change, i.e., processes which can be described as "nonreactions having no mechanism," if the terms reaction and mechanism are assigned their normal definitions.

The other point I want to mention here concerns the *hapto* nomenclature for organometallic compounds, which is now widely used and is more or less, though not finally, sanctioned by Chemical Abstracts and IUPAC. I was forced to invent this [36] in the winter of 1967-68, by a problem arising out of work on a fluxional organometallic molecule, $(C_5H_5)_3MoNO$. When I first conceived of preparing this molecule it was with the idea that it might have each C_5H_5 ring bonded differently to the metal, as in VI, since this structure allows an



(VI)

18-electron configuration on the metal atom. As it turned out, of course, the molecule does not have this structure, but that's another story [37]. The point was that in the old σ,π nomenclature there was no unambiguous way to name VI, and as I thought about other complex organometallic molecules, it became evident that some more articulate and systematic scheme was generally needed. After devising the scheme, I reflected that other notational proposals had failed because, owing to excessive paternal pride, their inventors had failed to subject them to criticism and modification before formally publishing them. Thus I first had an audience with the ACS Nomenclature Committee at the Spring Meeting in Atlantic City. This group suggested minor modifications, but generally found the scheme serviceable.

With the idea that notation is too important (and tricky) to be left solely to specialists, I decided to throw the whole thing to the merciless ministrations of my colleagues at the Joint Canadian—American Inorganic Chemistry meeting in Banff, in June 1968, before attempting to publish. Among the many memorable events of this meeting (such as an infinite stream of beverage containers proceeding at high ground speed from the hands of such celebrated high-livers as Fred Hawthorne to make inelastic collisions with the door of Bill Graham's room, while Bill tried manfully to get some sleep and ignore all the rowdies from south of his border) was a no-holds-barred critique of the *hapto* scheme. The proceedings were about as orderly as what Texas slang describes as a "Chi nese fire drill." All the would-be witticisms notwithstanding, however, I felt that the proposal had survived and so, in July, I submitted it to JACS.

It now appears that while most people use it, they also regard it as a Goc given right and constitutionally mandated obligation to change it in some way IUPAC has very constructively proposed using η instead of *h*, and I think this i good. They also propose other modifications about which I have reservations. The deliberations of Chemical Abstracts are still continuing. I think there is reason to hope that before long each of these institutions will produce a final version. I hope it is not tempting fate too recklessly to dream that they may even arrive at a *common* final version.

Epilog

I don't know whether the preceding ramblings are worth the space they take up. I, at least, have enjoyed sorting out some of these early goings on in my own mind. If I have got any of the facts, dates or attributions wrong, I apologize, and hope that I will be accused of nothing more sinister than having a faulty memory. I also think that this kind of humanistic, as opposed to technical, review of a field has value. Naturally, it should not be overdone, but scientists themselves, as well as the nonscientific public, tend to lose sight of the fact that science is a human enterprise. The results are supposed to have objective validity, but they are obtained by very human activities which are not without their own interest and importance.

References

1 F.A. Cotton, in L. Jackman and F.A. Cotton (Eds.), Dynamic Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1975, pp. 377-440.
2 R.D. Adams and F.A. Cotton, Ref. 1, pp. 489-522.
3 G. Wilkinson and T.S. Piper, J. Inorg. Nucl. Chem., 2 (1956) 32.
4 A. Conan Doyle, The Sign of the Four, Chapter 6.
5 U. Liddel and N.F. Ramsey, J. Chem. Phys., 19 (1951) 1608.
6 H.S. Gutowsky and A. Saika, J. Chem. Phys., 21 (1953) 1688; H.S. Gutowsky, D.W. McCall and C.P. Slichter, J. Chem. Phys., 21 (1953) 279.
7 See Ref. 1, p. 388.
8 W. Hieber, Advan. Organometal. Chem. 8 (1970) 1-28.
9 F.A. Cotton, A. Danti, J.S. Waugh and R.W. Fessenden, J. Chem. Phys., 29 (1958) 1427.
10 R.W. Berry, J. Chem. Phys., 32 (1960) 933.
11 R. Bramley, B.N. Figgis and R.S. Nyholm, Trans. Faraday Soc., 58 (1962) 1893.
12 T.A. Manuel and F.G.A. Stone, Proc. Chem. Soc., (1959) 90; J. Amer. Chem. Soc., 82 (1960) 366.
13 A. Nakamura and N. Hagihara, Bull. Chem. Soc. Jap., 32 (1959) 880.
14 M.D. Rausch and G.N. Schrauzer, Chem. Ind. (London), (1959) 957.
15 G. Wilkinson and R. Burton, Imperial College, never published.
16 F.A. Cotton, J. Chem. Soc., (1960) 400.
17 B. Dickens and W.N. Lipscomb, J. Amer. Chem. Soc., 83 (1961) 4062; J. Chem. Phys., 37 (1962) 2084.
18 H. Reihlen, A. Gruhl, G. von Hessling, and O. Pfrengle, Justus Liebig's Ann. Chem., 482 (1930) 161.

19 M. Saunders, Tetrahedron Lett., 25 (1963) 1699.

20 F.A. Cotton, Proc. Robert A. Welch Foundation Conf. Chem. Res., IX. Organometal. Chem.; W.O. Milligan (Ed.), Houston, Texas, 1966. pp. 213-214.

21 F.A. Cotton, Accounts Chem. Res., 1 (1968) 257.

22 F.A. Cotton, J.W. Faller and A. Musco, J. Amer. Chem. Soc., 90 (1968) 1438.

23 F.A. Cotton and A. Musco, J. Amer. Chem. Soc., 90 (1968) 1444. Cf. also Ph.D. Thesis, MIT, of J.W. Faller, 1966.

24 W.K. Bratton, F.A. Cotton, A. Davison, A. Musco and J.W. Faller, Proc. Nat. Acad. Sci., 58 (1967) 1324.

25 F.A. Cotton and R. Eiss, J. Amer. Chem. Soc., 91 (1969) 6593.

26 F.A. Cotton, A. Davison, T.J. Marks and A. Musco, J. Amer. Chem. Soc., 91 (1969) 6598.

27 F.A. Cotton, L. Kruczynski, B.L. Shapiro and L.F. Johnson, J. Amer. Chem. Soc., 94 (1972) 6191.

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

29 J.G. Bullitt, F.A. Cotton and T.J. Marks, J. Amer. Chem. Soc., 92 (1970) 2155.

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

31 R.D. Adams and F.A. Cotton, J. Amer. Chem. Soc., 95 (1973) 6589.

32 R.D. Adams, M.D. Brice and F.A. Cotton, Inorg. Chem., 13 (1974) 1080.

33 F.A. Cotton, L. Kruczynski and A.J. White, Inorg. Chem., 13 (1974) 1402.

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

35 J.P. Jesson and E.L. Muetterties, in L. Jackman and F.A. Cotton (Eds.), Dynamic Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1975. Chapter 8.