

Figure 8. Variation of the metal center in CH_3 ($M = \text{Y, Lu, Sc}$) complexes causes significant variation in the rate of the methane exchange reaction. The apparent bimolecular rate constants for exchange are $0.01 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (Sc), $0.460 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (Lu), and $2.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (Y).

exploration of new, highly reactive compounds. The olefin polymerization catalysis was extremely informative. Even though the types of complexes we explored are unlikely to have commercial application, they pro-

vide excellent models for study of coordination polymerization. The possible significance of paramagnetism in olefin insertion has not been established.

Beyond illustration of known processes, the lutetium model also called attention to generally unappreciated reaction pathways for termination of polymer chain growth. The termination and chain-transfer mechanism, β -alkyl extrusion, unknown for transition-metal alkyl compounds, will probably prove ubiquitous as we learn how to detect it. Indeed, it may become a model for catalytic C-C bond activation in hydrocarbons. The importance of both allylic and vinylic C-H bond activation in termination or chain transfer may be particularly important in the polymerization of α -olefins where chain propagation is much slower than for ethylene and alternative reactions of the olefins can compete.

The discovery of C-H bond reactions involving olefins, arenes, and even alkanes was important in the chemistry of the organolanthanides. In retrospect, it is reasonable that depriving a lanthanide complex of conventional donor ligands would create a fiercely electrophilic species and that such an electrophile might seize upon the C-H bond of a hydrocarbon as a source of electrons. The unexpected reaction of methane dramatically illustrated this point.

Metal-Pentadienyl Chemistry

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The cyclopentadienyl (C_5H_5) and allyl (C_3H_5) groups¹ are two of the most important ligands in inorganic and organometallic chemistry. Interestingly, these two ligands are important for two different reasons. The former, a closed, five-membered ligand, is noted for its great abilities as a stabilizing ligand, which can be well exemplified by the now classic metallocene compounds. As a result many detailed physical studies have been carried out on these systems and a great deal of information regarding structure and bonding is known. However, in chemical reactions the cyclopentadienyl ligand generally plays the role of an uninvolved spectator, although organic ring-substitution processes must not be overlooked.² In contrast, the open, three-membered allyl ligand can hardly be regarded as a stabilizing ligand. In particular, few homoleptic first-row transition-metal allyl compounds, $\text{M}(\text{allyl})_n$, are thermally stable.³ Hence, comparatively little detailed physical data has been gathered for these systems. However, the chemical and catalytic properties of these compounds can be characterized as nothing less than remarkable,⁴

even the very unstable compound tris(allyl)cobalt (decomp pt -40°C) showing versatile reaction chemistry.^{4a}

In comparison, the transition-metal chemistry of the open, five-membered pentadienyl ligand has been all but ignored until recently.⁵ It did not seem to be recognized that pentadienyl ligands, in and of themselves, should have much to contribute to transition-metal chemistry. However, some detailed comparisons (vide infra) involving the general features of a pentadienyl group and those of cyclopentadienyl and allyl groups suggested that the pentadienyl group should be capable of imparting thermal stability as well as chem-

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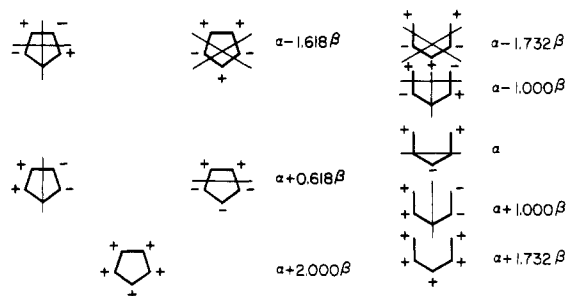
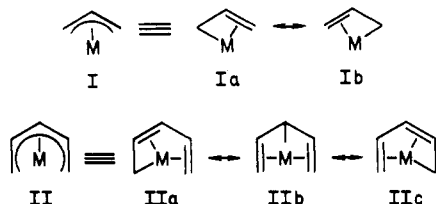


Figure 1. Comparison of the π -molecular orbitals of the "U" pentadienyl group with those of the cyclopentadienyl group.

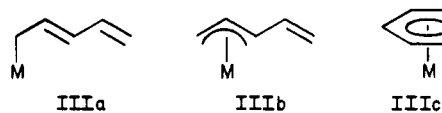
ical and catalytic reactivities into its metal complexes. Thus, even in the absence of "stabilizing" ligands, one should be able to carry out not only detailed physical studies but also various reactivity studies, with an ultimate goal of obtaining correlations between the two. Further, the knowledge obtained should help to build a unified understanding of the four possible open or closed, three- or five-membered ligand systems.

To understand the reasons for expecting thermal stability in metal-pentadienyl compounds, one can first compare the appropriate resonance hybrids involved in (η^3 -allyl)metal (I) and (η^5 -pentadienyl)metal (II) bonding. An η^3 -allyl-metal bond can be described as having



a σ M-C bond and one olefin-metal attachment in resonance hybrids Ia,b. The metal- η^5 -pentadienyl bond is similar but contains an extra olefin-metal attachment. Hence, a pentadienyl ligand is a better chelating ligand than the allyl group, and one therefore might expect higher thermal stability. A second indication of expected stability can be derived by comparing the π -molecular orbitals of a pentadienyl ligand in the U conformation with those of the cyclopentadienyl ligand (Figure 1). The similarity suggests that the bonding interactions between transition-metal valence orbitals and a cyclopentadienyl ligand may also occur between a transition metal and a pentadienyl ligand. Further, considering these groups as 6π -electron anions, the three filled orbitals of the pentadienyl ligand are on the average considerably higher in energy, while the two empty pentadienyl π -orbitals average considerably lower in energy, than those of the cyclopentadienyl ligand. Energetically, then, the pentadienyl ligand could be both a better donor and a better acceptor, although other considerations (e.g., overlap) will apply as well. Thus, the pentadienyl ligand under some circumstances could be more strongly bound than even the ubiquitous cyclopentadienyl ligand.

In addition to the above stability considerations, it became evident that metal-pentadienyl compounds should display a high degree of chemical and catalytic reactivity. Just as an allyl ligand may isomerize between η^1 (σ) and η^3 (π) configurations, a pentadienyl ligand may undergo isomerizations between η^1 (IIIa), η^3 (IIIb), and η^5 (IIIc) configurations, thereby providing a potentially great source of chemical versatility to its

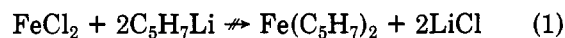


complexes. Of course there is an important question concerning how facile such interconversions should be. In comparing such processes for the allyl and cyclopentadienyl systems, Wilke and co-workers made use of the relative delocalization energies for the two anionic species.³ One can readily note that the loss in π -delocalization energy accompanying an $\eta^3 \rightarrow \eta^1$ allyl anion transformation is ca. 0.83β , compared with 1.64β for an $\eta^5 \rightarrow \eta^3$ transformation of the cyclopentadienyl anion.⁶ These differences are in clear accord with observed relative chemical behaviors of metal-allyl and metal-cyclopentadienyl compounds.^{1,3} In order to anticipate the chemical behavior of metal-pentadienyl compounds, it can be noted that an $\eta^5 \rightarrow \eta^3$ isomerization of a pentadienyl anion brings about a loss of ca. 0.64β ,⁶ smaller than that occurring for either the allyl or cyclopentadienyl systems. These initial indications strongly supported the idea that metal-pentadienyl chemistry should display a high degree of chemical reactivity, as well as thermal stability.⁷

The above considerations suggested that metal-pentadienyl chemistry should prove to be an important area in its own right. Since at that time very little was understood concerning transition metal-pentadienyl chemistry, the reasonable approach seemed to be to investigate pentadienyl complexes of a wide variety of transition metals. In this way important structural, stability, and other trends would be uncovered, and one could also learn reasonably quickly where the most interesting chemistry could likely be found. Similar approaches to transition metal-cyclopentadienyl and -allyl chemistry were in large part responsible for the rapid advances made in those fields.^{3,8} In the following sections will be described the major results we have obtained, the contributions to our understanding of metal-pentadienyl chemistry that have thereby been achieved, and some future prospects.

Open Ferrocenes and Open Ruthenocenes

Because of the preeminent importance of the thermally robust compound ferrocene, our first efforts centered on the preparation of bis(pentadienyl)iron compounds ("open ferrocenes"), including $\text{Fe}(\text{C}_5\text{H}_7)_2$ and various methylated derivatives.⁹ Several attempts to prepare $\text{Fe}(\text{C}_5\text{H}_7)_2$ from FeCl_2 and (pentadienyl)-lithium¹⁰ were unsuccessful (eq 1). However, we were



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(7) (a) Seyferth has independently made similar arguments,^{7b} while Jolly and Wilke have noted that pentadienyl ligands in the "W" conformation are favorably disposed for bonding to two metal atoms simultaneously.^{4b,5c,d} (b) Seyferth, D.; Goldman, E. W.; Pomet, J. *J. Organomet. Chem.* 1981, 208, 189.

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(10) (a) The pentadienyl anions were first conveniently prepared as part of Bates' now classic studies.^{10b} Other routes have since been reported as well.^{10c,d} (b) Bates, R. B.; Gosselink, D. W.; Kaczynski, J. A. *Tetrahedron Lett.* 1967, 199. (c) Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* 1976, 59, 453. (d) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* 1979, 52, 2036.

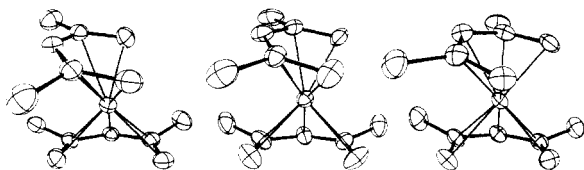


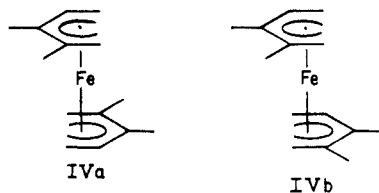
Figure 2. The observed structures for the bis(2,4-dimethylpentadienyl) complexes of vanadium, chromium, and iron in the solid state.

Table I.
Bonding Parameters

parameter	V	Cr	Fe
A. For $M(2,4-C_7H_{11})_2$ Compounds			
conformation angle	89.8	82.9	59.7
M-C(1,5)	2.179 (4)	2.166 (6)	2.108 (5)
M-C(2,4)	2.231 (4)	2.162 (5)	2.073 (4)
M-C(3)	2.236 (5)	2.167 (7)	2.084 (3)
M-C(av)	2.211 (2)	2.165 (4)	2.089 (1)
M-CM	1.632 (2)	1.594 (4)	1.508 (2)
C(1)···C(5)	3.05 (1)	2.93 (1)	2.785 (5)
B. For $M(C_5H_5)_2$ Compounds			
M-C	2.280 (5)	2.169 (4)	2.064 (3)
C-C	1.434 (3)	1.431 (2)	1.440 (2)
M-CM	1.928 (6)	1.798 (4)	1.660 (10)

^a Angles are given in degrees; distances are given in angstroms.

aware that methylation of (allyl)metal complexes could bring about dramatic increases in stability⁴ and so we did not abandon our efforts. Gratifyingly, the subsequent reaction of 2 equiv of (2,3-dimethylpentadienyl)lithium with ferrous chloride did lead to a good yield of reddish, essentially air-stable bis(2,3-dimethylpentadienyl)iron. Because of the complexity of its ¹H NMR spectrum, we presumed it to be a mixture of two isomers, ideally depicted as IVa and IVb, and this was confirmed by variable-temperature ¹³C NMR spectroscopy.



With the ice now broken, we soon prepared and characterized the 3-methyl and 2,4-dimethyl analogues and later found that the parent compound $Fe(C_5H_7)_2$ and its 2-methyl analogue could be isolated if one employed a (pentadienyl)zinc chloride reagent in place of alkali-metal pentadienides in the reaction with ferrous chloride. The zinc compound had earlier been reported and structurally characterized by Nakamura, Yasuda, and co-workers as part of their interesting studies of main-group metal-pentadienyl chemistry.¹¹

The open sandwich nature of these compounds was demonstrated by a single-crystal X-ray diffraction study of bis(2,4-dimethylpentadienyl)iron, $Fe[2,4-(CH_3)_2(C_5H_5)]_2$. The result is illustrated in Figure 2, along with later results for the vanadium and chromium analogues, and some pertinent bonding parameters may be found in Table I. The average Fe-C bond distance in the "open ferrocene" is 2.089 (1) Å, clearly longer than the

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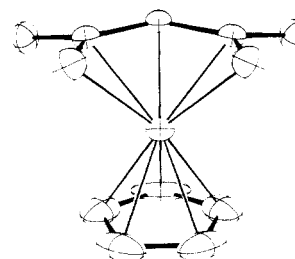


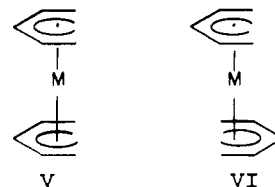
Figure 3. The solid-state structure of the "half-open ferrocene" $Fe(C_5H_5)(2,4-(CH_3)_2C_5H_5)$.

2.064 (3) Å value for ferrocene.¹² The longer distance in the pentadienyl complex is attributed to possible loss in metal-ligand overlap (due to the greater ligand size) and to increased interligand repulsions, resulting from a metal-ligand plane separation of only 1.50 Å, compared to 1.66 Å in ferrocene.

In view of the clearly short interligand nonbonded contacts present in $Fe(2,4-(CH_3)_2C_5H_5)_2$, it is notable that this compound contains essentially eclipsed pentadienyl ligands. To define a conformation angle, χ , one can construct for each ligand a plane composed of the metal atom, the carbon atom in the central position of the pentadienyl ligand, and the midpoint between the two terminal pentadienyl carbon atoms, i.e.



χ will be the angle formed between the two appropriate metal-ligand planes, with 0° assigned to the syn-eclipsed conformation V and 180° assigned to the anti-eclipsed form VI. The actual value of χ for the iron



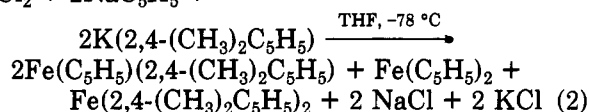
complex is 59.7°, virtually identical with the ideal 60° value for the gauche-eclipsed conformation. Interestingly, similar conformations have been found for pseudoferrocenes such as $Fe(\eta^5-C_7H_7)(\eta^5-C_7H_9)$.¹³ Clearly there must be a substantial electronic driving force responsible for the adoption of an eclipsed conformation in such crowded molecules. One reason for this could be the fact that in the gauche-eclipsed conformation there exists a nearly octahedral configuration of the formally charged carbon atoms. Of course, such a configuration would also be present for the anti-eclipsed conformation, but variable-temperature ¹H and/or ¹³C NMR spectra clearly demonstrated the presence of an unsymmetric ground state for these molecules, with ΔG^\ddagger for ligand oscillation being 8.4, 8.7, and 9.1 kcal/mol for the parent compound and its 3-methyl and 2,4-dimethyl analogues, respectively.⁸

Since interligand repulsions could be deleteriously affecting the metal-pentadienyl bonding in $Fe(2,4-(CH_3)_2C_5H_5)_2$, it was of interest to attempt the preparation

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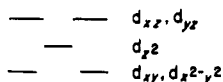
and isolation of a "half-open ferrocene", $\text{Fe}(\text{C}_5\text{H}_5)\text{-}(2,4\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_5)$, wherein both ligands should experience equivalent repulsive influences. We found, in fact, that the reaction depicted in eq 2 proceeded in nearly



the course shown, and the desired product could be isolated following fractional crystallization.¹⁴ An X-ray diffraction study revealed an "eclipsed" structure (Figure 3). The metal-carbon bonding to the pentadienyl ligand in $\text{Fe}(\text{C}_5\text{H}_5)(2,4\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_5)$ is now close to that of the cyclopentadienyl ligand (2.066 (4) vs. 2.062 (4) Å, respectively), in accord with the above expectations.

While the above information provided a good understanding of some important structural parameters,¹⁵ it revealed little concerning the metal-ligand bonding interactions taking place. We were therefore fortunate to become involved with Prof. Dr. Rolf Gleiter in some joint theoretical and experimental studies on a number of our compounds. Much information was obtained from a combination of INDO and extended Hückel theoretical calculations, which were correlated with photoelectron spectroscopic data.¹⁶ Most striking, perhaps, was the indication of greater mixing taking place between metal and ligand orbitals in the "open ferrocenes". In fact, substantial mixing between metal d orbitals took place as well. Also evident were much greater barriers to ligand rotation and increased δ bonding in the open systems. Finally, two local minima were observed, the anti-eclipsed and gauche-eclipsed conformations.

We were also fortunate that Professor Rolfe Herber of Rutgers University had an interest in obtaining Mössbauer spectra of these compounds, and once again important information was obtained.¹⁷ The most dramatic difference to be observed involved the much lower values of the quadrupole splitting parameter for the pentadienyl compounds (1.2–1.5 mm/s) compared to ferrocene itself (2.45 mm/s). These lower values actually correlate well with the relative d orbital populations obtained for ferrocene and the "open ferrocenes" in the theoretical study. Thus, in ferrocene the initial crystal field splitting pattern for the metal d orbitals is approximately as shown.¹⁸

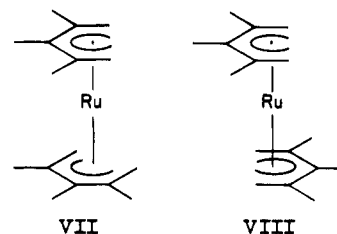


As molecular orbital calculations indicate that relatively little mixing takes place between the metal and ligand orbitals, the MO (ligand field) model is fairly similar. The particular d orbital populations shown would be expected to give rise to a large quadrupole splitting. However, greater mixing between metal and ligand

orbitals in the "open ferrocenes", as indicated by the MO studies, tends to equalize the d_{xy} , $d_{x^2-y^2}$, d_{xz} , and d_{yz} populations, bringing about a substantial decrease in the quadrupole splitting parameter, as observed. Thus, the experimental Mössbauer results can be seen to substantiate the general trends observed in the theoretical calculations.

Of course, a major reason for investigating these systems was the expectation that both thermal stability and chemical reactivity should be present. We have therefore begun to investigate the utilization of our complexes in various chemical reactions, using species with few methyl groups since methylation in general tends to increase thermal stability. Indeed, $\text{Fe}(\text{C}_5\text{H}_7)_2$ has proven to be a very active catalyst in bringing about the oligomerization of butadiene,¹⁹ yielding a product mixture similar to those obtained from other reported iron catalysts.²⁰ Further, in collaboration with Professor Robert Parry, we have found that $\text{Fe}(\text{C}_5\text{H}_7)_2$ reacts with PF_3 under very mild conditions to yield $\text{Fe}(\text{PF}_3)_5$.²¹ Clearly these compounds can take part in "naked" metal applications, and it is significant that even our most stable first-row transition-metal "open metallocene" system should be so active in these applications.

We later turned our attention to possible "open ruthenocenes" and soon found that $\text{Ru}(2,4\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_5)_2$ could be readily prepared by reaction of hydrated ruthenium trichloride with 2,4-dimethyl-1,3-pentadiene and zinc dust in ethanol,²² paralleling procedures for the preparation of bis(cyclohexadienyl)ruthenium, ruthenocene, and several related compounds.²³ The yellow, crystalline product is air-stable, soluble in organic solvents, and readily sublimable. However, this method did not prove successful for the preparation of complexes with fewer methyl groups, so we considered the possibility of preparing $\text{Ru}(2,3,4\text{-}(\text{CH}_3)_3\text{C}_5\text{H}_4)_2$. This molecule appeared particularly interesting since if it existed in the gauche-eclipsed conformation VII, there



would be two destabilizing eclipsing $\text{CH}_3\cdots\text{CH}_3$ interactions present, whereas an anti conformation, VIII, would be free of such interactions. Thus, if there were only a relatively small electronic preference for the gauche-eclipsed conformation relative to the anti form, the compound should be sterically forced into the anti conformation. After a practical synthesis of 2,3,4-trimethyl-1,3-pentadiene was worked out, the desired ruthenium complex was prepared and characterized by standard methods, including a single-crystal X-ray

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diffraction study. The solid-state structure of the compound was again found to be gauche-eclipsed, despite short intramolecular $\text{CH}_3\cdots\text{CH}_3$ repulsions. Interestingly, the value for χ is 52.5° , which seems to indicate that some ligand twisting has taken place in order to reduce these repulsions. Evidently for iron and ruthenium there is a significant preference for the gauche-eclipsed over the anti conformation, and consistent with these observations, variable-temperature ^1H NMR spectra for both $\text{Ru}(2,4\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_5)_2$ and $\text{Ru}(2,3,4\text{-}(\text{CH}_3)_3\text{C}_5\text{H}_4)_2$ indicated unsymmetric ground-state conformations, with barriers to ligand oscillation (ΔG^\ddagger) of 9.7 and 10.2 kcal/mol, respectively. The average ruthenium-carbon bond distance of 2.188 (3) Å compares quite well with that of 2.196 (3) Å in ruthenocene.²⁴

Open Vanadocenes and Open Chromocenes

It is well-known that a number of first-row metallocenes are stable even when an 18-electron configuration is not present,¹ and in fact a number of similar allyl complexes may be prepared, although their stabilities are generally low.³ It seemed likely, then, that other homoleptic bis(pentadienyl) compounds of first-row transition metals should be isolable, and indeed both bis(pentadienyl)chromium and bis(pentadienyl)nickel had been described in the literature.^{5b-d} Both reports appeared prior to 1970 but did not seem to spark any great interest in metal-pentadienyl chemistry. We have found that both $\text{Cr}(3\text{-CH}_3\text{C}_5\text{H}_6)_2$ and $\text{Cr}(2,4\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_5)_2$ can be readily prepared as green crystalline compounds from CrCl_2 and the appropriate pentadienyl anions, and each possesses two unpaired electrons.²⁵ These observations are comparable to those reported for $\text{Cr}(\text{C}_5\text{H}_7)_2$ and provide an interesting comparison with the scarlet chromocene, which also contains two unpaired electrons.²⁶ An X-ray study of $\text{Cr}(2,4\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_5)_2$ (Figure 2) demonstrated that this compound was indeed an open sandwich,²⁷ and the average Cr-C bond distance was found to be 2.165 (4) Å, essentially identical with the 2.169 (4) Å distance in chromocene.¹¹ As was the case for the "open ruthenocene", it seems that when a reasonably large metal is present, the interligand repulsion in a given "open metallocene" decreases sufficiently so that its metal-carbon bond distances become comparable to those of its metallocene counterpart. The value of χ for this structure is 82.9° , very different from those of the iron and ruthenium structures.

Interesting surprises were encountered when we turned our attention to vanadium. The open complex $\text{V}(2,4\text{-}(\text{CH}_3)_2\text{C}_5\text{H}_5)_2$ could be straightforwardly prepared from a divalent vanadium chloride complex and 2 equiv of the appropriate anion, but an initially puzzling circumstance was that this compound only possesses one unpaired electron,²⁶ whereas vanadocene has three.²⁶ Clearly this demonstrates a fundamental difference between the open and closed systems and one which should have a dramatic effect on the chemical and

physical properties of these compounds. The solid-state structure for this compound (Figure 2) exhibits several notable features.²⁷ First, the average vanadium-carbon bond distance of 2.211 (2) Å is substantially shorter than that in vanadocene, 2.280 (5) Å.¹² In this example, the metal-pentadienyl bonding interactions actually appear stronger than those in the metallocene itself! This could be easily explained, however, by the low-spin configuration for the former. A second interesting feature of this structure is that the conformation angle χ is 89.8° , indicative of an ideally staggered conformation. This also has to be regarded as highly significant in view of the strong preference for the gauche-eclipsed conformers in the iron and ruthenium complexes. As a result, the vanadium, chromium, and iron compounds form an interesting conformational series in which the structure ranges from ideally staggered (V, $\chi = 89.8^\circ$), through an intermediate stage (Cr, $\chi = 82.9^\circ$), and finally becoming virtually eclipsed (Fe, $\chi = 59.7^\circ$). Such rich conformational behavior is unknown for analogous allyl or cyclopentadienyl complexes.

It would naturally be of fundamental importance to account for the low-spin configuration of the "open vanadocene" and the interesting conformational variations. In fact, a simple, yet effective, model could be devised to explain these observations, based on relative d orbital populations, particularly the population of potential δ bonding orbitals as one moved from titanium toward iron.^{15,27,28} Further theoretical studies should greatly refine our present understanding of these trends. However, one dramatic surprise came recently from a structural examination of a phosphine adduct of a "half-open vanadocene", $\text{V}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_7)(\text{P}(\text{C}_2\text{H}_5)_3)$, in which the V-C bond distances to the pentadienyl ligand average ca. 2.21 Å, compared to 2.30 Å for the cyclopentadienyl ligand.²⁹ Clearly spin arguments cannot explain this very significant feature, which we hope to understand better in the future.

Open Titanocenes

In terms of metal-centered reaction chemistry, various titanocene-related compounds have proven to be some of the most versatile of all the metallocenes.³⁰ In part this may be attributed to the well-known instability of titanocene itself and of even decamethyltitanocene.³¹ Hence, it was of interest to pursue the synthesis, characterization, and reaction chemistry of open analogues of titanocene, and we soon found that the reaction of 2 equiv of the 2,4-dimethylpentadienyl anion with a reduced titanium(II) chloride led to a deep emerald green solution, from which a diamagnetic liquid product could be obtained. Exhaustive chemical and physical characterization of this compound demonstrated that this was, in fact, a monomeric 14-electron "open titanocene".³² The ^1H and ^{13}C NMR spectra each consisted of seven resonances, which indicated that the two 2,4-dimethylpentadienyl ligands were equivalent, but present in an unsymmetric environment, as

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(28) (a) Many classic examples are known of ligand eclipsing occurring in dinuclear metal complexes due to δ bonding.^{28b,c} Even though such compounds differ greatly from those mentioned herein, the general principles are similar. (b) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225. (c) Trogler, W. C.; Gray, H. B. *Ibid.* **1978**, *11*, 232.

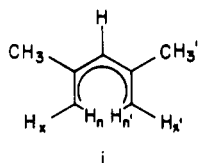
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indicated in i. At higher temperatures, coalescence to



a four-line pattern was observed for both the ^1H and ^{13}C NMR spectra. Analogous to $\text{Fe}(\text{2,4}-(\text{CH}_3)_2\text{C}_5\text{H}_5)_2$, the titanium complex also had to exist in a conformation other than syn-eclipsed or anti-eclipsed but appeared to have a higher energy barrier to ligand oscillation, which we have now determined to be $\text{ca. } 15.3 \pm 0.2$ kcal/mol. Most notably, spectra could be recorded at temperatures as high as 120°C for ca. 10 min or so without any observable decomposition taking place. Clearly we have another example in which an "open metallocene" is in some sense more stable (or more strongly bound) than the metallocene itself. The previously described approximate molecular orbital scheme predicts that an ideally staggered conformation be adopted, similar to that of the vanadium analogue. This expectation has also been supported by preliminary theoretical calculations on the $\text{Ti}(\text{2,4}-(\text{CH}_3)_2\text{C}_5\text{H}_5)_2$ compound.³³

Ligand Adducts of the "Open Metallocenes"

The coordination of Lewis bases to a metal atom or ion is a not uncommon phenomenon for early metallocenes, or related compounds.³⁴ Accordingly, the analogous reactions involving our bis(pentadienyl)metal compounds were studied, and indeed the titanium and vanadium compounds react almost instantaneously with CO or PF_3 .³⁵ However, reactions of the titanium compound with triethylphosphine and with trimethyl phosphite are reversible ($\Delta H = \text{ca. } -6.7$ and -8.9 kcal/mol, respectively). In the case of the vanadium compound, the formation of 17-electron mono(ligand) adducts was expected, analogous to vanadocene itself. Since the carbonyl ligand serves as a good indicator of the relative electron-withdrawing abilities of the accompanying ligands, it is very notable that the ν_{CO} for $\text{V}(\text{2,4}-(\text{CH}_3)_2\text{C}_5\text{H}_5)_2(\text{CO})$ was 1942 cm^{-1} , compared to 1884 cm^{-1} for $\text{V}(\text{C}_5\text{H}_5)_2(\text{CO})$.^{34a} Similarly, the ν_{CO} values for $\text{Mn}(\text{C}_5\text{H}_7)(\text{CO})_3$ reported by Seyferth et al. are also significantly higher than the values for $\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})_3$.^{7b} Thus, the open pentadienyl ligands seem to withdraw more electron density from the metal atom than does the cyclopentadienyl ligand. This came as quite a surprise since C_5H_5 has both a higher electron affinity (1.8 eV) and a higher ionization potential (8.7 eV) than C_5H_7 (0.9 and 7.8 eV, respectively).³⁶ The reasons for this apparent reversal are not clear at present.

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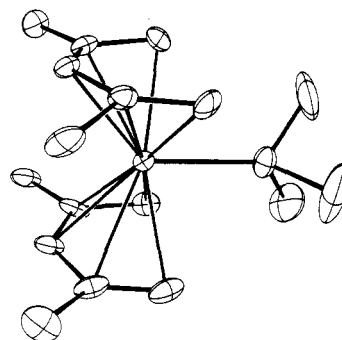


Figure 4. The solid-state structure of the trifluorophosphine adduct of bis(2,4-dimethylpentadienyl)titanium. The vanadium analogue is isostructural, and a similar configuration has been found for triethylphosphine adducts of zirconium and niobium.

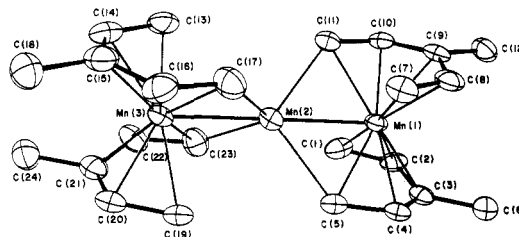


Figure 5. The structure of the unusual $\text{Mn}_3(\text{3-CH}_3\text{C}_5\text{H}_6)_4$ complex.

The CO and PF_3 adducts of $\text{Ti}(\text{2,4}-(\text{CH}_3)_2\text{C}_5\text{H}_5)_2$ also proved interesting. Whereas even $\text{Ti}(\text{C}_5(\text{CH}_3)_5)_2$ will form an 18-electron dicarbonyl complex,^{34d} the "open titanocene" would incorporate only one equivalent of CO or PF_3 , yielding a 16-electron complex.^{32,35} Both titanium adducts were found to be diamagnetic, and NMR spectroscopic considerations suggested a near syn-eclipsed conformation. The expected (crowded) structure pattern has been confirmed for $\text{Ti}(\text{2,4}-(\text{C}_5\text{H}_3)_2\text{C}_5\text{H}_5)_2(\text{PF}_3)$ and the isomorphous vanadium compound and some related molecules (Figure 4).¹⁹

Manganese and Cobalt Complexes

As is often the case, some of the most interesting observations involved reactions in which completely unexpected results were obtained. Such surprises were encountered in the reactions of either MnCl_2 or CoCl_2 with 2 equiv of methylated pentadienyl anions.^{25,37,38} Thus, an attempt to prepare $\text{Mn}(\text{3-CH}_3\text{C}_5\text{H}_6)_2$ led instead to a very unusual trinuclear complex, $\text{Mn}_3(\text{3-CH}_3\text{C}_5\text{H}_6)_4$ (Figure 5), which we initially formulated as an associated salt of high-spin Mn^{2+} and two 18-electron $\text{Mn}(\text{3-CH}_3\text{C}_5\text{H}_6)_2^-$ counterions. The complex was, in fact, found to contain five unpaired electrons. Further, the various Mn-C bond distances for the terminal manganese atoms were essentially identical with those of the 18-electron "open ferrocene" complex $\text{Fe}(\text{2,4}-(\text{C}_5\text{H}_3)_2\text{C}_5\text{H}_5)_2$, although the value of χ for this compound was 35.6° , close to a staggered conformation. The coordination environment of the central manganese atom was quite unusual and can best be described as edge-bicapped tetrahedral. Since this precludes an 18- (or any other reasonable) electron configuration, the formulation of the central manganese atom as the essentially ionic Mn^{2+} seemed reasonable. An interesting

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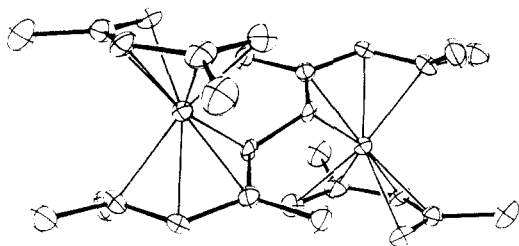
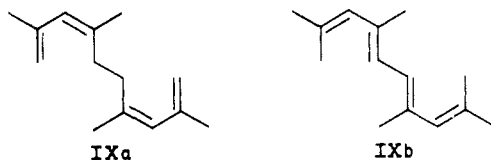


Figure 6. Perspective view of the observed dimer of bis(2,4-dimethylpentadienyl)cobalt.

contrast was obtained, however, from complementary theoretical calculations, carried out by Professor Gleiter's group.³⁸ These calculations suggest that substantial net positive charge resides on the two outer manganese atoms, while the central one bears substantial negative charge.

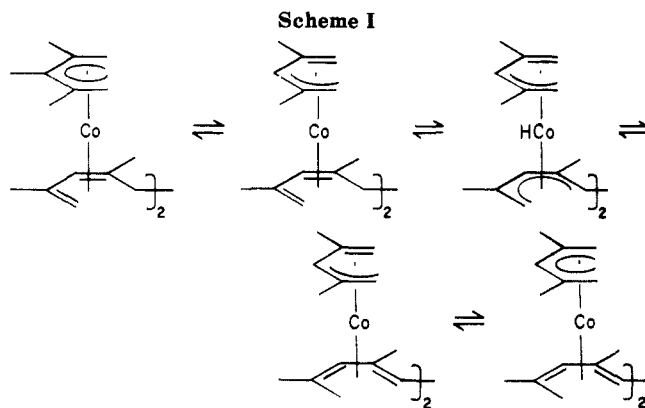
The reaction of cobaltous chloride with 2 equiv of the 2,4-dimethylpentadienyl anion led to a dimeric product, although a monomeric species was believed to exist as an intermediate. Because of the known dimerization of $(C_5H_7)Fe(CO)_3$ (and more recently, of $(2,4-(CH_3)_2C_5H_5)Fe(CO)_3$) on reduction of the cation,^{39a-c} the formation of an analogous cobalt dimer was not unexpected. However, a single-crystal X-ray diffraction study demonstrated that the dimeric ligand here was dramatically different (Figure 6). The expected form, IXa (neglecting possible cis/trans isomerism), contains



two 1,3-butadiene units which are not conjugated with one another.³⁹ In the form observed here, IXb, the two 1,3-butadiene units have each shifted inward by one bond, becoming mutually conjugated. As such isomerizations are not observed for complexes like $[(C_5H_7)Fe(CO)_3]_2$, its occurrence here could well result from the presence on each cobalt atom of an unaltered η^5 -2,4-dimethylpentadienyl ligand. The conversion of the η^5 -bound ligand to an η^3 form could lead to a coordinately unsaturated Co(I) center, which could then bring about the observed isomerization, as depicted in Scheme I. Here, then, is another selective transformation brought about by a metal-pentadienyl complex and one which seems to indicate that $\eta^5 \rightarrow \eta^3$ pentadienyl interconversions should be facile enough to allow for rich catalytic and reaction chemistry in these systems.⁴⁰

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(40) It should be noted that a number of (η^3 -pentadienyl)metal compounds are also known: (a) Hegedus, L. S.; Varaprath, S. *Organometallics* 1982, 1, 259. (b) Paz-Sandoval, M. d. l. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Ibid.* 1984, 3, 1026. (c) Bleeke, J. R.; Peng, W.-J. *Ibid.* 1984, 3, 1422. (d) Leyendecker, M.; Kreiter, C. G. *J. Organomet. Chem.* 1983, 249, C31. (e) Lehmkuhl, H.; Naydowski, C. *Ibid.* 1982, 240, C30. (f) At least one η^1 complex is also known. See: Yasuda, H.; Nagasuna, K.; Akitu, M.; Lee, K.; Nakamura, A. *Organometallics* 1984, 3, 1470.



Prospects and Concluding Remarks

Our initial studies have abundantly confirmed our early predictions that metal-pentadienyl complexes could possess reasonable thermal stability as well as chemical and catalytic reactivities. In some cases the metal-ligand bonding in these compounds, judged by thermal behavior and metal-carbon bond distances, may even exceed those of their cyclopentadienyl counterparts, and we have now gathered physical data on these compounds extensive enough that major bonding trends are beginning to be understood. On the other hand, even some of the "open ferrocene" complexes are very reactive (including electrochemically⁴¹), and we have already observed a number of unique chemical transformations in various metal systems. It is clear that the bis(pentadienyl) compounds of the first-row transition metals are very crowded, which leads to greatly constrained chemistry, as exemplified by reversible 14-16-electron reactions in the "open titanocene" system. In some respects, then, the most versatile chemistry might be exhibited by the less crowded complexes of various second-row metals such as zirconium.⁴² It seems that a great deal of metal-pentadienyl chemistry remains to be explored, and perhaps the best is yet to come.

It is a sincere pleasure to thank my student co-workers, particularly Teddy H. Cymbaluk, Robert W. Gedridge, Michael S. Kralik, Ju-Zheng Liu, Huairang Ma, Lothar Stahl, and David R. Wilson, for their efforts and perseverance through the course of this work. In addition, the competent and insightful collaborations with Charles F. Campana, Christoph Elschenbroich, Rolf Gleiter, Rolfe H. Herber, Robert Parry, and B. Stanley Pons are gratefully acknowledged. This work has been supported by the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, a Pennwalt Corp. grant of Research Corp., the University of Utah Research Committee, and NATO travel grants (with Prof. Dr. Rolf Gleiter).

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