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Structural and Reactivity Patterns in Transition-Metal–Pentadienyl Chemistry

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Contents

The area of metal–pentadienyl chemistry has recently been attracting growing attention, and a number of reviews covering various aspects of this field have appeared.[1] As a result of the increasing interest in this field, many new facets of metal–pentadienyl chemistry have been uncovered leading to a greater appreciation for, and understanding of, what this field has to offer. Once again, therefore, it seems appropriate to try to summarize and put into perspective the advances made in this area. In this review, the focus will first center on the physical and structural natures of these complexes, particularly how they relate to similar systems, e.g., allyl, butadiene, and cyclopentadienyl complexes. However, ligand-centered structural features such as C–C distances, C–C–C angles, and their variations with substituents have already been discussed in detail and for the most part will not be presented again.[2] Emphasis for the structural treatment in this review will be given to η^5-bound pentadienyl complexes, as structural parameters for η^3- and η^1-bound species can be expected to reflect the bonding of metal–allyl and metal–alkyl complexes, respectively. Subsequently, attention will turn to reaction chemistry involving major transformations of pentadienyl ligands.

I. Introduction

In many respects it is surprising that the potential usefulness of metal–pentadienyl compounds had not been appreciated earlier. After all, the closed, five-membered cyclopentadienyl ligand and the open, three-membered allyl ligand have proven to be of immense importance in both fundamental and practical senses.[3] The cyclopentadienyl ligand is well-renowned for its utility as a "stabilizing ligand", as it has yielded many very thermally stable compounds. Most notable among these are the metallocenes or bis(cyclopentadienyl)metal complexes.[4] In addition to the quite stable complexes of iron, ruthenium, and osmium (which obey the 18-electron rule), stable species are known also for vanadium, chromium, manganese, cobalt, and nickel, whose complexes possess electron counts in the range of 15–20. In contrast, while homoleptic allyl compounds of the first-row transition metals from titanium to nickel have been prepared, the most stable examples, of chromium and nickel, still decompose at room temperature.[5] Despite, and in fact perhaps because of, this much lower thermal stability, metal–allyl compounds have been utilized in a tremendous number of important synthetic and catalytic applications.[6]

While a number of reports dealing with metal–pentadienyl complexes had appeared prior to 1980 (vide infra), there was little if any indication or recognition that pentadienyl ligands by themselves might lead to a variety of potentially useful carbon–carbon bond-forming (coupling) reactions. However, a close comparison of the pentadienyl fragment, and particularly its molecular orbitals[7] (see Figure 1), to the related

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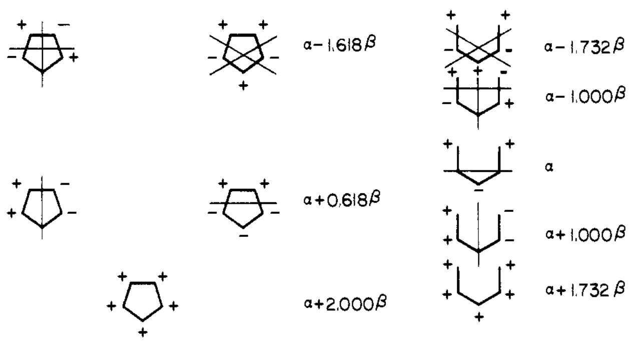


Figure 1. Comparison of the π-molecular orbitals of the pentadienyl and cyclopentadienyl groups.

cyclopentadienyl and allyl fragments, has suggested that the pentadienyl ligand should be capable of imparting thermal stability to a wide variety of metal complexes and that pentadienyl complexes should readily undergo "allyl-like" transformations (e.g., η^5–η^3–η^1 interconversions) and reactions (coupling and "naked metal" chemistry). It was also proposed that in some cases metal–pentadienyl bonding might actually be stronger than the renowned metal–cyclopentadienyl bonding,[1a,b] even though earlier publications had explicitly pointed out that metal–cyclohexadienyl bonding appeared weaker than metal–cyclopentadienyl bonding.[8] In fact, in both "half-open vanadocene" and "half-open titanocene" complexes, this has now been demonstrated, and even with the stronger metal–pentadienyl bonding, the pentadienyl ligand remains the more active center for coupling reactions (vide infra).

While the primary focus of this review relates to metal complexes of open pentadienyl ligands, it must be noted that a large number of metal complexes of cyclohexadienyl, cycloheptadienyl, and cyclooctadienyl (hereinafter collectively referred to as cyclo-dienyl for simplicity, although even between these species there may be significant differences[9]) ligands had been prepared early on, although few of these were homoleptic species and, with some notable exceptions,[10] little concerted effort had been devoted to reaction chemistry of these complexes. Nonetheless, some early observations did serve to foreshadow part of the future course of metal–pentadienyl chemistry, and it is appropriate that some of these be included, particularly when they represent species not yet observed for pentadienyl complexes or demonstrate behavior much different from that of otherwise related pentadienyl species.

The first complex of a pentadienyl ligand, $Fe(C_5H_7)(CO)_3^+$, was prepared in 1962 by protonation of the neutral Fe(η^4-pentadienol)$(CO)_3$ complex.[11] In 1960 the related cyclohexadienyl complex, $Fe(C_6H_7)(CO)_3^+$, had been reported to result from formal hydride abstraction from Fe(η^4-1,3-C_6H_8)$(CO)_3$,[12] while the isoelectronic $Mn(C_6H_7)(CO)_3$ had been prepared through the reaction of 1,3-cyclohexadiene with $Mn_2(CO)_{10}$[13] or from the reaction of $NaBH_4$ with $Mn(C_6H_6)(CO)_3^+$. Similarly, for most other early cyclo-dienyl complexes, the method of preparation utilized (η^4-diene)- or (η^6-arene)metal complexes as starting materials rather than utilizing the direct interaction of organic anions (pentadienyl, cyclohexadienyl, etc.) with metal complexes. While most of the resulting products involved η^5-dienyl coordination, a number of η^3-dienyl complexes had also been reported. Representative examples are depicted below

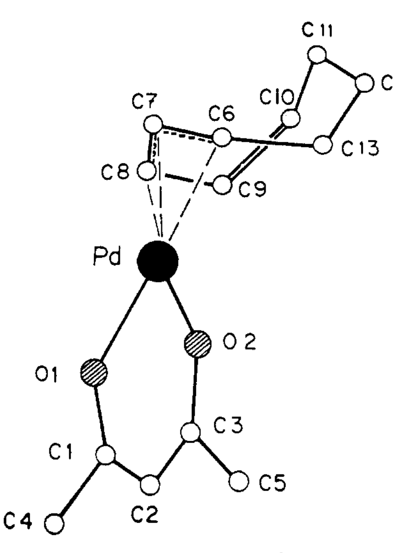


Figure 2. Solid-state structure of Pd(η^3-C_8H_{11})(acac) (reprinted from ref 14c; copyright 1966 American Chemical Society).

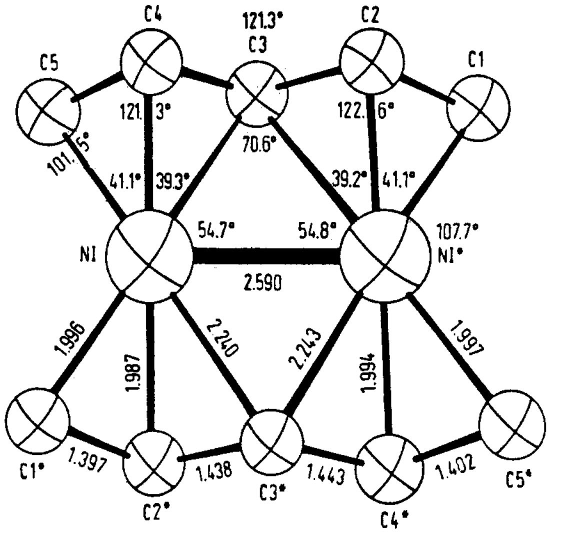
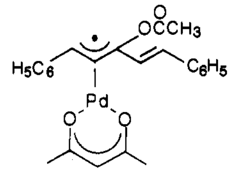
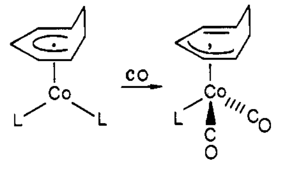


Figure 3. Molecular structure of $Ni_2(C_5H_7)_2$ (reprinted from ref 15; copyright 1969 VCH (Weinheim)).



and in Figure 2,[14] while the structure of the unusual $Ni_2(C_5H_7)_2$ may be seen in Figure 3.[15]

In addition to these isolated examples of η^3- and η^5-bound dienyl complexes, at least several examples of transformations between the η^3- and η^5-bonding modes had been observed. For example, Rinze reported the following η^5–η^3 conversion (eq 1, L = $P(C_6H_5)_3$).[16]



(1)

Mann and Maitlis observed that a variety of neutral and

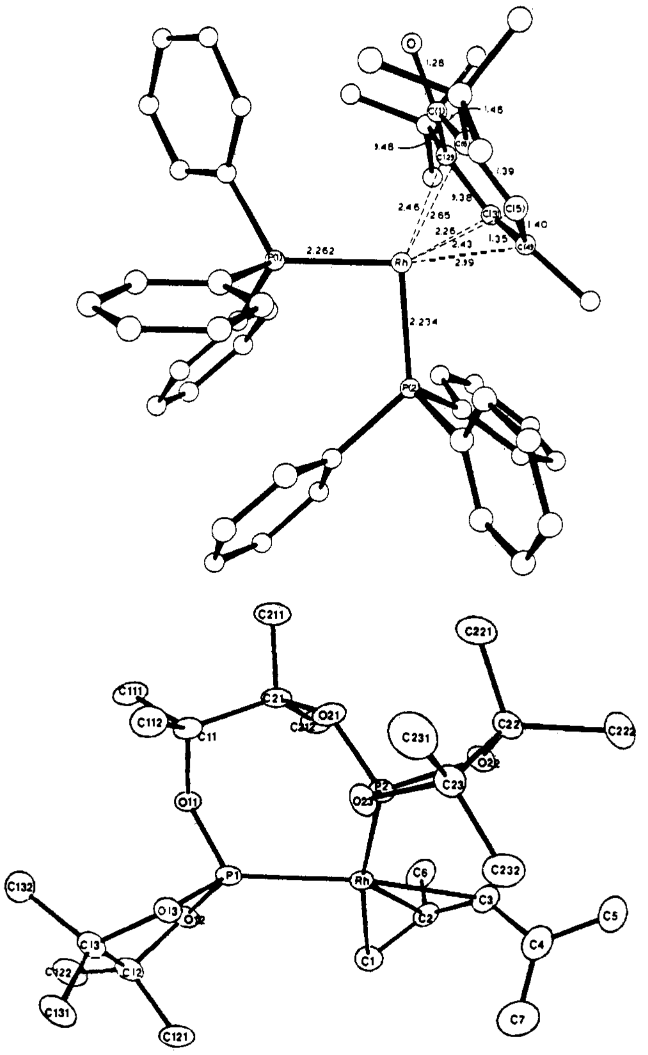
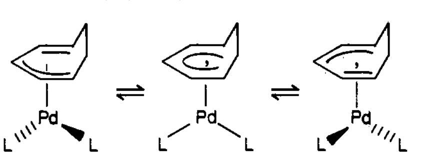


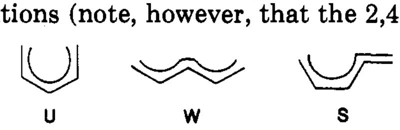
Figure 4. Comparison of the structures of Rh(η^5-C_6H_6O)(P($C_6H_5)_3)_2$ and Rh(η^3-2,4-C_7H_{11})(pinacop) (reprinted from ref 20 and 21; copyright 1980 Elsevier Sequoia and 1988 American Chemical Society).

cationic 16-electron η^3-cycloheptadienyl complexes of palladium displayed fluxional behavior that could be attributed to η^3–η^5–η^3 interconversions, e.g., eq 2.[17] These observations were subsequently supported by molecular orbital studies.[18]



(2)

Although not the case in the example above, in general one might expect that cyclo-dienyl complexes should exhibit a greater preference toward η^5 coordination than would pentadienyl complexes, as the former will be held relatively rigid in the U conformation, while pentadienyl fragments tend to prefer **W** and **S** (sickle) configurations (note, however, that the 2,4-dimethyl-



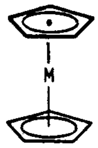
pentadienyl fragment is an exception, preferring the U conformation).[19] In fact, a good illustration of this may be found in some rhodium chemistry. Thus, while a Rh(cyclohexadienyl)(P($C_6H_5)_3)_2$ complex has been formulated as an η^5-bound complex,[20] an analogous open pentadienyl complex has been found to adopt an η^3 configuration (Figure 4).[21]

In a number of cases, the reaction chemistry of metal–pentadienyl complexes has also been paralleled by earlier work with cyclo-dienyl compounds, and such situations will be discussed in the appropriate sections. In addition, however, it should be noted that some very important and extensive applications have been developed for (cyclohexadienyl)metal chemistry in organic synthesis.[10]

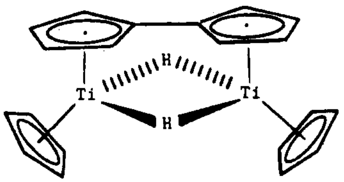
II. Syntheses, Spectroscopy, and Structural Data

A. Open Metallocenes

While a number of organic fragments, perhaps most notably CO, may be incorporated into various series of homoleptic complexes of transition metals,[22] cyclopentadienyl has been for some time quite unique. All first-row transition metals from vanadium to nickel form thermally stable metallocenes



despite the fact that their electron configurations range from 15 to 20. Of these metals, only for iron is the 18-electron rule obeyed. Despite cyclopentadienyl's reputation as a stabilizing ligand, however, the simple titanocene analogue is known to be quite unstable, and attempts at its isolation have led instead to a myriad of dimeric species, perhaps most commonly 1, and to nitrogen adducts.[23]



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The first "open metallocene" to be reported seems to be bis(pentadienyl)chromium, Cr($C_5H_7)_2$, although its potential significance relative to the metallocenes was not recognized.[24] However, two "pseudoferrocenes", bis(6-R-1,3,5-trimethylcyclohexadienyl)iron (R = C_6H_5, t-C_4H_9), were reported at about the same time,[25] and while the potential relationship with ferrocene was suggested, the conformational and bonding natures of these species were essentially unknown. Subsequently, a metal atom vapor reaction led to Fe(η^5-C_7H_7)(η^5-C_7H_9) (C_7H_7 = cycloheptatrienyl; C_7H_9 = cycloheptadienyl).[26] That unsymmetric structures were adopted by these complexes was demonstrated by X-ray diffraction (Figure 5).[26,27] Isoelectronic cationic complexes of rhodium and iridium were reported at about the same time.[28]

In the early 1980s, it was proposed that pentadienyl ligands should be capable of imparting thermal stability as well as favorable chemical and catalytic reactivities to their transition-metal complexes and that in some cases pentadienyl might even bond more strongly than

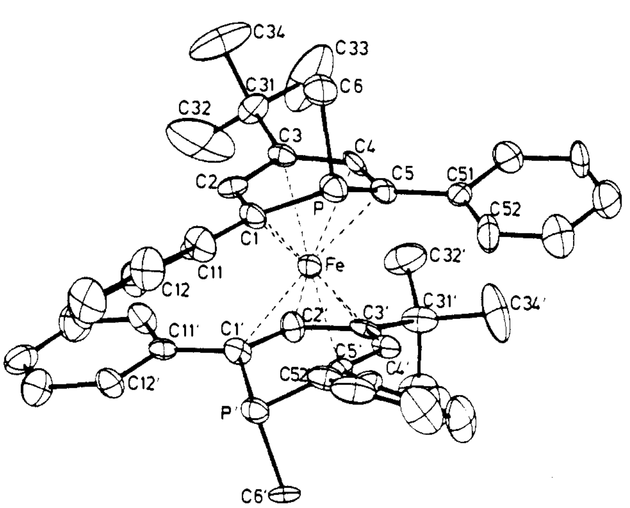
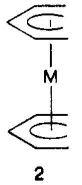


Figure 5. Structure of the pseudoferrocene Fe[η^5-1,5-$(C_6H_5)_2$-3-(*t*-C_4H_9)$C_5H_2P(CH_3)$]$_2$ (reprinted from ref 27b; copyright 1985 American Chemical Society).

cyclopentadienyl.[29] In accord with these expectations, it was found that direct reaction of 2 equiv of the 2,4-dimethylpentadienyl anion with divalent titanium, vanadium, chromium, and iron chlorides or chloride complexes led straightforwardly to the formation of the respective "open metallocenes" M(2,4-C_7H_{11})$_2$ (M = Ti, V, Cr, Fe).[29a,b,30] Products could also be isolated from reactions involving manganese and cobalt dichlorides, but much different courses were followed, and the products are described later.

Because of their close relationship with ferrocene, the open ferrocenes have provided a nice opportunity for comparisons through physical studies. Most of these studies can be more effectively understood in relation to results for the half-open ferrocene Fe(C_5H_5)(2,4-C_7H_{11}) and hence their discussion will be postponed until section II.C. Structures of Fe(2,4-C_7H_{11})$_2$ (Figure 6) and Fe(2,3,4-C_8H_{13})$_2$ have been determined,[31] and in each case a nearly gauche-eclipsed conformation was adopted, with the average Fe–C bond distances of 2.089 (2) and 2.087 (1) Å, respectively, being longer than the average distance of 2.064 (3) Å in ferrocene.[32] To discuss the conformations properly, one can define a conformation angle, χ, as being 0° for the syn-eclipsed conformation **2** and 180° for the anti-eclipsed form **3**.



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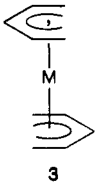

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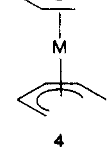
With this definition, the value of χ for the gauche-eclipsed form **4** should be 60°. The respectively values for the two iron complexes are 59.7 and 55.1°, and the deviation from 60° for the latter complex can readily be ascribed to intramolecular $CH_3 \cdots CH_3$ repulsions. While a second gauche-eclipsed form, **5**, is possible, until recently (vide infra) it had appeared to be quite unlikely and was generally omitted from consideration. While something close to this form has now been observed for Zr(2,4-C_7H_{11})$_2$(CO)$_2$, it is still likely to be uncommon, and any unqualified reference to a gauche-eclipsed form will refer to that of **4**. It can be noted that structural determinations for "pseudo-ferrocenes", as in Figure 6, also have revealed gauche-eclipsed ligand orientations, although recent spectroscopic data for bis(6,6-dimethylcyclohexadienyl)iron have led to the proposal that it exists in the anti-eclipsed form **3**.[33]



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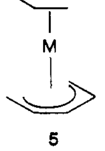

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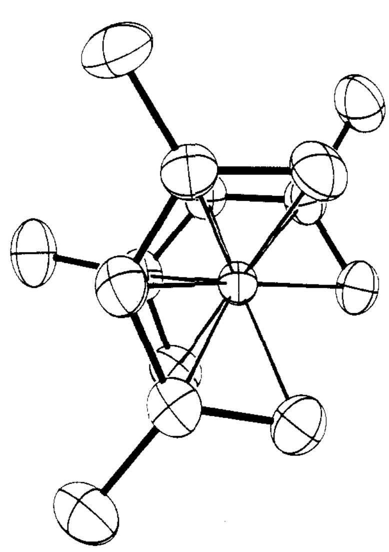
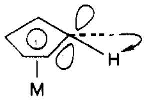


Figure 6. Structure of the open ferrocene Fe(2,4-C_7H_{11})$_2$ (reprinted from ref 31a; copyright 1983 American Chemical Society).

It is notable that the Fe–C bonds for the "open ferrocenes" are slightly longer than those in ferrocene itself. This observation is consistent with early structural observations for other η^5-dienyl complexes.[8] For the "open ferrocenes" at least, the longer distances were attributed to the presence of significant interligand steric repulsions and to decreased Fe–pentadienyl overlap.[31] Support for both of these possibilities would be found from the structural data. Regarding the overlap argument, it can be noted that a tilting of 3.7 (9)° by the hydrogen atom substituents toward iron has been observed for ferrocene, **6**, and attributed to an attempt to improve metal–ligand overlap by pointing the carbon atoms' p orbitals more toward the metal center,[32] whereas for vanadium, the tilt appeared to take place in the opposite direction. For comparison, tilts of substituents in the "open metallocenes" are generally in the range of 6–12°, suggesting that more tilting is required to bring about reasonable overlap.



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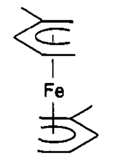
In accord with structural results, variable-temperature ^1H and ^{13}C NMR spectroscopic studies have demonstrated that the ground states of Fe(C_5H_7)$_2$, Fe(3-C_6H_9)$_2$, Fe(2,4-C_7H_{11})$_2$, and Fe(2,3,4-C_8H_{13})$_2$ are all unsymmetric (presumably gauche-eclipsed) in solution phase.[31,34] The barriers to the ligand oscillation processes have been determined (Table I) and can be seen

TABLE I. Rotational Barriers ($\Delta G^{\neq}$ at the Coalescence Temperature, kcal/mol) for Various Open Metallocenes[a]

	Fe[b]	Ru[c]	Os[d]
C_5H_7	8.4		
3-C_6H_9	8.7		
2,4-C_7H_{11}[e]	9.1	9.7	13.4
2,3,4-C_8H_{13}	9.4	10.2	

[a] Uncertainties are ca. 0.1–0.2 kcal/mol. [b] References 31 and 34. [c] Reference 48. [d] Reference 34. [e] The barrier for Ti(2,4-C_7H_{11})$_2$ is 15.3 kcal/mol.

to increase with the addition of methyl substituents. For the unsymmetric complexes possessing the 2-methyl- or 2,3-dimethyl-substituted ligands, variable-temperature NMR spectra indicate the presence of two isomers, such as 7 and 8, depicted in the anti-eclipsed form for clarity, although for both the actual ground states will be gauche-eclipsed. The presence of two isomeric forms, 7 and 8, has been further confirmed recently through ^{57}Fe NMR spectroscopy.[35]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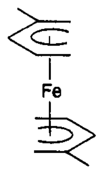
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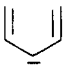
Molecular orbital studies have been carried out on the open ferrocenes, utilizing both the extended Hückel (EH) and INDO methods, and the results correlated with photoelectron spectroscopic data.[36] Several significant differences were noted between the open ferrocenes and ferrocene. Thus, calculations for the anti-eclipsed, syn-eclipsed, and gauche-eclipsed conformations for the former compound reveal in each case the presence of three orbitals having comparable (30–70%) metal and ligand character, whereas no such orbitals are found for ferrocene. According to the EH method, the anti-eclipsed form is favored over the observed gauche-eclipsed form by 22 kJ/mol. While this is at oods with structural and spectroscopic results, it is in accord with the observation that the barriers to ligand rotation in those species are significantly larger than those for the metallocenes. The lower degree of π orbital stabilization for pentadienyl relative to cyclopentadienyl appears most reponsible for the higher degree of mixing. However, the lower molecular symmetry may also contribute somewhat. In any event, as a direct result of the greater orbital mixing, the iron d orbital populations in the open ferrocenes become much more symmetric in accord with much lower quadrupole splittings observed in the Mössbauer spectra.[37]

The lower stabilization of C_5H_7 is responsible for several other features. Despite the large size of pentadienyl, which leads to poorer metal–ligand overlap and increased ligand–ligand steric repulsion and therefore to longer Fe–C bonds than in ferrocene, the Wiberg indices for the eclipsed Fe(C_5H_7)$_2$ (Fe–C(1,5) = 0.351, Fe–C(2,4) = 0.193, Fe–C(3) = 0.342) average slightly more than the value of 0.281 for ferrocene. Thus, any weakening of the Fe–pentadienyl bonding that results from overlap and steric problems seems to be more than compensated for by the energetic favorability of metal–pentadienyl bonding. The internal and external C–C bond indices are 1.27 and 1.39, respectively, which is consistent with many structural results, and the resonance hybrid



Other interesting trends have also been uncovered. While δ (Fe $\rightarrow$ L) bonding in ferrocene appears very modest, the δ bonding in the open ferrocenes seems quite significant and perhaps is largely responsible for the slightly higher charge on iron found by the theoretical studies (0.434 vs 0.416 in Fe(C_5H_5)$_2$). The carbon atom charges are greatest for the terminal atoms, −0.478 which can be compared to the respective values of 0.033 and −0.312 for the C(2,4) and C(3) atoms in Fe(C_5H_7)$_2$, and −0.173 for the carbon atoms in ferrocene. Actually, spectroscopic studies of various metal pentadienyl carbonyl complexes generally reveal higher C–O stretching frequencies compared to their C_5H_5 analogues, suggesting that pentadienyl is the better accepting ligand, despite the fact that C_5H_5 has both a higher electron affinity and ionization potential than C_5H_7.[38] It might be that the large size of the pentadienyl ligands, and the closer approach of their planes to the metal centers, tend to promote the δ interaction, and possibly pentadienyl ligands may function as significant δ-accepting ligands in many of these compounds. Perhaps this type of interaction might be responsible for the observation that metal pentadienyl complexes are most favored for low metal oxidation states, although other factors (pentadienyl vs metal ion size or resonance stabilization of the pentadienyl radical) might also be important.

The theoretical studies also indicate that methylation brings about significant changes in the Fe–C bonding including a net destabilization of the compounds. Thus, the Fe–C(3) bond index for Fe(3-C_6H_9)$_2$ is smaller than that for Fe(C_5H_7)$_2$ (0.24 vs 0.28), and similarly the Fe–C(2,4) index for Fe(2,4-C_7H_{11})$_2$ is smaller than that of Fe(C_5H_7)$_2$ (0.21 vs 0.23). In accord with these observations, the orbital ionizations observed by photoelectron spectroscopy are significantly lower in energy for the complexes having the higher degrees of methylation.[36] Note, however, that the kinetic stabilities (e.g., thermal) of these compounds generally *increase* with higher degrees of methylation (cf. Co(allyl)$_3$ complexes[39]).

Some final observations may be made regarding the molecular HOMO's and LUMO's. For the pentadienyl anion itself one observes a fairly small separation between the HOMO and LUMO, 1.00β. In comparison, the separation for the cyclopentadienyl anion is much larger at 2.24β. This indicates that pentadienyl should function as a "softer" ligand than cyclopentadienyl,[40] in accord with the theoretical studies indicating greater metal–ligand orbital mixing. Paralleling the results for the isolated anions, theoretical studies also indicate that Fe(C_5H_7)$_2$ has both a higher energy HOMO and a lower energy LUMO than ferrocene, leading to a smaller HOMO/LUMO separation. In accord with these results, the open ferrocenes have been found to undergo electrochemical oxidation more readily than ferrocene[41] (section II.C).

Detailed magnetic and structural data have been obtained for open chromocenes and open vanadocenes (Figures 7 and 8, Table II).[29,42] Analogous to chro-

TABLE II. Pertinent Bonding Parameters for Metallocenes and Open Metallocenes

parameter	V[a]	Cr[b]	Fe[c]
A. For $M(2,4\text{-}C_7H_{11})_2$ Compounds			
conformatn angle, deg	89.8	82.2	59.7
M–C(1,5), Å	2.179 (4)	2.155 (5)	2.108 (5)
M–C(2,4), Å	2.231 (4)	2.171 (4)	2.073 (4)
M–C(3), Å	2.236 (5)	2.163 (6)	2.084 (3)
M–C(av), Å	2.211 (2)	2.163 (3)	2.089 (1)
M–CM, Å	1.632 (2)	1.599 (3)	1.508 (2)
C(1)···C(5), Å	3.05 (1)	2.92 (2)	2.785 (5)
B. For $M(C_5H_5)_2$ Compounds[d]			
M–C, Å	2.280 (5)	2.169 (4)	2.064 (3)
M–CM, Å	1.928 (6)	1.798 (4)	1.660 (10)

[a] Reference 49. [b] Reference 42. [c] Reference 31a. [d] Reference 32.

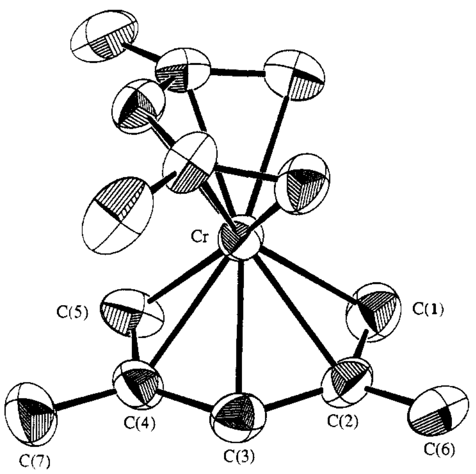


Figure 7. Structure of the open chromocene $Cr(2,4\text{-}C_7H_{11})_2$ (reprinted from ref 42; copyright 1987 American Chemical Society).

mocene,[43] open chromocenes such as $Cr(C_5H_7)_2$, $Cr(3\text{-}C_6H_9)_2$, $Cr(2,4\text{-}C_7H_{11})_2$, and $Cr(1,5\text{-}(SiMe_3)_2C_5H_5)_2$ all possess two unpaired electrons.[29,44] Surprisingly, however, $V(2,4\text{-}C_7H_{11})_2$ was found to possess only one unpaired electron, compared to vanadocene's three. Subsequently, several open titanocenes, including $Ti(2,4\text{-}C_7H_{11})_2$, $Ti(2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5)_2$, and $Ti(1,5\text{-}(SiMe_3)_2C_5H_5)_2$ have also been found to be low spin (diamagnetic),[45] whereas $Ti(C_5Me_5)_2$ possess two unpaired electrons.[23d]

The structural determination for $Cr(2,4\text{-}C_7H_{11})_2$ revealed an unsymmetric pentadienyl ligand orientation, for which the conformation angle is 82.2°.[42] Interestingly, the average Cr–C distance was found to be 2.163 (3) Å, reasonably similar to, if not actually slightly shorter than, the value of 2.169 (4) Å for chromocene.[46,47] Clearly, compared to the Fe(II) complexes, the metal bonding to the pentadienyl ligand has gained relative to cyclopentadienyl, and this may readily be understood on the basis of the sizes of the metal centers. Thus, while in the "open ferrocene" the metal–pentadienyl bonding is hindered by both a loss in metal–pentadienyl overlap and the presence of pentadienyl–pentadienyl repulsions, both of these problems will be relieved somewhat as one substitutes a larger metal atom for iron. A similar observation was also made for the larger ruthenium complex (vide infra), with the metal–pentadienyl bonding again appearing to be marginally shorter than the metal–cyclopentadienyl bonding, 2.188 (2) vs 2.196 (3) Å.[48] Although these results seem to demonstrate at least some gain for metal–pentadienyl bonding, subsequent results for $V(2,4\text{-}C_7H_{11})_2$ came as quite a surprise.[49] A nearly staggered conformation (χ = 89.8°) was observed, with the average V–C distance being 2.211 (2) Å, much shorter than the 2.280 (5) Å value for vanadocene.[47,50] It would be convenient to interpret the shorter V–C(pentadienyl) distances as indicating stronger V–pentadienyl bonding, as this would then help explain the remarkable thermal stability of the "open-titanocenes". However, it is well recognized that low-spin configurations can give rise to M–C bond distances which may be shortened, but not necessarily strengthened. A good example of such a situation involves 1,1′-dimethylmanganocene, which has been found to exist as an equilibrium mixture of low- and high-spin species (one and five unpaired electrons, respectively).[51] As the equilibrium between these two forms is close to being balanced, there is little difference in stability between them, yet the average Mn–C distances for the two forms are 2.14 and 2.433 (8) Å, respectively. Hence, the short average M–C distance in $V(2,4\text{-}C_7H_{11})_2$ did not necessarily reflect stronger bonding relative to vanadocene. However, subsequent results with half-open vanadocene and half-open titanocene complexes, in which spin complications have been removed, have now revealed that the metal–pentadienyl bonding has become stronger than the metal–cyclopentadienyl bonding in these species (vide infra).

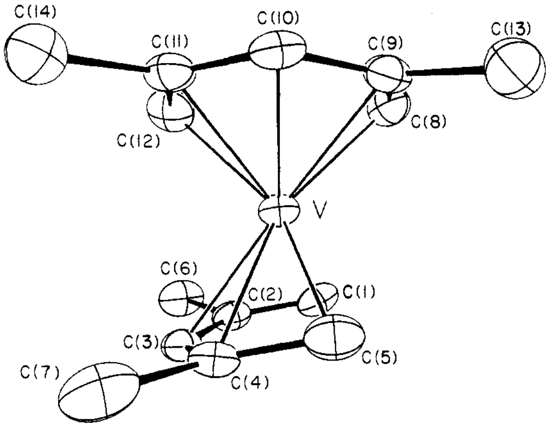


Figure 8. Structure of the open vanadocene $V(2,4\text{-}C_7H_{11})_2$ (reprinted from ref 49; copyright 1984 American Chemical Society).

Some interesting comparisons may be drawn for the three $M(2,4\text{-}C_7H_{11})_2$ structures. As can be seen in Table II, the shortest Fe–C(pentadienyl) bonds are those involving the formally uncharged 2- and 4-positions, while the longest ones are to the 1- and 5-positions. For chromium, all bonds are similar, while for vanadium the shortest bonds involve the 1- and 5-positions. One way of rationalizing this trend would be to propose that bonding for the earlier metals is principally π (ligand→metal) in nature and hence would be more localized at the charged positions, particularly at the open edge of the pentadienyl ligand. As one proceeds to the right of the periodic table, one adds electrons to the metal center, which could then promote δ (metal→ligand) bonding, which should involve primarily the 2- and 4-positions. The presence of greater δ bonding for the later open metallocenes could also be used to explain the adoption of the sterically demanding gauche-eclipsed conformation for iron, the smallest metal in the series. Also notable in the $M(2,4\text{-}C_7H_{11})_2$

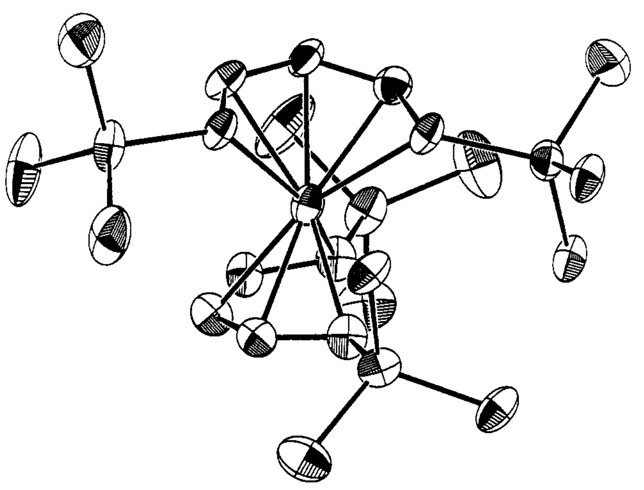


Figure 9. Molecular structure of an open titanocene Ti[1,5-$(SiMe_3)_2C_5H_5]_2$.[45]

series (M = V, Cr, Fe) is the fact that the pentadienyl ligands are themselves quite deformable. Thus, for the largest complex (M = V), one observes a C(1)···C(5) separation of 3.05 (1) Å, while for M = Cr, the separation becomes 2.92 (2) Å, and for the smallest case (M = Fe), it is only 2.785 (5) Å. For Fe(2,3,4-$C_8H_{13})_2$, this separation drops further, to 2.706 (9) Å. As the pentadienyl ligands seem to be too large for optimal bonding with metal centers (vide supra), it appears that these ligands are contracting more and more as the metal size decreases, in order to promote better overlap. This trend is reminiscent of the previously mentioned substituent tilt effects, and a similar skeletal deformability has been noted for metal-allyl compounds.[52]

As Ti(2,4-$C_7H_{11})_2$ is a liquid at room temperature, a single-crystal X-ray diffraction study could not be routinely carried out.[30] Variable-temperature ^1H and ^{13}C NMR spectroscopy did reveal that the molecule possesses an unsymmetric ground state, presumably similar to the "staggered" 90° form found for V(2,4-$C_7H_{11})_2$, with the barrier ($\Delta G^{\ddagger}$) to the ligand oscillation process being 15.3 ± 0.2 kcal/mol. Interestingly, MO calculations indicate that the syn-eclipsed conformation ($\chi = 0$) is lower in energy than the anti-eclipsed form, just the opposite of the situation for iron.[36c] In order to obtain structural data for an open titanocene, we sought to prepare analogous species having bulkier substituents such as t-C_4H_9 (cf. t-C_4H_9OH vs CH_3OH). Indeed, 2,4-(t-$C_4H_9)_2$-1,3-pentadiene could be prepared in straightforward fashion, from which K[2,4-(t-$C_4H_9)_2C_5H_5$] and finally Ti[2,4-(t-$C_4H_9)_2C_5H_5]_2$ could be prepared.[45] The latter compound is in fact a solid at room temperature, and despite the much bulkier substituents present, still has a barrier to ligand oscillation which is quite similar to that of Ti(2,4-$C_7H_{11})_2$. However, good single crystals were difficult to obtain, and ultimately resort was made to the 1,5-bis(trimethylsilyl)pentadienyl anion, which had previously been reported by Nakamura, Yasuda, et al.[53] From the reaction with "$TiCl_2$", a solid product was again obtained, which was indeed Ti[1,5-$(SiMe_3)_2C_5H_5]_2$ (eq 3).

$$\text{“}TiCl_2\text{”} + 2K[1,5\text{-}(SiMe_3)_2C_5H_5] \rightarrow Ti[1,5\text{-}(SiMe_3)_2C_5H_5]_2 \quad (3)$$

Interestingly, while ^1H and ^{13}C NMR signals for the other two "open titanocenes" display significant broadening even at room temperature, those for Ti[1,5-$(SiMe_3)_2C_5H_5]_2$ remain sharp even to 107°, suggesting a much higher barrier to the ligand oscillation process. Whether this is due to a steric or electronic effect is not yet clear. In any event, a solid-state structural determination could be carried out, and the result (Figure 9) clearly confirms the fact that the open titanocenes are indeed stable, monomeric, 14-electron open-sandwich compounds.[45] The conformation is close to the expected staggered form, with $\chi = 82.5°$. Quite possibly the twist from 90° occurs as a result of $SiMe_3$···$SiMe_3$ repulsions. The average Ti-C distance of 2.275 (2) Å is actually quite similar to the average V-C distance of 2.280 (5) Å in vanadocene and much shorter than the 2.33 Å distance that has been estimated for decamethyltitanocene.[32] The Ti-C(5) distance is actually longer than the Ti-C(1) distance (2.315 (5) vs 2.264 (5) Å) probably a result of silyl-silyl steric interactions. The Ti-C(2-4) distances are 2.268 (4) 2.278 (6), and 2.248 (5) Å, respectively.

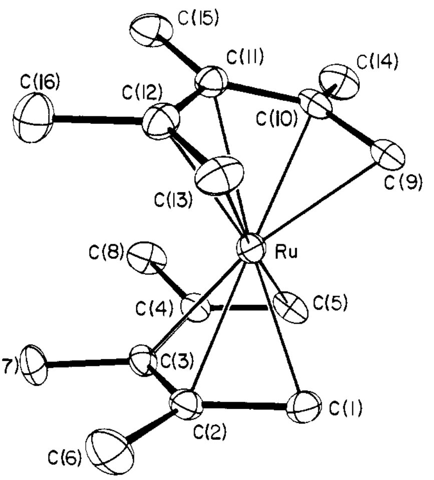


Figure 10. Solid-state structure of the open ruthenocene Ru-(2,3,4-$C_8H_{13})_2$ (reprinted from ref 48; copyright 1983 American Chemical Society).

The only stable second- and third-row metallocenes are those of ruthenium and osmium, which possess 18-electron configurations and exist in eclipsed (D_{5h}) structures.[54] Not surprisingly, open analogues of these species could be obtained through the routes[55] indicated in eq 4 and 5.[34,48]

$$RuCl_3{\cdot}nH_2O + \text{2,4-dimethyl-1,3-pentadiene} \xrightarrow{\text{Zn, EtOH}} Ru(2,4\text{-}C_7H_{11})_2 \quad (4)$$

$$Na_2OsCl_6 + \text{2,4-dimethyl-1,3-pentadiene} \xrightarrow{\text{Zn, EtOH}} Os(2,4\text{-}C_7H_{11})_2 \quad (5)$$

Replacement of 2,4-dimethyl-1,3-pentadiene in eq 4 by the 2,3,4-trimethyl analogue leads to the isolation of Ru(2,3,4-$C_8H_{13})_2$. Variable-temperature NMR spectroscopy indicated that each of these species exists in an unsymmetric conformation, and the barriers to the ligand oscillation processes are listed in Table I. In accord with these results, single-crystal X-ray diffraction studies revealed nearly gauche-eclipsed conformations for both Ru(2,3,4-$C_8H_{13})_2$ and Os(2,4-$C_7H_{11})_2$ (Figures 10 and 11), with the respective values of χ being 52.5° and 48.2°, cf. 59.7° for Fe(2,4-$C_7H_{11})_2$. One can note a steady twist from the gauche-eclipsed toward the syn-eclipsed form as one proceeds down the iron

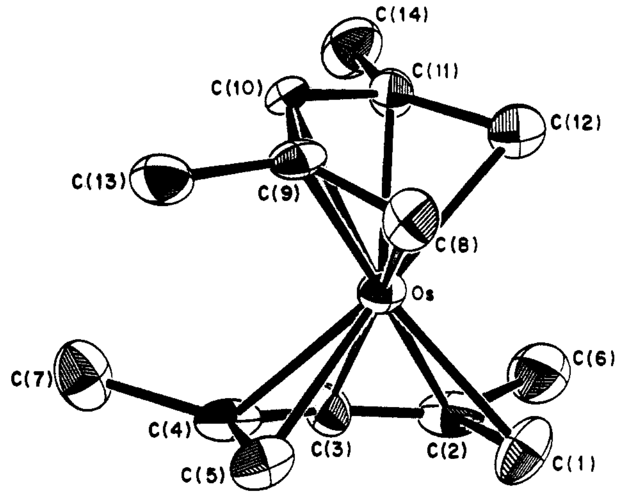


Figure 11. Structure of the open osmocene $Os(2,4\text{-}C_7H_{11})_2$ (reprinted from ref 34; copyright 1987 Elsevier Sequoia).

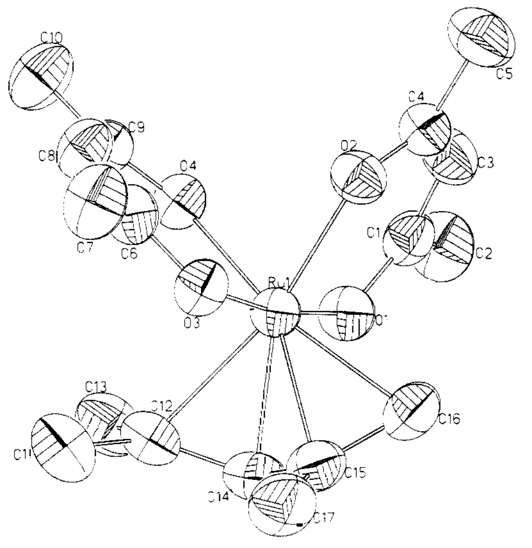


Figure 12. Perspective view of $Ru(\eta^4\text{-}trans\text{-}2,4\text{-}(CH_3)_2\text{-}1,3\text{-}C_5H_6)(acac)_2$.[57]

triad, but an explanation for this is not obvious. The average Ru–C and Os–C distances in those structures were found to be 2.188 (3) and 2.200 (7) Å, respectively, similar to the value of 2.196 (3) Å in ruthenocene.[56]

As the yields for the preparations of the open ruthenocenes varied substantially with the quality of the $RuCl_3{\cdot}nH_2O$ used, a related reaction was attempted utilizing $Ru(acac)_3$, which had previously been used for the preparation of ruthenocene.[4a] Indeed, the $Ru(acac)_3$ analogue of eq 4 did lead to a much cleaner reaction, but the product was not an open ruthenocene, but instead $Ru(\eta^4\text{-}2,4\text{-dimethyl-}1,3\text{-pentadiene})(acac)_2$ (Figure 12),[57] which is notable for its possession of η^4-*trans*-diene coordination. Such coordination has been observed in $Zr(C_5H_5)_2$(diene) and $Mo(C_5H_5)(NO)$(diene) complexes, but only for the latter case is the *trans*-diene coordination thermodynamically favored.[58] The diene ligands in the $Ru(diene)(acac)_2$ complexes may readily be replaced by appropriate ligands (e.g., phosphines).[57]

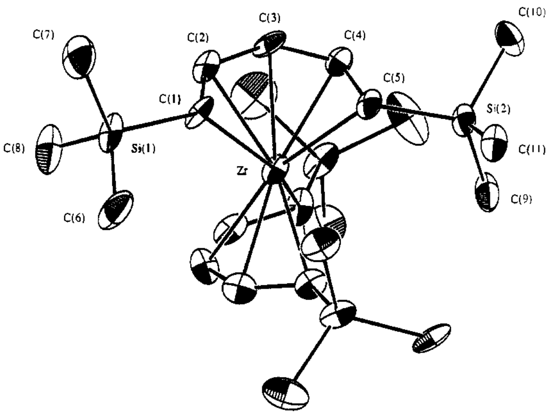
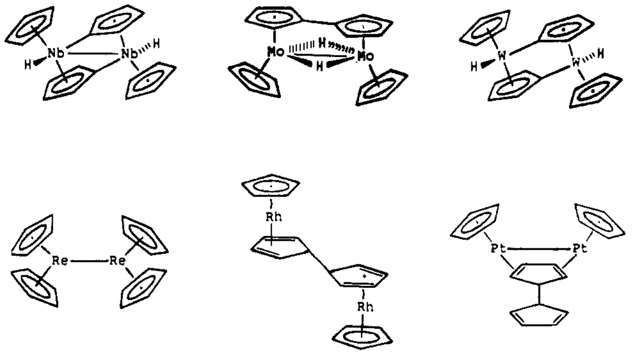


Figure 13. Structure of a 14-electron open zirconocene $Zr[1,5\text{-}(SiMe_3)_2C_5H_5]_2$.[60]

It is notable that despite the "stabilizing" nature of the cyclopentadienyl ligand, no second- or third-row metallocenes have been isolated which violate the 18-electron rule. Rather, various dimers are generally isolated, such as those depicted below.[59]



Given this fact, even we were surprised when it proved possible to isolate a deep red, 14-electron open zirconocene through the route of eq 6,[60] which involves a

$$ZrCl_4(THF)_2 + 4[1,5\text{-}(SiMe_3)_2C_5H_5]^- \rightarrow Zr[1,5\text{-}(SiMe_3)_2C_5H_5]_2 \quad (6)$$

spontaneous reduction of Zr(IV) to Zr(II). This complex, like its green titanium analogue, is diamagnetic and quite stable thermally, being isolable by sublimation at 125 °C. Variable-temperature NMR spectroscopic studies yielded similar results to those obtained for the titanium analogue, indicating a high barrier to ligand oscillation. An interesting comparison may be made regarding the air sensitivity of the open titanocenes and open zirconocene. While $Ti(2,4\text{-}C_7H_{11})_2$ is extremely air-sensitive, smoldering and even setting fire to paper, $Ti[1,5\text{-}(SiMe_3)_2C_5H_5]_2$ is only slightly so. The larger $Zr[1,5\text{-}(SiMe_3)_2C_5H_5]_2$, however, is extremely air-sensitive.

The monomeric, 14-electron open-sandwich configuration proposed for $Zr[1,5\text{-}(SiMe_3)_2C_5H_5]_2$ has been confirmed by X-ray diffraction (Figure 13).[60] The complex is isomorphous with its titanium analogue, has nearly an identical conformation (χ = 82.2°), and possesses an average metal–carbon bond distance of 2.396 (3) Å, consistent with the 0.13 Å difference in size between these two metals.[61] It is interesting that the conformation for $Zr[1,5\text{-}(SiMe_3)_2C_5H_5]_2$ is similar to that of its titanium analogue while that for $Ru(2,3,4\text{-}C_8H_{13})_2$ is similar to those of its iron analogues. This would suggest that structural trends observed for the first transition series open metallocene complexes (M = Ti, V, Cr, Fe) also will apply for second- or third-row open metallocenes (e.g., M = Nb, Mo, Re), should such species prove isolable.

B. Ligand Adducts of Open Metallocenes

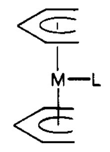
While metallocene-related species such as $M(C_5H_5)_2(L$ or $X)$ and $M(C_5H_5)_2X_3$ are known,[62] the $M(C_5H_5)_2(L)_2$ and $M(C_5H_5)_2X_2$ complexes are much more common.[63] In contrast, for the open metallocenes the mono(ligand) adducts dominate, probably as a result of the great steric crowding brought on by pentadienyl (cone angle of 180–190° vs 126° for C_5H_5 and 165° for C_5Me_5—see Figure 14).[64] For the first-row metal complexes, these adducts are most commonly prepared by the direct coordination of the ligand to the open metallocene, e.g., eq 7 and 8.[30,64,65] For all com-

$$Ti(2,4\text{-}C_7H_{11})_2 + L \rightarrow Ti(2,4\text{-}C_7H_{11})_2(L) \quad (7)$$

$L = CO, PF_3, P(OCH_2)_3CCH_3, PMe_3, PMe_2C_6H_5, P(OMe)_3, P(OEt)_3, PEt_3$

$$V(2,4\text{-}C_7H_{11})_2 + L \rightarrow V(2,4\text{-}C_7H_{11})_2(L) \quad (8)$$

$L = CO, PF_3, PMe_3, P(OMe)_3, PEt_3$



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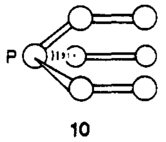

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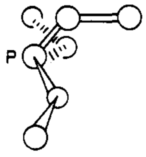

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plexes, it is assumed that a syn-eclipsed conformation is adopted, as in **9**, and ^1H and ^{13}C NMR spectroscopy for the titanium adducts are in accord with these symmetric structures. For the titanium complexes, reversiblity of complex formation has been demonstrated, and ΔH values of 17.4 ± 0.8, 14.5 ± 0.8, 12.9 ± 0.5, 11.4 ± 0.9, 10.6 ± 0.6, and 10.0 ± 0.1 kcal/mol have been found for the dissociation of PF_3, PMe_3, $PMe_2C_6H_5$, $P(OMe)_3$, $P(OEt)_3$, and PEt_3, respectively (the ΔS values range from 27.4–34.1 eu).[64] The ΔH values have been correlated entirely with steric effects (not surprising in view of the fact that the open metallocenes are crowded even without supplemental ligand coordination), once a correction for the cone angle of phosphite ligands had been made to account for the fact that conformations such as the previously assumed form **10** are not feasible sterically, and the smallest accessible form is actually more like 11. An alternative route to some of these species, and to a number of complexes for which the open metallocenes are not available, involves the direct reaction of pentadienyl anions with "MCl_2" in the presence of phosphine (eq 9–11, M = Ti, V).[64,66] Subsequently, the PEt_3 may be replaced by CO

$$\text{"}MCl_2\text{"} + 2C_5H_7^- + PEt_3 \rightarrow M(C_5H_7)_2(PEt_3) \quad (9)$$

$$\text{"}MCl_2\text{"} + 2(3\text{-}C_6H_9^-) + PEt_3 \rightarrow M(3\text{-}C_6H_9)_2(PEt_3) \quad (10)$$

$$\text{"}VCl_2\text{"} + 2(1\text{-}C_6H_9^-) + PEt_3 \rightarrow V(1\text{-}C_6H_9)_2(PEt_3) \quad (11)$$

or else by a phosphine or phosphite ligand having a smaller cone angle than PEt_3. Interestingly, the PEt_3 coordination in $Ti(C_5H_7)_2(PEt_3)$ and $Ti(3\text{-}C_6H_9)_2(PEt_3)$ is much stronger than that in $Ti(2,4\text{-}C_7H_{11})_2(PEt_3)$. The value of ΔH for the 3-methylpentadienyl complex is 14.6 ± 0.7 kcal/mol, while that for the pentadienyl complex could not be measured directly as decomposition occurred prior to detectable dissociation.[64] These data indicate that ligand coordination to the methylated open titanocenes is hindered by the ensuing $CH_3\cdots CH_3$ repulsions in the syn-eclipsed structures, and hence, these repulsions may also contribute somewhat to the isolability of 14-electron open titanocenes. It should be noted that while chromocene will (reversibly) form a mono(carbonyl) adduct,[67] the open chromocenes have not yet been observed to undergo simple adduct formation; prolonged exposure to CO, $t\text{-}C_4H_9NC$,[4] or dmpe leads instead to $Cr(CO)_6$, $Cr(CN(t\text{-}C_4H_9))_6$, or $Cr(dmpe)_3$ (vide infra).[42]

Structural data have been obtained for a number of the above complexes, including $Ti(2,4\text{-}C_7H_{11})_2(L)$ (L = PF_3, PMe_3, $P(OEt)_3$), $V(2,4\text{-}C_7H_{11})_2(L)$ (L = CO, PF_3), $V(3\text{-}C_6H_9)_2(CO)$, and $V(1\text{-}C_6H_9)_2(CO)$, and in each case the expected syn-elipsed configuration has been found (Figures 15 and 16).[68] Not surprisingly, the Ti–P bond distance in the PF_3 adduct is much shorter than that in the PMe_3 adduct, 2.325 (1) vs 2.550 (2) Å, while the V–PF_3 distance is still shorter at 2.250 (1) Å. The V–CO distances are reasonably similar at ca. 1.92 (1) Å. For $V(1\text{-}C_6H_9)_2(CO)$, only one of the expected isomers could be isolated as a solid at room temperature (Figure 16), which interestingly possesses eclipsed methyl groups. Spectroscopic (IR) data suggested that another isomer of this formula was also present, presumably **12**, but as

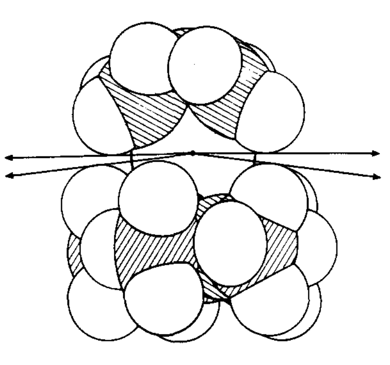


Figure 14. Approximate space-filling model of $Cr(C_5Me_5)(C_5H_7)$. The cone angle of C_5H_7 (above) may be seen to be larger than that of C_5Me_5 due to the closer approach of the metal atom to the C_5H_7 plane.

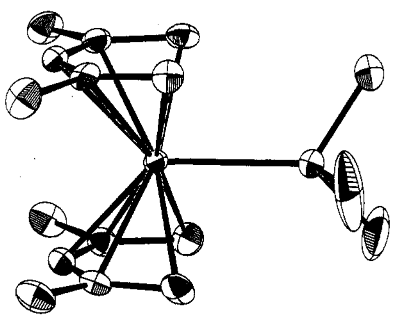


Figure 15. Perspective view of the syn-eclipsed $Ti(2,4\text{-}C_7H_{11})_2(PMe_3)$.[68]

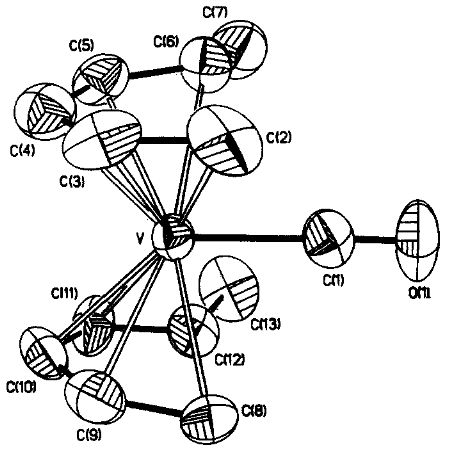


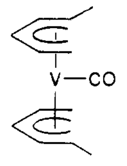
Figure 16. Molecular structure of one isomer of $V(1\text{-}C_6H_9)_2(CO)$.[68]

TABLE III. C–O Stretching Frequencies for the Monocarbonyl Adducts of Open Titanocenes and Open Vanadocenes (Hexane Solution)[a]

methylated positions	Ti	V
(none)	1964.2	1961.9
1		1943.8
2		1958.0
3	1957.4	1952.0
2,3		1945.9
2,4	1951.7	1948.3

[a] Reference 66.

it appeared to be an oil at room temperature, structural characterization was not feasible.



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Kinetic studies on the exchange of coordinated with free CO have been carried out for carbonyl adducts of various vanadocenes, open vanadocenes, and half-open vanadocenes.[66a] The CO exchange reactions for $V(C_5H_5)_2(CO)$ and $V(C_5Me_5)_2(CO)$ are reasonably facile and first order in both CO and metal complex concentrations. The activation parameters for these reactions are consistent with an associative process, having $\Delta H^\ddagger$ = ca. 6 and 8.9 kcal/mol and $\Delta S^\ddagger$ = ca. −30 and −21 eu, respectively. While one would expect that associative processes would be further promoted for a pentadienyl complex, due to more facile η^5–η^3 transformations, the exchange processes for $V(C_5H_7)_2(CO)$, $V(2,4\text{-}C_7H_{11})_2(CO)$, $V(C_5H_5)(C_5H_7)(CO)$, and $V(C_5H_5)(2,4\text{-}C_7H_{11})(CO)$ were in fact found to occur about 10^3–10^4 times more slowly, involving only a slight dependence on CO concentration. Activation parameters for the CO-independent process were fairly similar for each of these species, with $\Delta H^\ddagger$ ranging from 27 to 29 kcal/mol and $\Delta S^\ddagger$ ranging from 2 to 11 eu. The corresponding values for the CO-dependent pathway for $V(C_5H_7)_2(CO)$ are 22.7 kcal/mol and −2 eu.

With a reasonable variety of methylated open vanadocene carbonyl complexes available, it appeared worthwhile to probe relative positional effects on C–O stretching frequencies.[66b] Pertinent data are summarized in Table III. It can be seen that 1-methylation brings about the largest effect, perhaps due to the ability of this substituent to bend furthest out of the pentadienyl plane, thereby improving overlap with the metal center. The next largest effect is brought about by the other charged (3) position, even though, or perhaps in part because, substituents in the 3-position tend to bend least out of the pentadienyl plane. The smallest effect is brought about by placement of substituents in the 2- and 4-positions. Quite parallel results have been obtained for carbonyl adducts of the half-open vanadocenes (vide infra).[60] For comparison, the C–O stretching frequencies for $V(C_5H_5)_2(CO)$, $V(CH_3C_5H_4)_2(CO)$, and $V(C_5Me_5)_2(CO)$ are 1893, 1889, and 1850 cm^{-1}, respectively, in hydrocarbon solution.[66]

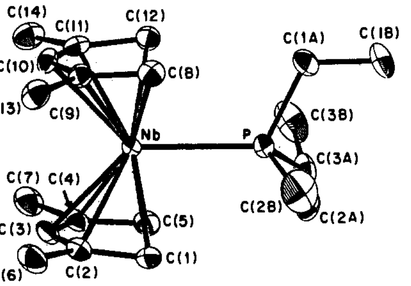


Figure 17. Structural configurations for the $M(2,4\text{-}C_7H_{11})_2(PEt_3)$ complexes (M = Zr, Nb, and (by NMR) Hf.

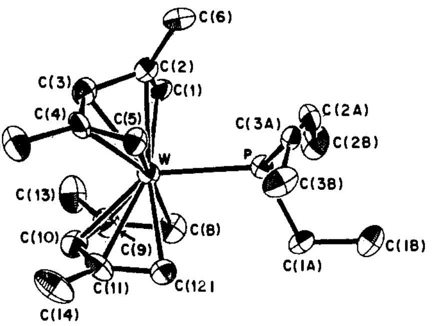


Figure 18. Alternative structural pattern adopted by $M(2,4\text{-}C_7H_{11})_2(PEt_3)$ complexes (M = Mo, W).[69] Similar η^5-S-pentadienyl coordination has also been structurally demonstrated for $Cr(C_5H_5)(C_5H_7)(CNR)$ (R = $2,6\text{-}(CH_3)_2C_6H_3$).

Related open metallocene adducts for zirconium, hafnium, niobium, molybdenum, and tungsten may be prepared by the routes of eq 12 and 13.[69] Except for

$$MCl_4(PEt_3)_2 + 4(2,4\text{-}C_7H_{11}^-) \rightarrow M(2,4\text{-}C_7H_{11})_2(PEt_3) \quad (12)$$

$$M = Zr, Nb, Mo, W$$

$$\text{“}HfCl_3(PEt_3)_2\text{”} + 3(2,4\text{-}C_7H_{11}^-) \rightarrow Hf(2,4\text{-}C_7H_{11})_2(PEt_3) \quad (13)$$

the niobium compound, all species are diamagnetic. Spectroscopic (NMR) data for the zirconium and hafnium complexes are in accord with the expected syn-eclipsed conformations, which has in fact been subsequently confirmed structurally for zirconium as well as the paramagnetic (17-electron) niobium complex (Figure 17). In contrast, however, the ^1H and ^{13}C NMR spectra for $Mo(2,4\text{-}C_7H_{11})_2(PEt_3)$ and $W(2,4\text{-}C_7H_{11})_2(PEt_3)$ indicated quite unsymmetric structures. Solid-state structural determinations for these complexes revealed in each case one normal (U-shaped) η^5-2,4-C_7H_{11} ligand with the other η^5-2,4-C_7H_{11} ligand present

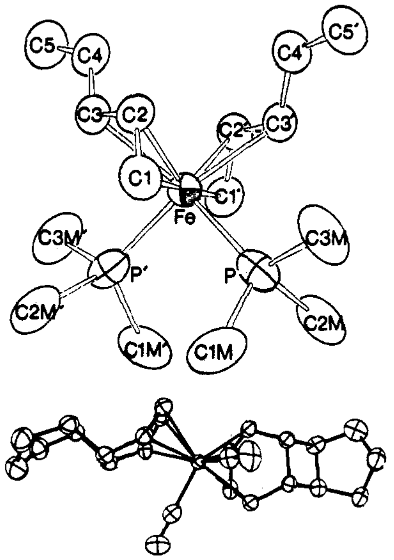
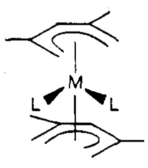


Figure 19. Views of the ligand arrangements in $Fe(\eta^3-C_5H_7)_2(PMe_3)_2$ (reprinted from ref 75a; copyright 1984 American Chemical Society) and $Mo(\eta^4-C_{11}H_{14})_2CO)_2$ (reprinted from ref 75b; copyright 1974 Munksgaard).

in the unusual sickle shape (Figure 18). Notably, a structurally characterized complex of the type $W(\eta^5$-**S**-dienyl)(Br)$(CO)_3$ was reported at about the same time.[70] Other complexes with open η^5-**S**-pentadienyl ligands had been generated earlier, but either would readily rearrange to the usual **U** conformation or, as for $Fe(1,1,5-(CH_3)_3C_5H_4)(CO)_3^+$ would exist in an equilibrium with the **U** conformation.[71] A partially closed $Mo(C_5H_5)(\eta^5$-**S**-dienyl)(CO) complex had also been reported, for which the **U** form was inaccessible,[72] and subsequently a related open complex was also found to contain an η^5-**S**-dienyl ligand.[71g] An example of η^5-**W** coordination (through one sulfur and four carbon atoms) has been observed in an unusual tungsten complex.[73]



13

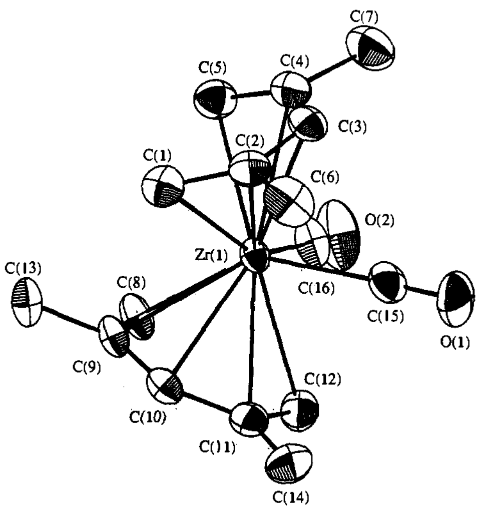


Figure 20. Structure of $Zr(2,4-C_7H_{11})_2(CO)_2$.[74]

Despite steric crowding in the $M(2,4-C_7H_{11})_2(PEt_3)$ (M = Zr, Nb) complexes, addition of smaller phosphine or phosphite ligands leads to almost immediate replacement of the PEt_3. Presumably this comes about as a result of partial phosphine dissociation, yielding small quantities of the 14- or 15-electron open metallocenes in solution. With CO, however, much different results are obtained. For zirconium, a facile equilibrium is established, involving $Zr(2,4-C_7H_{11})_2(PEt_3)$, $Zr(2,4-C_7H_{11})_2(CO)_2$, and a monocarbonyl adduct.[74] In general, the dicarbonyl adduct is only isolable once the freed PEt_3 is removed. The dicarbonyl adduct may subsequently be converted to $Zr(2,4-C_7H_{11})_2(CO)$ under static vacuum. While the ^1H and ^{13}C NMR spectra of $Zr(2,4-C_7H_{11})_2(CO)$ are typical of the highly symmetric syn-eclipsed conformation, spectra for $Zr(2,4-C_7H_{11})_2(CO)_2$ reveal a completely unsymmetric structure. Actually, on the basis of $M(allyl)_2L_2$ and $M(diene)_2L_2$ structures such as in Figure 19[75] one could well have expected a related configuration, **13**, for $Zr(2,4-C_7H_{11})_2(CO)_2$.[76] However, variable-temperature ^1H and ^{13}C NMR spectra demonstrate an unsymmetric ground-state incompatible with **13**. A solid-state structural determination revealed quite an unusual structure (Figure 20). An angle of 140.7° exists between the two pentadienyl ligand planes (cf. 143.4° in $Zr(C_5H_5)_2(CO)_2$[77]) and the value of $\chi = 106°$. Thus, the ligand orientation is closest to the unexpected gauche-eclipsed form **5** (120°), although the large angle between pentadienyl ligand planes probably renders this parameter less meaningful. One of the carbonyl ligands is situated by an open edge of a pentadienyl ligand (as in the allyl and diene analogues above), while the other carbonyl ligand is situated by the back end of the other pentadienyl ligand. The average Zr–C(pentadienyl) bond distances average 2.531 (1) and 2.502 (1) Å for the two ligands, while the Zr–CO distances are 2.208 (4) and 2.236 (3) Å, respectively (ordered according to number). The barrier to the ligand oscillation process was found to be 11.6 kcal/mol. Notably, $Zr(C_5H_7)_2(dmpe)$ has been found to adopt a structure like **13**, suggesting that a methyl substituent in the dicarbonyl may be blocking one of the sites by an open pentadienyl edge.[78] In contrast to the results for zirconium, the reaction of $Nb(2,4-C_7H_{11})_2(PR_3)$ complexes (PR_3 = PEt_3 or $PMe_2C_6H_5$) with CO leads to $Nb(2,4-C_7H_{11})(CO)_3(PR_3)$ complexes, which will be discussed subsequently.[74]

A very interesting series of pseudo-metallocenes (to follow the nomenclature proposed previously) has also been reported.[33] While the cyclohexadienyl anion is unstable toward loss of benzene,[79] the 6,6-dimethylcyclohexadienyl anion is quite stable and was found to react readily with metal halides to yield the respective $M(6,6-(CH_3)_2C_6H_5)_2$ complexes (M = Ti, V, Cr, Fe, and possibly Mn). As with the open metallocenes, the pseudo-titanocene and pseudo-vanadocene possess low-spin states. In many respects these species behave in ways intermediate between the metallocenes and open metallocenes. Thus, a smaller barrier to ligand oscillation is observed for their titanium complex (10.8 kcal/mol) relative to $Ti(2,4-C_7H_{11})_2$ (15.3 kcal/mol, vide supra), while a barrier for their iron complex was not detectable. The colors of their chromium (crimson) and vanadium (scarlet) complexes much more closely resemble those of chromocene (crimson) and vanadocene (purple) than those of the respective open metallocenes,

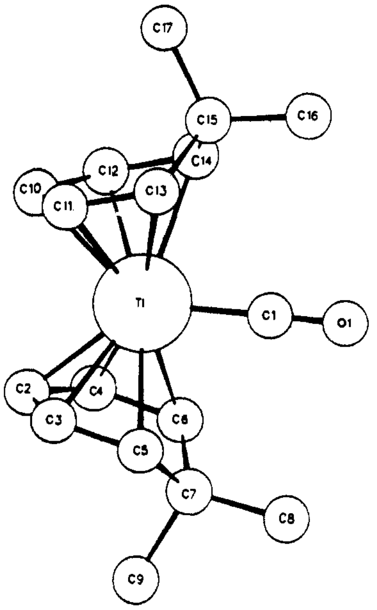


Figure 21. Molecular structure of $Ti[6,6\text{-}Me_2C_6H_5]_2(CO)$ (reprinted from ref 33; copyright 1987 American Chemical Society).

which are each green. Both their titanium and vanadium complexes readily form monocarbonyl adducts as well as related PMe_3 and PF_3 complexes, and once again spectral parameters are intermediate between those of the metallocene carbonyls and the open metallocene carbonyls. Thus, the C–O stretching frequency for $V(6,6\text{-}(CH_3)_2C_6H_5)_2(CO)$ is 1912 cm^{-1}, compared to 1881 cm^{-1} for $V(C_5H_5)_2(CO)$ and 1942 cm^{-1} for $V(2,4\text{-}C_7H_{11})_2(CO)$. A structural determination for $Ti(6,6\text{-}(CH_3)_2C_6H_5)_2(CO)$ was carried out (Figure 21), revealing a syn-eclipsed structure similar to those often seen for ligand adducts of the open metallocenes (vide infra). Even though the cyclohexadienyl anion itself is subject to decomposition, it was possible for the authors to use it to prepare the parent pseudo-ferrocene, $Fe(C_6H_7)_2$, although this was found to be thermally unstable, decomposing to $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}1,3\text{-}C_6H_8)$.

C. Half-Open Metallocenes

Although the open metallocenes have provided for some very interesting comparisons with the metallocenes, it is very clear that a number of difficulties arise in attempting to gain an understanding regarding the origin of these differences. While one might expect that differences in size and orbital energies for pentadienyl and cyclopentadienyl would be especially important, it is clear that other complications exist as well. For example, pentadienyl ligands are far bulkier than C_5H_5 or even C_5Me_5 ligands, and as they are also situated closer to the metal center (1.51 Å for $Fe(2,4\text{-}C_7H_{11})_2$ with d(Fe–C) = 2.089 (3) Å vs 1.66 Å for $Fe(C_5H_5)_2$ with d(Fe–C) = 2.064 (3) Å), significantly greater interligand repulsions are expected, which would lead to lengthened M–pentadienyl bonding parameters. Secondly, the symmetries of the metallocenes are quite high (eclipsed, D_{5h}; staggered, D_{5d}; otherwise D_5 for parallel planes), whereas the open metallocenes generally only possess C_2 symmetry. Conceivably, the higher symmetry for the metallocenes could retard metal–ligand orbital mixing. Finally, as noted earlier for both titanium and vanadium, the open metallocenes may adopt low-spin configurations which could give rise to artificially shorter M–C bonds. With these three additional complications, it clearly becomes difficult to make meaningful comparisons between the metallocenes and the open metallocenes. One way in which these complications may be removed would be to prepare a series of half-open metallocenes, in which one pentadienyl and one cyclopentadienyl ligand are both present. In such complexes, the steric, symmetry, and spin complications mentioned above are nicely eliminated, so that only relative ligand sizes and orbital energies remain as likely differentiating parameters.

A very large number of $M(C_5H_5)$(cyclo-dienyl) (cyclo-dienyl = cyclohexadienyl etc.) complexes had already been prepared, especially for the iron and cobalt triads, and not surprisingly their syntheses generally involved indirect routes, such as nucleophilic addition to $M(C_5H_5)(arene)^+$ complexes.[80] Half-open metallocenes of iron, ruthenium, and osmium could be prepared by using variations of the routes used to make their open metallocenes, except that either mixtures of dienyl anions or of dienes were employed (i.e., eq 14–16).[41,69b,81a] For the preparation of $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$,

$$4FeCl_2 + 4C_5H_5^- + 4(2,4\text{-}C_7H_{11}^-) \rightarrow 2Fe(C_5H_5)(2,4\text{-}C_7H_{11}) + Fe(C_5H_5)_2 + Fe(2,4\text{-}C_7H_{11})_2 \quad (14)$$

$$RuCl_3{\cdot}nH_2O + 0.9C_5H_6 + \text{excess diene} \rightarrow Ru(C_5H_5)(\text{dienyl}) \quad (15)$$

diene = $2,4\text{-}(CH_3)_2\text{-}1,3\text{-}C_5H_6$, $2,3,4\text{-}(CH_3)_3\text{-}1,3\text{-}C_5H_5$;
dienyl = $2,4\text{-}C_7H_{11}$, $2,3,4\text{-}C_8H_{13}$, respectively

$$Na_2OsCl_6{\cdot}nH_2O + 0.9C_5H_6 + \text{excess } 2,4\text{-}(CH_3)_2\text{-}1,3\text{-}C_5H_6 \rightarrow Os(C_5H_5)(2,4\text{-}C_7H_{11}) \quad (16)$$

the reaction proceeded nearly statistically as shown, and the $Fe(2,4\text{-}C_7H_{11})_2$ contaminant could readily be removed due to its higher solubility. Careful crystallization of the remaining solution can lead to readily separable clumps of ferrocene and $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$, which may then be finally purified by a second recrystallization. The ruthenium and osmium preparations proceed quite selectively, yielding no metallocene if the C_5H_6/M ratio is kept to just below one. Apparently the first equivalent of cyclopentadiene is rapidly picked up by the metal complexes, and should there only be an acyclic diene (2,4-dimethyl-1,3-pentadiene) remaining in solution thereafter, it must subsequently be incorporated.

In the NMR spectra of each of these compounds, the ^1H and ^{13}C resonances for the cyclopentadienyl ligand experience downfield shifts relative to the metallocenes, while most of the pentadienyl resonances are shifted upfield relative to the open metallocenes. The structures for the iron and ruthenium complexes appear to be predominantly eclipsed (Figure 22), although the large thermal motion for the C_5H_5 ligands indicates that there could be a contribution from slightly staggered forms (cf. $Cr(C_5Me_5)(C_5H_7)$, vide infra). For the osmium complex, however, there was clear evidence for the contribution of both eclipsed and staggered forms. In accord with the notion that steric crowding might be deleteriously affecting the metal–pentadienyl bonding, in each of these half-open metallocenes the

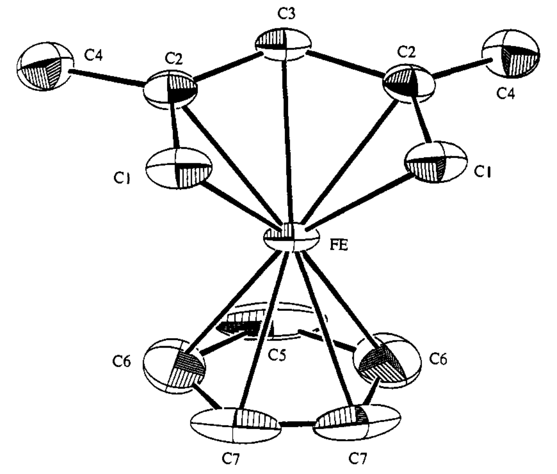


Figure 22. Structure of the half-open ferrocene $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$.[68]

TABLE IV. Comparative Physical Data for $Fe(C_5H_5)_2$ (I), $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$ (II), and $Fe(2,4\text{-}C_7H_{11})_2$ (III)

parameters	I	II	III
E°(0/+), vs SCE[a]	0.49	0.29	0.11
g values (ESR)[a]	1.28	2.0020	2.0165
	4.36	2.1033	2.0712
		2.2255	2.1793
δ(^{57}Fe NMR), vs $Fe(CO)_5$[b]	1532	2277	2639
Mössbauer			
IS,[c] mm/s	0.542	0.474	0.498
QS,[c] mm/s	2.453	1.946	1.516
Fe–C, Å	2.064 (3)	2.06 (1)	2.089 (3)
		2.06 (1)	

[a] Reference 41. [b] Reference 35b. [c] Reference 37.

bonding to pentadienyl has gained relative to comparisons involving the metallocenes and open metallocenes. Thus, while the average Fe–C distance of 2.089 (3) Å for $Fe(2,4\text{-}C_7H_{11})_2$ is clearly longer than the value of 2.064 (3) Å for ferrocene, the bonding to each ligand in the half-open ferrocene is essentially equivalent at 2.06 (1) Å, while for $Ru(C_5H_5)(2,4\text{-}C_7H_{11})$ the pentadienyl ligand appears favored (2.168 (3) vs 2.178 (3) Å).

In a subsequent report, a route to $Fe(C_5H_5)(C_5H_7)$ has been developed, based on photolytic loss of CO from $Fe(C_5H_5)(\eta^1\text{-}C_5H_7)(CO)_2$.[82] An interesting comparison may be made to another half-open ferrocene, $Fe(C_5H_5)(\eta^5\text{-}C(CF_3)_2CHC(CF_3)CFC({=}C(CF_3)_2))$, which was prepared from the reaction of $Fe(C_5H_5)(CO)_2^-$ with $(CF_3)_2C{=}C{=}C(CF_3)_2$.[83] The average Fe–C distance to the cyclopentadienyl ligand is 2.09 (1) Å, while the respective distances to the pentadienylidene ligand are 2.14 (1), 2.04 (1), 2.06 (1), 2.01 (1), and 1.91 (1) Å. It would appear that the electronegative substituents have significantly strengthened the Fe–pentadienyl bonding at the apparent expense of the Fe–cyclopentadienyl bonding.

Some revealing physical and spectroscopic parameters for $Fe(C_5H_5)_2$, $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$, and $Fe(2,4\text{-}C_7H_{11})_2$ may be seen in Table IV. For the most part, the data for $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$ fall right between those for ferrocene and $Fe(2,4\text{-}C_7H_{11})_2$, suggesting that symmetry effects are small. One exception to this involves the ESR data for the radical cations of these species. As a result of its high symmetry, the ferrocence radical cation formally possesses a degenerate electronic ground state, leading to much different behavior than seen for the other two radical cations, which possess nondegenerate electronic ground states.[41] Photoelectron spectra have been obtained for these compounds and correlated with molecular orbital studies.[81a]

It can be noted that both the open ferrocene and the half-open ferrocene are oxidized more readily than ferrocene. The products, however, are not isolable, and the redox process for $Fe(2,4\text{-}C_7H_{11})_2$ requires low temperatures and rapid scan rates for reversibility.[41] These observations suggested the possibility that pentadienyl–pentadienyl coupling reactions occurred for the radical cations, probably being intramolecular for $Fe(2,4\text{-}C_7H_{11})_2^+$ and intermolecular for $Fe(C_5H_5)(2,4\text{-}C_7H_{11})^+$. In fact, attempts to prepare the isoelectronic manganese analogues $(Mn(3\text{-}C_6H_9)_2$ and $Mn(C_5H_5)(2,4\text{-}C_7H_{11})$ appeared also to lead to such coupling reactions (vide infra),[84] and more recent kinetic studies have demonstrated that the decomposition of $Fe(2,4\text{-}C_7H_{11})_2^+$ follows first-order kinetics, while that for $Fe(C_5H_5)(2,4\text{-}C_7H_{11})^+$ is second-order.[85] In both cases, pentadienyl dimers are isolated in high yields.

Isoelectronic, cationic complexes of cobalt, rhodium, and iridium had actually been prepared earlier from the protonation of $M(C_5H_5)(\eta^4\text{-}1,3\text{-dien-5-ol})$ complexes.[86] A variety of such species was reported, possessing substituents on the pentadienyl carbon atoms in the 1-, 2-, and 5-positions. For the case in which the respective substituents are CH_3, H, and H, complexes of all three metals were described. For rhodium and iridium, the (C_6H_5, H, *t*-C_4H_9), (C_6H_5, H, C_6H_5), and (C_6H_5, CH_3, C_6H_5) combinations were reported, while for rhodium alone the (CH_3, H, C_6H_5) and (C_6H_5, CH_3, *p*-$CH_3OC_6H_4$) combinations were described, and for iridium alone, the (C_6H_5, H, *p*-$CH_3OC_6H_4$) combination was reported. Interestingly, for the "symmetrical" (C_6H_5, H, C_6H_5) combinations, the expected equivalence of one end of the pentadienyl ligand to the other was not observed, and this was attributed to an unsymmetrical orientation of the C_6H_5 substituents, one being endo and the other exo. Related species have also been prepared by the protonation of η^4-hexatriene complexes. Thus, protonation of $Rh(C_5H_5)(\eta^4\text{-}1\text{-}C_6H_5\text{-}6\text{-}(C_6H_5C(O))\text{-hexatriene})$ leads to $Rh(C_5H_5)(\eta^5\text{-}1\text{-}C_6H_5\text{-}5\text{-}C_6H_5C(O)\text{-}CH_2C_5H_5)^+$. In contrast, protonation with HBF_4 of $Rh(C_5H_5)(\eta^4\text{-}1\text{-}(C_6H_5C(O))\text{-}6\text{-}C_6H_5\text{-hexatriene})$ leads to $Rh(C_5H_5)(\eta^1,\eta^3\text{-}1\text{-}C_6H_5C(O)CH_2\text{-}C_6H_5C_5H_5)^+$, in which both η^3-dienyl and acyl lone-pair coordination are present. In contrast, HCl or HBr yield the η^3-dienyl complexes $Rh(C_5H_5)(\eta^3\text{-}1\text{-}C_6H_5C(O)CH_2\text{-}5\text{-}C_6H_5C_5H_5)(X)$ (X = Cl, Br). Subsequently, various related $Rh(C_5H_5)(\eta^5\text{-}1\text{-}RC_5H_6)^+$ and $Rh(C_5H_5)(\eta^3\text{-}5\text{-}RC_5H_6)(X)$ (X = Cl, Br, I; R = H, *m*-$CH_3C_6H_4$, *m*-$CH_3OC_6H_4$, *p*-$CH_3OC_6H_4$, *p*-FC_6H_4) species were similarly prepared. A structural study of $Rh(C_5H_5)(1\text{-}C_6H_5C_5H_6)^+$ revealed very similar Rh–C bonding for the two ligands, 2.158 vs 2.154 Å, respectively.

The related cobalt complex $Co(C_5H_5)(2,4\text{-}C_7H_{11})^+$ has been prepared by formal hydride abstraction from $Co(C_5H_5)(\eta^4\text{-}2,4\text{-dimethyl-}1,3\text{-pentadiene})$.[87] This species and its rhodium and iridium analogues above are notable in that metal–pentadienyl complexes tend to be stable for metal centers in low formal oxidation states, and few complexes have even trivalent metal centers. A single-crystal diffraction study revealed the same eclipsed structural type as observed for the related iron and ruthenium complexes and apparently similar

Co–C bonding for the C_5H_5 and 2,4-C_7H_{11} ligands (2.047 (9) vs 2.056 (7) Å, respectively).

Monomeric, 16-electron half-open chromocenes could be prepared by a number of routes, those given in eq 17 and 19 being reasonably useful.[44,88] A wide variety

$$CrCl_2 + C_5H_5^- + 2,4\text{-}C_7H_{11}^- \rightarrow Cr(C_5H_5)(2,4\text{-}C_7H_{11}) \quad (17)$$

$$Cr(C_5H_5)Cl_2 + \tfrac{1}{2}Mg \rightarrow \text{“}Cr(C_5H_5)Cl\text{”} \quad (18)$$

$$\text{“}Cr(C_5H_5)Cl\text{”} + C_5H_7^- \rightarrow Cr(C_5H_5)(C_5H_7) \quad (19)$$

of half-open chromocenes has been prepared this way, including $M(C_5H_5)$(pentadienyl) (pentadienyl = C_5H_7, 3-C_6H_9, 2,3-C_7H_{11}, 2,4-C_7H_{11}, 1,5-$(SiMe_3)_2C_5H_5$, 1,5-$(C_6H_5)_2C_5H_5$) and $M(C_5Me_5)$(pentadienyl) (pentadienyl = C_5H_7, 3-C_6H_9, 2,3-C_7H_{11}, 2,4-C_7H_{11}) species. Additionally, an unusual complex, $Cr(C_5H_5)(1,2,3\text{-}(CH_3)_3\text{-}4\text{-}(aryl)C_5H_3)$, has been prepared indirectly through coupling reactions involving acetylenes.[89] A structural determination for $Cr(C_5Me_5)(C_5H_7)$ revealed a structure twisted ca. 6° from eclipsed with significantly shorter bonding to pentadienyl (2.117 (3) vs 2.194 (3) Å).[88b]

An interesting feature of these complexes is that they have a greater tendency, relative to $Cr(C_5H_5)_2$ or $Cr(2,4\text{-}C_7H_{11})_2$, to undergo coordination by additional Lewis bases. As this tendency extends also to their titanium and vanadium analogues, it appears to reflect a general property of the half-open metallocenes. It is recognized that Lewis base coordination to the metallocenes requires that the two cyclopentadienyl ligand tilt from their favored parallel orientation, while coordination to the open metallocenes generally entails a twist to the unfavored syn-eclipsed orientation. Both of these processes are unfavorable and can be expected to impede Lewis base coordination. In contrast, coordination to a half-open metallocene will require very little distortion, and this could quite easily account for their greater tendency to undergo Lewis base coordination. In any event, the half-open chromocenes listed above react instantly with CO, PF_3, $P(OCH_2)_3CCH_3$, or $t\text{-}C_4H_9NC$ to yield 18-electron mono(ligand) adducts, although prolonged exposure reversibly yields dicarbonyl complexes also, e.g., the crystallographically characterized $Cr(C_5H_5)(\eta^3\text{-}C_5H_7)(CO)_2$. In some cases, phosphine and phosphite adducts may also be isolated. Surprisingly, NMR spectroscopy of the monocarbonyl complexes indicates that the pentadienyl ligands are present in unsymmetric environments, suggesting the adoption of the η^5-sickle conformation.[88] This has been confirmed structurally for the related $Cr(C_5H_5)(C_5H_7)(CN(2,6\text{-}(CH_3)_2C_6H_3))$.[88b]

A wide variety of half-open vanadocenes may also be prepared, although the presence of an additional ligand (carbonyl, phosphine, or isocyanide) appears generally necessary to allow for stability.[60,66a] For most adducts, the reported $[V(C_5H_5)Cl(PEt_3)_2]_2$ serves as a convenient starting material, e.g., eq 20. The coordinated PEt_3

$$\tfrac{1}{2}[V(C_5H_5)(Cl)(PEt_3)_2]_2 + \text{pentadienyl}^- \rightarrow V(C_5H_5)(\text{pentadienyl})(PEt_3) \quad (20)$$

$$\text{pentadienyl} = C_5H_7,\ 3\text{-}C_6H_9,\ 2,4\text{-}C_7H_{11}$$

may readily be replaced by smaller phosphines or phosphites, CO, or $t\text{-}C_4H_9NC$. For larger ligands such as $P(C_6H_5)_3$, an alternative route employing THF-solvated $V(C_5H_5)I$ may be used (eq 21). EPR spectroscopy has proven particularly useful in characterizing these species and in probing their electronic natures.

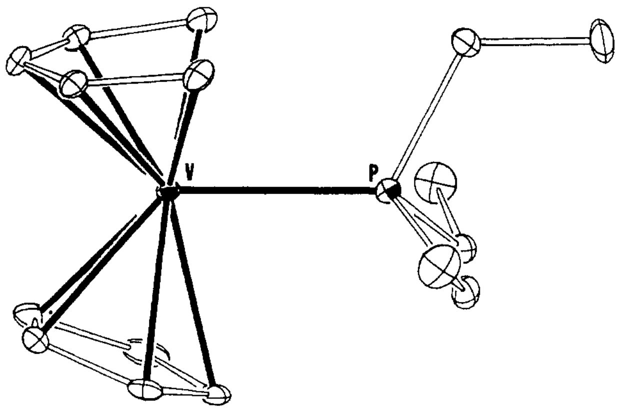


Figure 23. Perspective view of $V(C_5H_5)(C_5H_7)(PEt_3)$.[60]

$$V(C_5H_5)(I)(THF) + 2,4\text{-}C_7H_{11}^- + P(C_6H_5)_3 \rightarrow V(C_5H_5)(2,4\text{-}C_7H_{11})(P(C_6H_5)_3) \quad (21)$$

For the phosphine adducts, coupling to both the vanadium ($I = {}^7/_2$) and phosphorus ($I = {}^1/_2$) nuclei is observed. The magnitude of the phosphorus coupling is greatest for π-accepting ligands (e.g., ca. 59 G in $V(C_5H_5)(2,4\text{-}C_7H_{11})(PF_3)$) and decreases with increasing donor character (e.g., 40.6 G in $V(C_5H_5)(2,4\text{-}C_7H_{11})(P(OMe)_3)$, 30.1 G in $V(C_5H_5)(2,4\text{-}C_7H_{11})(PMe_3)$). In addition, the decreases in phosphorus hyperfine couplings are accompanied by increases in the vanadium hyperfine couplings (ca. 59, 66, and 67 G). For the carbonyl adducts, methylation effects on the IR spectra followed a pattern quite similar to that observed for the open vanadocene carbonyls (vide supra). Thus, compared to $V(C_5H_5)(C_5H_7)(CO)$ (1938.0 cm^{-1} as a Nujol mull), 2,4-dimethylation and 3-methylation were found to bring about decreases in the C–O stretching frequency of 3.4 and 2.3 cm^{-1}, respectively.

It is notable that the additional donor ligands in these adducts appear to be an integral part of the complexes. Attempts to prepare related half-open vanadocenes without such ligands have not proven successful. Furthermore, these additional ligands appear quite strongly bound, even though vanadocene is not coordinated by phosphines, and open vanadocenes are coordinated only weakly by them. Nevertheless, even with the presence of the extra ligand, these half-open vanadocene complexes have resolved an important question regarding metal–pentadienyl bonding. As noted earlier, the average V–C distance in $V(2,4\text{-}C_7H_{11})_2$ was found to be much shorter than that in $V(C_5H_5)_2$, 2.211 (2) vs 2.280 (5) Å, but the difference could be attributed to the low-spin configuration of the former and hence did not necessarily reflect stronger V–pentadienyl bonding. However, the structure of the half-open vanadocene $V(C_5H_5)(C_5H_7)(PEt_3)$ (Figure 23) revealed a very similar pattern, with the average V–C distances being 2.207 (4) vs 2.299 (4) Å.[60] Hence, it is clear that the differences did not arise simply as a result of spin influences, and the large difference in the bonding parameters provides a convincing demonstration that the V–pentadienyl bonding is actually stronger than the V–cyclopentadienyl bonding.

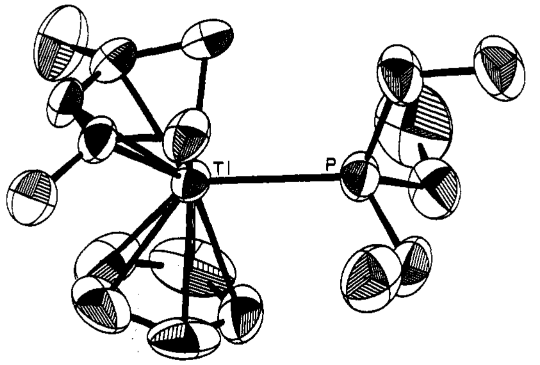


Figure 24. Solid-state structure of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$ (reprinted from ref 90; copyright VCH (Weinheim)).

While the more common pentadienyl ligands (e.g., C_5H_7 and methylated derivatives) do not appear capable of existing in simple $V(C_5H_5)$(pentadienyl) complexes, the use of the $1,5\text{-}(SiMe_3)_2C_5H_5$ ligand seems to have allowed isolation of $V(C_5H_5)(1,5\text{-}(SiMe_3)_2C_5H_5)$, through the reaction of $V(C_5H_5)(I)$ with the appropriate anion. However, it has not yet been structurally characterized, and it appears subject to disproportionation under some conditions. Presumably, its stability derives from steric retardation of the coordination of additional ligands, although one can observe some coordination with appropriate ligands such as CO. Quite possibly, the presence of the $SiMe_3$ substituents also helps to retard any disproportionation reactions.[60]

A related series of half-open titanocenes may also be prepared, as indicated in eq 22.[90] Other phosphines

$$Ti(C_5H_5)(Cl)_2(THF)_2 + 2PEt_3 + 2\text{pentadienyl}^- \rightarrow Ti(C_5H_5)(\text{pentadienyl})(PEt_3) \quad (22)$$

$$\text{pentadienyl} = C_5H_7,\ 2,4\text{-}C_7H_{11}$$

such as PMe_3 may similarly be employed, or alternatively, complexes with smaller phosphine or phosphite ligands may be prepared by direct replacement of PEt_3. All of these 16 electron complexes are diamagnetic, and ^1H and ^{13}C NMR spectroscopy reveal the presence of symmetric U-shaped pentadienyl ligands, as in their vanadium (but not chromium) analogues.

As both the half-open chromocenes and half-open vanadocenes possess much shorter M–C distances to the pentadienyl ligand compared to the cyclopentadienyl ligand, such a difference would be expected to hold also for titanium. Indeed, a structural determination for $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$ (Figure 24) revealed the expected trend, with the average Ti–C bond distances being 2.346 (4) Å for the C_5H_5 ligand and 2.240 (3) Å for the pentadienyl ligand, yielding a difference of 0.106 (5) Å.[90,91] Now that half-open metallocenes have been structurally characterized for titanium, vanadium, chromium, iron, and the cobalt cation (a manganese relative will be described later), it should be possible to reach some general conclusions regarding metal–pentadienyl and metal–cyclopentadienyl bonding. As noted earlier, energetic comparisons would suggest that metal–pentadienyl bonding should generally be favored (even though such a preference had previously not been observed[8]), due to the fact that the aromatic nature of the cyclopentadienyl anion leads to significant stabilization, which would tend to decrease its tendency to engage in further bonding interactions. However, two factors might be expected to impede metal–pentadienyl bonding, both of which are direct geometric consequences of its greater girth. As it is recognized that the C_5H_5 ligand possesses a larger size than optimum for bonding to iron[32] (if not to larger metals as well), even poorer overlap must be expected for metal–pentadienyl bonding, and the presence of larger substituent tilts seems to confirm this expectation (vide supra). In addition, the larger girth of the pentadienyl ligand leads to a much closer approach to the metal center (and larger cone angle), even when M–C distances are comparable to those for the C_5H_5 ligand. Thus, steric crowding will be significantly greater for pentadienyl ligands compared to C_5H_5 and even C_5Me_5. Therefore, despite an expected general energetic favorability for metal–pentadienyl bonding, there are two complications which are metal-dependent. Both differences, overlap and steric, as well as differences in spin configurations, need to be accounted for when one compares metallocenes with open metallocenes, but of these only the overlap effect should carry over to comparisons within the half-open metallocene series.

TABLE V. Average Metal-Carbon Bond Distances (Å) in $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$, $V(C_5H_5)(C_5H_7)(PEt_3)$, $Cr(C_5Me_5)(C_5H_7)$, $Mn_2(C_5H_5)_2(2,4\text{-}C_7H_{11})$, $Rh(C_5H_5)(1\text{-}C_6H_5C_5H_6)^+$, and $M(C_5H_5)(2,4\text{-}C_7H_{11})$ Complexes (M = Fe, Co^+, Ru)

M	M–C_5H_5	M–pentadienyl
Ti[a]	2.346 (4)	2.240 (3)
V[b]	2.299 (4)	2.207 (4)
Cr[c]	2.194 (3)	2.117 (3)
Mn[d,e]	2.083 (3)	2.093 (3)
Fe[f]	2.06 (1)	2.06 (1)
Co[g]	2.047 (9)	2.056 (7)
Rh[h]	2.158 (10)	2.154 (10)
Ru[i]	2.178 (3)	2.168 (3)

[a] Reference 90. [b] Reference 60. [c] Reference 88b. [d] Reference 84b. [e] Distances quoted are for the formal Mn(I) center. [f] Reference 68. [g] Reference 87. [h] Reference 86c. [i] Reference 81a.

In fact, observed average M–C bond distances for these systems can readily be rationalized in light of these considerations. Beginning with the half-open metallocenes, one does indeed observe (Table V) that the average M–C bond distances for the pentadienyl ligands are shorter than those to the cyclopentadienyl ligands, except for the smaller iron and cobalt complexes (as well as $Mn_2(C_5H_5)_2(2,4\text{-}C_7H_{11})$). That the metal–pentadienyl bonding is not enhanced relative to the metal–cyclopentadienyl bonding for these smaller metal centers may be taken as an indication of a loss in metal–ligand overlap. In accord with this, it has already been noted that the pentadienyl ligands tend to contract themselves for these smaller metals, perhaps in an attempt to improve overlap.[1a] If we now turn our attention to the metallocene/open metallocene comparisons, it is most straightforward to begin with the chromium and iron complexes, for which there are no differences in spin configurations. It can readily be seen that while the Fe–pentadienyl and Fe–cyclopentadienyl bonding are reasonably comparable in $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$, the Fe–pentadienyl bonding in $Fe(2,4\text{-}C_7H_{11})_2$ appears weaker (at least, it is longer) than the bonding in $Fe(C_5H_5)_2$. Similarly, while the Cr–pentadienyl bonding in $Cr(C_5Me_5)(C_5H_7)$ seems stronger than the Cr–C_5Me_5 bonding, when one compares $Cr(2,4\text{-}C_7H_{11})_2$

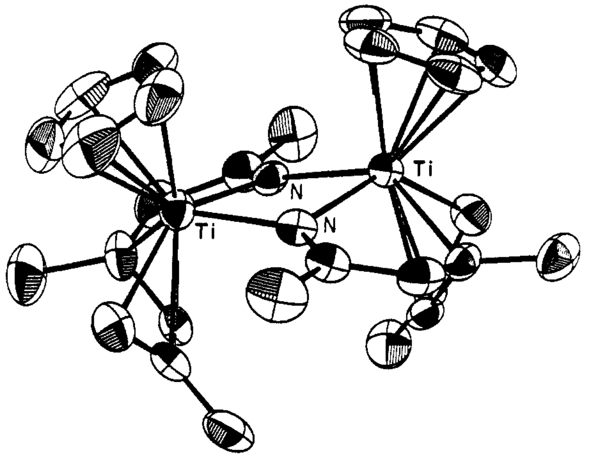


Figure 25. Structure of the acetonitrile–half-open titanocene coupling product $[Ti(C_5H_5)(C_9H_{14}N)]_2$ (reprinted from ref 90; copyright VCH (Weinheim)).

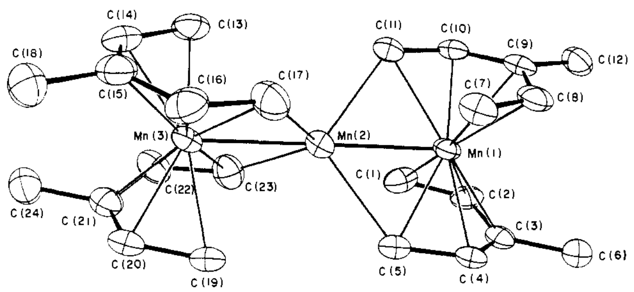
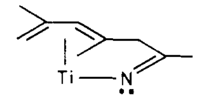


Figure 26. Structure of $Mn_3(3\text{-}C_6H_9)_4$ (reprinted from ref 84a; copyright 1983 American Chemical Society).

with $Cr(C_5H_5)_2$, the Cr–pentadienyl and Cr–cyclopentadienyl bonding appear comparable. In both cases, then, the M–pentadienyl bonding appears to become weaker relative to the M–cyclopentadienyl bonding when one passes from comparisons for the half-open metallocenes to comparisons between the metallocenes and open metallocenes. This may readily be ascribed to a steric contribution, due to pentadienyl–pentadienyl repulsions in the open metallocenes. In accord with this, it can be noted that for both chromium and iron, the M–pentadienyl bonding in the open metallocene appears weaker than the pentadienyl bonding in the half-open metallocene. Finally, as one reaches titanium and vanadium, one notes that the metal–pentadienyl bonding appears stronger than the metal–cyclopentadienyl bonding whether one deals with the half-open metallocene comparisons or the metallocene/open metallocene comparisons. As we are now dealing with even larger metal centers, steric and overlap considerations will become even less important and perhaps at some point overlap may even favor the pentadienyl ligands over cyclopentadienyl (vide supra). As the M–C(pentadienyl) bonds in $Cr(C_5Me_5)(C_5H_7)$, $V(C_5H_5)(C_5H_7)(PEt_3)$, and $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$ are all notably shorter than their respective $M\text{–}C(C_5H_5)$ distances, it is clear that metal–pentadienyl bonding may be favored even without the intervention of spin differences. To what extent, if any, the low-spin configurations in open vanadocenes, titanocenes, and zirconcenes may bring about some shortening of their M–C bond distances remains unclear; possibly a structural determination on $V(C_5H_5)(1,5\text{-}(SiMe_3)_2C_5H_5)$ or a related complex might shed further light on this question. It must be kept in mind, however, that while a low-spin configuration may bring about shorter (not necessarily stronger) M–C bonds, it could actually be that the presence of stronger M–C bonds in the open metallocenes of titanium, vanadium, and zirconium was responsible for their adoption of low-spin configurations.

Despite the presence of stronger metal–pentadienyl bonding in $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$, it is already clear that the pentadienyl ligand has retained its generally higher reactivity relative to the C_5H_5 ligand. Thus, the half-open titanocene complex reacts instantly with CH_3CN to yield a dimeric complex (Figure 25) in which coupling between the pentadienyl and CH_3CN groups has taken place[90]



Of particular interest in the complex is the sickle shape of the former pentadienyl fragments.

D. Open and Half-Open Manganocenes

Of the first-row metallocenes, half-open metallocenes, and open metallocenes, the complexes of manganese behave particularly uniquely. Manganocene itself is a polymer in the solid state,[92] while in the vapor phase it is monomeric, possessing a high-spin (five unpaired electrons) configuration and behaves essentially as an ionic compound.[93] Substitution of methyl groups on the cyclopentadienyl ligands, however, can stabilize low-spin configurations, and decamethylmanganocene exists in fact exclusively in the low-spin (*one* unpaired electron) form with short Mn–C distances (2.112 (3) Å),[94] while 1,1′-dimethylmanganocene exists in an equilibrium involving both low- and high-spin monomeric forms in the gas phase (d(Mn–C) = 2.14 and 2.433 (8) Å, respectively).[51] Attempts to prepare an analogous open manganocene, $Mn(3\text{-}C_6H_9)_2$, led instead to an apparent intramolecular coupling reaction ("naked manganese" chemistry) and the isolation of $Mn_3(3\text{-}C_6H_9)_4$ (Figure 26).[84a] Detailed magnetic studies of this complex revealed the presence of five unpaired electrons, while structural results revealed that the bonding involving the terminal manganese atoms is quite similar to the bonding in the open ferrocenes, with d(Mn–C) averaging 2.114 (2) Å vs 2.089 (3) Å in $Fe(2,4\text{-}C_7H_{11})_2$, while the central manganese atom possesses whay may be described as an edge-bicapped tetrahedral coordination environment, in which the central manganese atom interacts weakly with a formally charged, terminal carbon atom from each of the pentadienyl ligands (d(Mn–C) averaging 2.331 (4) Å) and with the two terminal manganese atoms (d(Mn–Mn) averaging 2.516 (1) Å). Together, the above data suggested that the compound could be best formulated as an associated salt of high-spin Mn^{2+} and $Mn(3\text{-}C_6H_9)_2^-$, the latter being isoelectronic with the open ferrocenes.

While magnetic studies reveal the presence of five unpaired electrons (a sextet configuration) for $Mn_3(3\text{-}C_6H_9)_4$, MO studies indicate that two low-lying states exist, one a doublet and the other a sextet only 0.8 kJ/mol higher in energy. A quartet state was found to be 124.8 kJ/mol higher than the doublet state. As opposed to the $Mn^{2+}[Mn(3\text{-}C_6H_9)_2^-]_2$ formulation with

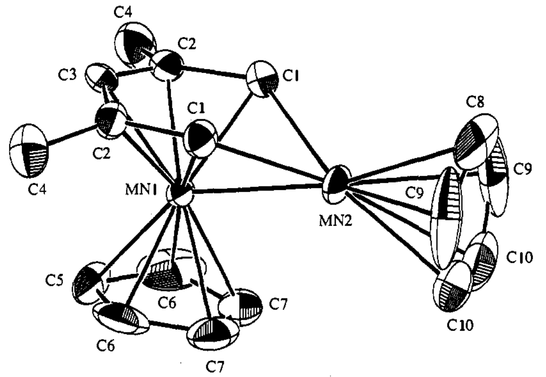


Figure 27. Perspective view of $Mn_2(C_5H_5)_2(2,4\text{-}C_7H_{11})$.[84b]

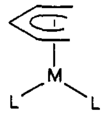
five unpaired electrons on the unique manganese center, the MO calculations indicate Mn(2)'s spin to be $+^3/_2$, with spins of $+^1/_2$ being contributed by each of the other two manganese centers. For the doublet state, these spins are $+^3/_2$ and $-^1/_2$, respectively, while for the quartet, they are all $+^1/_2$. Furthermore, the calculations indicate that substantial negative charge resides on the central manganese atom, with the terminal manganese atoms being positively charged. Despite the rather large differences in energy and spins, the Wiberg bond indices for all three states are rather similar. Thus, in each case the Mn–Mn indices are ca. 0.03, while the Mn(2)–C(1) and Mn(2)–C(5) indices (and their equivalents) average ca. 0.02 and 0.08, respectively. The terminal manganese center indices average 0.31, 0.21, 0.34, 0.25, and 0.40, respectively, for the C(1–5) types of atoms. While the MO formulation differs somewhat from the ionic one initially proposed, the results may, however, be reconciled in that charge and oxidation state are not identical, two good cases being the hydride ligand, which even in the same complex may behave as either a protic or a hydridic species,[95] and in fact some lithium compounds, which have been proposed to contain contributions of an Li^- sort.[96] It could easily be imagined, however, that coordination of strong Lewis bases to the central manganese center would lead to stabilization of the initially proposed formulation.

As the above complex seemed to be formed via an intramolecular coupling reaction, it appeared that perhaps a half-open manganocene might be preparable, as any pentadienyl–pentadienyl coupling would need to occur intermolecularly. Such a species would then allow for at least some understanding of manganese–pentadienyl bonding in a hypothetical open manganocene. The reaction of $MnCl_2$ with equimolar amounts of the cyclopentadienyl and 2,4-dimethylpentadienyl anions did lead to the clean formation of a single product, but this species was not a simple half-open manganocene (Figure 27).[84b] As can be seen, a net loss of pentadienyl has again occurred, most likely via an intermolecular coupling reaction, yielding $Mn_2(C_5H_5)_2(2,4\text{-}C_7H_{11})$. In almost every respect, this species is quite analogous to $Mn_3(3\text{-}C_6H_9)_4$. Once again, five unpaired electrons are present, and the bonding in the $Mn(C_5H_5)(2,4\text{-}C_7H_{11})$ portion of the molecule is quite similar to that in the half-open ferrocene $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$ (Figure 22). The other manganese center possesses quite long bonds to its own cyclopentadienyl ligand, not unlike those found in high-spin manganocene complexes (2.351 vs 2.433 (8) Å, respectively). In addition, the other manganese atom also interacts with two terminal carbon atoms from the $2,4\text{-}C_7H_{11}$ ligand (d(Mn–C) = 2.394 Å), with the first manganese atom (d(Mn–Mn) = 2.459 Å), and perhaps weakly also with two carbon atoms of the other cyclopentadienyl ligand. As for the first manganese complex, this species may also be formulated as an associated salt of high-spin Mn(II) with an anionic 18-electron fragment, i.e., $[Mn(C_5H_5)]^+[Mn(C_5H_5)(2,4\text{-}C_7H_{11})]^-$.

E. Mono(η^5-pentadienyl) Complexes

In some sense, the simplest example of a mono(pentadienyl)metal complex is $[Ni(C_5H_7)]_2$ (Figure 3).[15] Formally, the nickel coordination spheres appear similar to that of $Ni(C_3H_5)_2$, except that the nickel centers in the former receive five instead of six electrons from the organic ligands, and the deficiency might be expected to be satisfied by formation of a Ni–Ni bond (2.590 (1) Å). Actually, however, MO calculations on $[Ni(C_5H_7)]_2$ reveal a very weak Ni–Ni interaction, with much stronger Ni–C(1), Ni–C(2), and Ni–C(3) bonds (Wiberg bond indices = 0.089, 0.248, 0.110, and 0.146, respectively).[97] Interestingly, there is far less charge transferred from nickel to the organic ligands in the dimer relative to $Ni(C_3H_5)_2$. As a result, the net charge on the nickel centers is only 0.545 for the dimer, compared to 0.783 in $Ni(C_3H_5)_2$. The extra metal-centered electron density leads to significant destabilization of orbitals possessing high d character, so that the lowest energy ionization events involve the formal metal orbitals, whereas for $Ni(C_3H_5)_2$ the lowest energy ionizations involve ligand orbitals.

Ligated mono(pentadienyl)metal complexes, M(pentadienyl)(L)$_n$, have been described for n = 2, 3, and 4. Theoretical studies have indicated that the ligand orientations shown, 14–16, should be favored,[98] and



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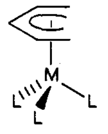

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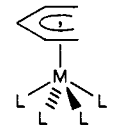

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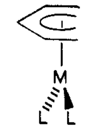
subsequent structural data have generally confirmed such expectations, although in a few cases the presence of η^5-sickle pentadienyl ligands leads to somewhat altered configurations. For the relatively common species 15 and their η^5-cyclo-dienyl analogues,[99] one observes a significant tilting of the unique ligand (L) up toward the pentadienyl plane, which may lead to significant electronic differences for the three L sites.[42] A few complexes which may be considered as members of the M(pentadienyl)(L)$_5$ family have also been reported and may be regarded as pseuedooctahedral complexes (vide infra), analogous to lanthanide, actinide, and transition-metal complexes, e.g., $U(C_5H_4CH_3)Cl_3(THF)_2$,[100] $Zr(C_5H_5)Cl_3(DME)$,[101] and $Er(C_5H_5)Cl_2(THF)_3$.[102] The various mono(pentadienyl) complexes will be considered sequentially from n = 2 to n = 5.

1. M(η^5-pentadienyl)(L)$_2$

A variety of M(η^5-pentadienyl)(L)$_2$ complexes has been reported, as well as cyclohexadienyl, cycloheptadienyl, and cyclooctadienyl analogues. Various accompanying ligands (L) have been incorporated, including CO, halide, phosphines, phosphites, and olefins.

In general, structural determinations for such complexes have revealed the expected ligand orientation (above), although theoretical considerations suggest that placement of electronegative atoms in, or electron-withdrawing substituents on, the formally charged 1-, 3-, and/or 5-positions might lead to the adoption of an alternative orientation, 17.[18] In fact, such a structure has been found for at least one species, a Rh(η^5-cyclodienyl)(P(C_6H_5)$_3$)(CO) complex.[103]



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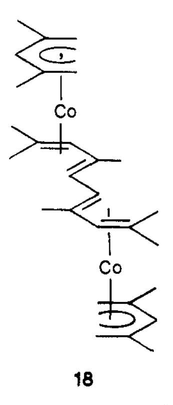
By far the most common examples of these complexes involve metals in the cobalt triad. Thus, the reaction of cobaltous chloride with 2 equiv of the 2,4-dimethylpentadienyl anion (2,4-$C_7H_{11}^-$) leads to a dimeric complex, 18, in which each cobalt center is bonded to an η^5-2,4-C_7H_{11} ligand and to an η^4-diene portion of the 2,4,7,9-tetramethyl-2,4,6,8-decatetraene bridging unit which was formed from the coupling of two pentadienyl units.[104] An unusual isomerization of the bridging unit has evidently taken place, and this is described in greater detail in section II.H.1. Somewhat related cycloheptadienyl and cyclooctadienyl analogues for cobalt and iridium have also been reported, containing either 1,3- or 1,5-diene ligands.[105] Exposure of Co(η^5-C_7H_9)(η^4-1,5-C_8H_{12}) (C_7H_9 = cycloheptadienyl; C_8H_{12} = cyclooctadiene) to CO was found to lead to Co(η^5-C_7H_9)(CO)$_2$.



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A wide variety of bis(phosphine) adducts of mono(pentadienyl)cobalt complexes has been reported. The cycloheptadienyl complex Co(η^5-C_7H_9)(P(C_6H_5)$_3$)$_2$ has been prepared from CoH(N_2)(PC_6H_5)$_3$)$_3$ and cycloheptatriene, and its reaction with CO to yield Co(η^3-C_7H_9)(CO)$_2$(P(C_6H_5)$_3$) has already been mentioned (vide supra).[16] A number of related phosphine and phosphite complexes employing the 2,4-dimethylpentadienyl ligand have subsequently been reported. Thus, the reaction of $CoCl_2$ with K(2,4-C_7H_{11}) in the presence of a reducing agent (Zn or K(2,4-C_7H_{11})) and PEt_3 or pinacop[106] leads to Co(2,4-C_7H_{11})(PEt_3)$_2$ or Co(2,4-C_7H_{11})(pinacop), respectively.[21,107] A structural determination revealed essentially the expected geometry, although a slight distortion (a twist of 3.7°) of one of the phosphorus centers was observed (P2, Figure 28). The Co–P(1) and Co–P(2) distances were found to differ, being 2.149 (1) and 2.180 (1) Å, respectively. A similar structure was found for Co(2,4-C_7H_{11})(pinacop), with analogous Co–P(1) and Co–P(2) distances being 2.078 (2) and 2.105 (2) Å, respectively. The Co–pentadienyl bonding appears slightly weaker in the more crowded PEt_3 complex.

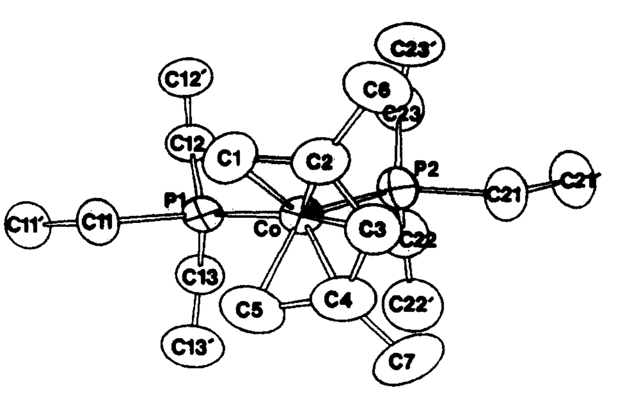


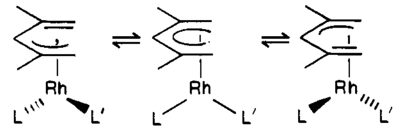
Figure 28. Solid-state structure of Co(2,4-C_7H_{11})(PEt_3)$_2$ (reprinted from ref 107; copyright 1984 American Chemical Society).

The complex Co(2,4-C_7H_{11})(PEt_3)$_2$ may readily be converted to other η^5-2,4-C_7H_{11} complexes.[107] Exposure to P(n-Pr)$_3$ leads to the establishment of an equilibrium mixture of phosphine complexes, believed to proceed via dissociative processes, and evacuation leads to preferential removal of PEt_3, allowing isolation of Co(2,4-C_7H_{11})(P(n-Pr)$_3$)$_2$. On the other hand, exposure to smaller ligands such as P(OMe)$_3$ or PMe_3 was found to lead to Co(η^3-2,4-C_7H_{11})(L)$_3$ complexes. The L = PMe_3 species could also be isolated from the reaction of CoCl(PMe_3)$_3$ with K(2,4-C_7H_{11}). In both cases, the complexes were isolated as mixtures of two isomers, proposed to possess η^3-2,4-C_7H_{11} ligands in the U and W conformations. These species were found to equilibrate rapidly by NMR spectroscopy, and a mechanism involving an η^1-2,4-C_7H_{11} ligand, bonded through the central carbon atom, was proposed.

The electron-rich Co(I) complexes may readily be oxidized to 17-electron Co(II) species.[107] Thus, reaction of Co(2,4-C_7H_{11})(PEt_3)$_2$ with H^+ or Ag^+ leads to Co(2,4-C_7H_{11})(PEt_3)$_2^+$, while reaction with AgI, CH_3I, or NH_4I leads to Co(2,4-C_7H_{11})(I)(PEt_3). Co(2,4-C_7H_{11})(PEt_3)$_2^+$ revealed a larger twist distortion (9.8°) relative to the neutral species, as well as longer Co–P distances of 2.204 (1) and 2.292 (1) Å, the shorter of the two again corresponding to the phosphine ligand under the open pentadienyl edge. The average Co–C bond distance of 2.155 Å may be compared to the analogous value of 2.099 Å in the neutral complex. A structural study for Co(2,4-C_7H_{11})(I)(PEt_3) revealed that the PEt_3 ligand is located by the open edge of the pentadienyl group, leaving the iodide ligand by the pentadienyl ligand's C(3) atom. Interestingly, the respective Co–P and average Co–C bond distances of 2.158 (1) and 2.120 Å much more clearly resemble those in Co(2,4-C_7H_{11})(PEt_3)$_2$ than those in Co(2,4-C_7H_{11})(PEt_3)$_2^+$.

Treatment of the 17-electron Co(2,4-C_7H_{11})(PEt_3)$_2^+$ with PMe_3 was found to lead to Co(η^3-2,4-C_7H_{11})(PMe_3)$_3^+$, which could also be isolated from the oxidation of Co(η^3-2,4-C_7H_{11})(PMe_3)$_3$ with $AgBF_4$.[107] Addition of phosphites to the various 17-electron Co(II) complexes led to expulsion of the pentadienyl ligand and formation of 18-electron cationic complexes. Thus, reactions of Co(2,4-C_7H_{11})(I)(PEt_3), Co(2,4-C_7H_{11})(PEt_3)$_2^+$, and Co(η^3-2,4-C_7H_{11})(PMe_3)$_3^+$ with 5, 4 and 4 equiv of P(OMe)$_3$ lead respectively to Co(P(OMe)$_3$)$_5^+$, Co(PEt_3)(P(OMe)$_3$)$_4^+$, and Co(PMe_3)$_2$(P(OMe)$_3$)$_3^+$.

From reactions of $[RhCl(PR_3)_2]_2$ complexes (R = Me, Et, *i*-Pr, *i*-Bu) with $K(2,4\text{-}C_7H_{11})$, 16-electron $Rh(\eta^3\text{-}2,4\text{-}C_7H_{11})(PR_3)_2$ complexes may be isolated,[108] clearly differing from their 18-electron $Co(\eta^5\text{-}2,4\text{-}C_7H_{11})(PR_3)_2$ or $Rh(phenoxide)(P(C_6H_5)_3)_2$ analogues (Figure 4) but similar to isoelectronic 16-electron $Pd(cycloheptadienyl)(L)_2^+$ species noted previously.[17] In solution, two isomers were observed for each complex, the major component being attributed to the **U**-shaped $2,4\text{-}C_7H_{11}$ ligand, while the minor component was assigned as having a **W**-shaped $2,4\text{-}C_7H_{11}$ ligand (similar assignments had also been made for $Co(\eta^3\text{-}2,4\text{-}C_7H_{11})(PMe_3)_3$ complexes, vide supra). Analogous to observations made for various $Pd(cycloheptadienyl)(L)_2^+$ species, variable-temperature NMR spectroscopy indicated that the $U\text{-}2,4\text{-}C_7H_{11}$ complexes undergo η^3–η^5–η^3 interconversions such that the ends of the pentadienyl ligands become equivalent without an interchange of the two phosphorus atoms. At somewhat higher temperatures, equilibration of the **U** and **W** isomers was observed to take place, and a sickle- (**S**-) shaped intermediate was proposed. More recently, the 16-electron $Rh(\eta^3\text{-}2,4\text{-}C_7H_{11})(pinacop)$ complex has been prepared and also found to exist as two isomers in solution.[21] Notably, however, a solid-state structural determination (Figure 4) for $Rh(\eta^3\text{-}2,4\text{-}C_7H_{11})(pinacop)$ revealed that the $2,4\text{-}C_7H_{11}$ ligand was not present in either the **W** or the **U** conformation but was present in the syn-**S**[109] (sickle) form.



Outside of the above-mentioned examples for the cobalt triad, relatively few well-characterized M(pentadienyl)$(L)_2$ complexes involving other groups have been reported. The 16-electron $Pd(\eta^3\text{-}cycloheptadienyl)(L)_2^+$ species have been shown by variable-temperature NMR spectroscopy to undergo interconversion via a *higher energy* 18-electron η^5-pentadienyl intermediate, with the observed values of $\Delta G^{\ddagger}$ being ca. 7–17 kcal/mol.[17] Anionic complexes of the formulas $Fe(cycloheptadienyl)(CO)_2^-$ and $Fe(2,4\text{-}C_7H_{11})(CO)_2^-$ have been generated in situ and characterized in part spectroscopically but have not been structurally characterized.[110] However a strong ESR signal for $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$ in solution suggests extensive homolysis to 17-electron $Fe(2,4\text{-}C_7H_{11})(CO)_2$ species, in accord with structural data for the dimer,[111] which was found to be much more crowded than $[Fe(C_5H_5)(CO)_2]_2$.

2. *M(η^5-pentadienyl)(L)$_3$*

The $M(\eta^5\text{-}pentadienyl)(L)_3$ families are by far the most common examples of mono(pentadienyl)metal complexes. As is generally the case, the examples involving η^5-cyclo-dienyl ligands are far more numerous than those with the pentadienyl ligand itself and for the chromium triad include such general types as $M(\eta^5\text{-}cyclo\text{-}dienyl)(L)_2(allyl)$ (L = CO, PR_3),[112] $M(\eta^5\text{-}cyclo\text{-}dienyl)(CO)_2(NO)$,[113] $M(\eta^5\text{-}cyclo\text{-}dienyl)(CO)_3^{n-}$ (n = 0, 1),[114] $[M(\eta^5\text{-}cyclo\text{-}dienyl)(CO)_3]_2$,[115] $M(\eta^5\text{-}cyclo\text{-}dienyl)(CO)_3\text{–}M(C_5H_5)(CO_3)$,[116] and $M(\eta^5\text{-}cyclo\text{-}dienyl)(\eta^7\text{-}C_7H_7)$,[117] some of which could also be considered as $M(\eta^5\text{-}pentadienyl)(L)_4$ complexes.

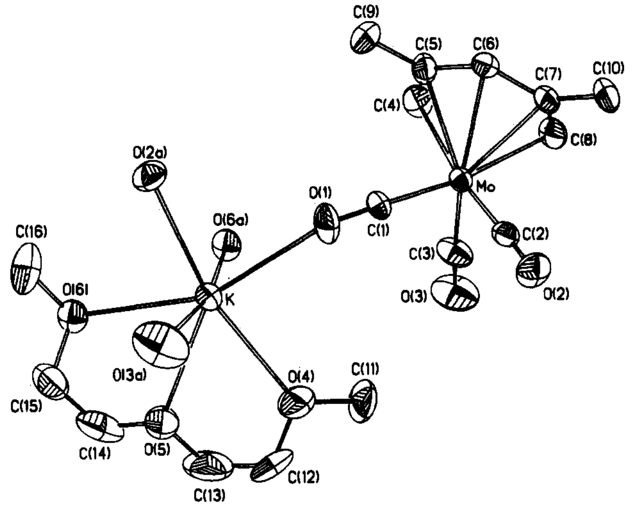
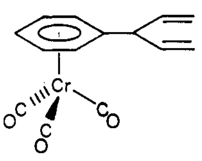


Figure 29. Partial view of the three-dimensional structure of $K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ illustrating the isocarbonyl coordination.[119b]

For the open pentadienyl ligands, the carbonyl anions seem important. Thus, proton abstraction from the arene complex **19** leads initially to the detectable dienyl complex **20**, which subsequently rearranges to the $(\eta^5\text{-}3\text{-}phenylpentadienyl)$chromium tricarbonyl anion.[118] From the reaction of $Mo(diglyme)(CO)_3$ with $K(2,4\text{-}C_7H_{11})$ a related complex, $K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3$, may be isolated.[119] Structural characterization revealed a polymeric network involving isocarbonyl coordination to the potassium ions in addition to a novel bridging coordination exhibited by the diglyme ligands (Figure 29). Analogous reactions involving $Cr(CH_3CN)_3(CO)_3$ and $W(C_2H_5CN)_3(CO)_3$ have led to their respective anionic complexes, which upon reaction with $Hg(CN)_2$ yielded the $Hg[M(2,4\text{-}C_7H_{11})(CO)_3]_2$ species (M = Cr, Mo, W), which were readily isolated and characterized. $Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ undergoes a wide range of other reactions, such as oxidation with $Fe(C_5H_5)_2^+$ or I_2 to yield $[Mo(2,4\text{-}C_7H_{11})(CO)_3]_2$ and $Mo(2,4\text{-}C_7H_{11})(I)(CO)_3$, respectively, or formation of unsymmetric metal–metal bonded complexes, e.g., $Mo(2,4\text{-}C_7H_{11})(CO)_3\text{–}Mo(C_5H_5)(CO)_3$ upon reaction with $Mo(C_5H_5)(I)(CO)_3$.[120] Other reactions leading to coupling products or an unusual molybdenabenzene complex will be discussed later (sections II.H.2 and II.H.3). The paramagnetic, 16-electron complex $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$ has been prepared either by the reaction of $CrCl_2(dmpe)_2$ with 1 equiv of $K(2,4\text{-}C_7H_{11})$ or in low yield from the reaction of $Cr(2,4\text{-}C_7H_{11})_2$ with 1 equiv of an amine hydrochloride in the presence of dmpe. A structural determination revealed an unsymmetric ligand orientation, with one phosphorus atom under the pentadienyl open edge. The compound was found to react with $LiCH_3$, leading to the similar $Cr(2,4\text{-}C_7H_{11})(CH_3)(dmpe)$ complex.



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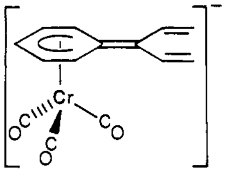
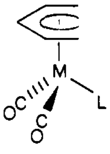


20

A variety of (η^5-cyclo-dienyl) complexes of manganese and rhenium has been reported, especially of the types

M(η^5-cyclo-dienyl)(arene) (M = Mn, Re),[121] M(η^5-cyclo-dienyl)$(CO)_3$,[13,122] Mn(η^5-cyclo-dienyl)$(CO)_2(P(C_6H_5)_3)$,[123] M(η^5-cyclo-dienyl)$(CO)_x(P(OCH_2)_3CEt)_{3-x}$ (M = Mn, Re; x = 1, 2),[124] [Mn(η^5-cyclo-dienyl)$(CO)_2(NO)^+$],[125] [Mn(η^5-cyclo-dienyl)$(CO)(P(C_6H_5)_3)(NO)^+$],[125] and Mn(η^5-cyclo-dienyl)(dppe)$(CO)^{n+}$) (n = 0, 1).[99b] Often these complexes are prepared by nucleophilic addition to cationic metal arene complexes. Thus, addition of H^- to $Mn(C_6H_6)(CO)_3^+$ yields Mn(η^5-C_6H_7)$(CO)_3$,[13] while addition of PR_3 (R = n-Bu) yields [Mn(η^5-$C_6H_6(PR_3)$)$(CO)_3]^+$, which may be considered as a phosphonium salt.[122a] Interestingly, for the M(η^5-cyclo-dienyl)$(CO)_2(P(OCH_2)_3CEt)$ complexes, mixtures of the two possible isomers **21** and **22** were observed, whereas for the M(η^5-cyclo-dienyl)(CO)$(P(OCH_2)_3CEt)_2$ species, only the unsymmetric form **23** was observed. Barriers to the ligand oscillation process for the latter unsymmetric species were ca. 10 kcal/mol for either manganese or rhenium, whereas the barriers to the interconversions of **21** and **22** were ca. 10–11 kcal/mol. These barriers are larger than those for isoelectronic, cationic iron and ruthenium species, and they also noted that an increase in the dienyl ring size would lead to a larger barrier. The ^{31}P resonances for phosphorus nuclei residing by the open pentadienyl edge (as in **21**) were found at lower field than those in the alternate position (e.g., **22**). In contrast, the Mn(η^5-cyclo-dienyl)(dppe)$(CO)^{n+}$ species were found by structural studies to exist in the symmetric form.[99b]



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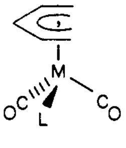

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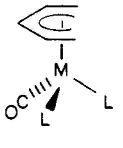
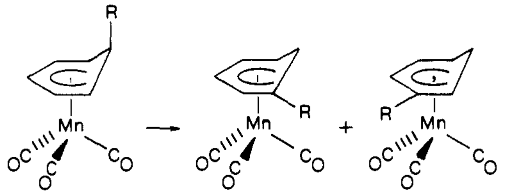


23

An interesting isomerization pathway for the cyclohexadienyl complexes, unavailable to noncyclic pentadienyl analogues, involves a hydrogen atom shift from the 6-position to other locations, as indicated below.



The conversions were suggested to take place via Mn(η^4-arene)(H)$(CO)_3$ intermediates, which would also explain the observation that in arene solvents, the original cyclohexadienyl ligand may be replaced by another cyclohexadienyl ligand, derived from the arene and a hydride ligand.[122b,126]

The earliest known pentadienyl analogues of these species are the tricarbonyls, such as Mn(1-C_6H_9)$(CO)_3$ and $M(C_5H_7)(CO)_3$ (M = Mn, Re), which were all prepared from reactions of $M(CO)_5Br$ with an appropriate SnR_3(pentadienyl) compound.[29c,127] A larger series of these complexes, Mn(η^5-dienyl)$(CO)_3$ (dienyl = C_5H_7, 1-C_6H_9, 2-C_6H_9, 2,4-C_7H_{11}), has been synthesized, through the thermolysis of Mn(η^3-dienyl)$(CO)_4$ precursors, which were prepared by photolysis of $Mn_2(CO)_{10}$ with appropriate dienes.[128] Alternatively, the reaction of $NaMn(CO)_5$ with *trans*-1-bromo-2,4-pentadiene has been found to lead initially to Mn(η^1-C_5H_7)$(CO)_5$, which could subsequently be converted to Mn(η^3-W-C_5H_7)$(CO)_4$ and $Mn(C_5H_7)(CO)_3$.[129] Related oxodienyl complexes, such as Mn[2-(C_6H_5)-5-(CH_3)O-C_4H_3]$(CO)_3$, Mn[2-($C_6H_5CH_2$)-4-(CH_3)-5-$C_6H_5OC_4H_2$]$(CO)_3$, Mn[2-C_6H_5-5-$C_2H_5OC_4H_3$]$(CO)_3$, and Re(O-C_4H_5)(CO)$(P(C_6H_5)_3)_2$, have been reported,[130] as has an unusual complex formed from the reaction of $Mn_2(CO)_{10}$ with tropone (Figure 30).[131]

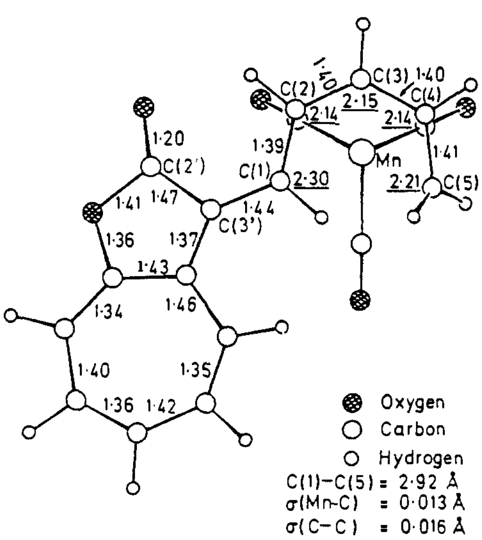


Figure 30. Perspective view of $Mn(1\text{-}(C_9H_5O_2)C_5H_6)(CO)_3$ (reprinted from ref 131; copyright 1971 Royal Society of Chemistry).

$Mn(C_5H_7)(CO)_3$ has been found to react readily at room temperature with strongly basic phosphines (PMe_3, $PMe_2(C_6H_5)$ and $P(n\text{-}C_4H_9)_3$) to yield Mn(η^3-C_5H_7)$(CO)_3$(L) complexes, although under reflux in cyclohexane, the formal replacement of CO is achieved, yielding Mn(η^5-C_5H_7)$(CO)_2$(L) complexes, for L = PMe_3, $PMe_2(C_6H_5)$, $P(C_6H_{11})_3$, $P(C_6H_5)_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OC_6H_5)_3$, and $As(C_6H_5)_3$.[132] Qualitative observations indicated that the rates of substitution were dependent on ligand concentration and on the ligand itself, with PMe_3 (fastest) $\simeq$ $PMe_2(C_6H_5) > P(OC_6H_5)_3 \simeq P(C_6H_5)_3 \simeq P(C_6H_{11})_3 > P(OMe)_3 \simeq P(OEt)_3$. Interestingly, pure products could not be isolated if an excess of ligand were present, possibly an indication of the formation of η^1-pentadienyl products, as have been found for the analogous rhenium system, for which two isomers of $Re(C_5H_7)(CO)_3(PEt_3)_2$ could be isolated (see section II.F). The C–O stretching frequencies in the $Mn(C_5H_7)(CO)_2$(L) compounds fell in a reasonable order, with $P(OC_6H_5)_3 > P(OMe)_3 > P(OEt)_3 > P(C_6H_5)_3 > PMe_3 > PMe_2(C_6H_5) > P(C_6H_{11})_3 > As(C_6H_5)_3$. Both ^1H and ^{13}C NMR spectral data were reported and in these the pentadienyl ligands seemed symmetric, one end being equivalent to the other (cf. **21**). However, the presence of some broad resonances may be an indication that unsymmetric conformations (cf. **22**) are present in at least some cases, which may be obscured by relatively low barriers to pentadienyl ligand oscillation. Interestingly, photoelectron spectroscopic data indicate that little difference exists between the ionization energies of the metal d levels of the $M(C_5H_5)(CO)_3$ and $M(C_5H_7)(CO)_3$ (M = Mn or Re) complexes,[133] a situation entirely different from that observed for the open ferrocenes.

More recently, a series of phosphine analogues has been reported. While the reaction of $MnBr_2$ with 2 equiv of K(2,4-C_7H_{11}) in the presence of PMe_3 leads to

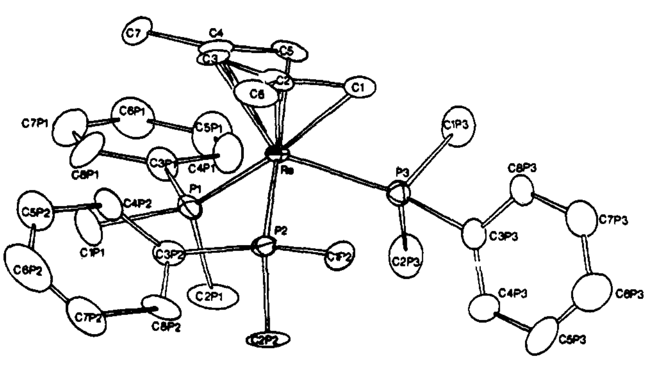


Figure 31. Structure of $Re(2,4-C_7H_{11})(PMe_2(C_6H_5))_3$ (reprinted from ref 136a; copyright 1986 American Chemical Society).

an intramolecular coupling reaction (vide infra), the use of chelating polyphosphine ligands leads instead to compounds of the type $Mn(C_5H_7)L_3$ and $Mn(2,4-C_7H_{11})L_3$, for which L_3 = $(Me_2PCH_2)_3CMe$ or $(Et_2PCH_2CH_2)_2PC_6H_5$.[134] For $Mn(C_5H_7)[(Et_2PCH_2CH_2)_2PC_6H_5]$ an unsymmetric structure was adopted, such that a terminal phosphorus atom was located by the open pentadienyl edge. As a result, variable-temperature NMR studies could be utilized to determine the barrier to pentadienyl ligand oscillation, which is 18.3 ± 0.5 kcal/mol compared to 17.3 ± 0.2 kcal/mol for $Mn(2,4-C_7H_{11})[(Et_2PCH_2CH_2)_2PC_6H_5]$. For $Mn(C_5H_7)[(Me_2PCH_2)_3CMe]$ and $Mn(2,4-C_7H_{11})[(Me_2PCH_2)_3CMe]$, analogous barriers of 11.4 ± 0.6 and 10.9 ± 0.2 kcal/mol were found. However, a simple oscillation or rotation of the pentadienyl ligand was not favored by the authors. Rather, they preferred a process involving an initial η^5–η^3 conversion for the pentadienyl ligand, followed by its oscillation or rotation.[135] Structural studies for $Mn(C_5H_7)[(Et_2PCH_2CH_2)_2PC_6H_5]$ and $Mn(2,4-C_7H_{11})((Me_2PCH_2)_3CMe)$ were undertaken and revealed the expected η^5-dienyl coordination environments (cf. 21–23). For both compounds, the Mn–P distances were fairly similar, ranging from 2.197 (2) to 2.229 (2) Å. For the former compound, the Mn–C (pentadienyl) distances to the 2- and 4-positions were shortest, averaging 2.102 (5) Å, while those to the 1- and 5-positions were longest, averaging 2.181 (5) Å, and the Mn–C(3) distance was intermediate at 2.140 (7) Å.

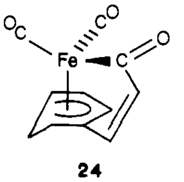
From the reaction of $ReCl_3(PMe_2(C_6H_5))_3$ with 3 equiv of KC_5H_7 or $K(2,4-C_7H_{11})$, the respective complexes $Re(C_5H_7)(PMe_2(C_6H_5))_3$ and $Re(2,4-C_7H_{11})(PMe_2(C_6H_5))_3$ have been isolated.[136] Variable-temperature NMR spectroscopy indicated barriers to pentadienyl ligand rotation of 16.4 ± 0.2 and 13.6 ± 0.3 kcal/mol for these complexes, respectively. As in the case of the related manganese complexes, the exchange processes were proposed to involve an η^5–η^3 conversion of the pentadienyl ligand prior to rotation rather than simple rotation of the η^5-bound ligand. A solid-state structural determination (Figure 31) revealed all Re–P distances to be essentially identical at 2.352 (4) Å, while the Re–C distances averaged 2.28 (1) Å. As with other η^5-cyclo-dienyl and pentadienyl complexes, the ligand residing by the open pentadienyl edge lies substantially closer to the pentadienyl plane, in this case the separations being 2.24 vs 3.22 Å.

The iron triad contributes by far the most members to the M(pentadienyl)L_3 class of compounds, and most of these involve the η^5-cyclo-dienyl ligands. An overwhelming number of such compounds is known, important examples of which include the general types $[M(\eta^5\text{-cyclo-dienyl})(CO)_3^+]$,[10,12] $[M(\eta^5\text{-cyclo-dienyl})(phosphine)_3^+]$,[137] $M(\eta^5\text{-cyclo-dienyl})(CO)_2(L)^+$ (L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$, C_5H_5N, CH_3CN, NH_3),[138] $M(\eta^5\text{-cyclo-dienyl})(CO)_x(P(OCH_2)_3CEt)_{3-x}$ (x = 1, 2),[124] $[M(\eta^5\text{-cyclo-dienyl})(CO)(P(OMe)_3)_2^+]$,[139] $[M(\eta^5\text{-cyclo-dienyl})(arene)^+]$,[9b,55,140] $[M(\eta^5\text{-cyclo-dienyl})(diene)(CO)^+]$,[141] $M(\eta^5\text{-cyclo-dienyl})(phosphine)(L_2)^+$ (L_2 = 2,2-bipyridine, 1,10-phenanthroline),[142] $M(\eta^5\text{-cyclo-dienyl})(H)(phosphine)_2$,[143] $M(\eta^5\text{-cyclo-dienyl})(X)(CO)_2$ (X = Cl, Br, I, CN, SR, alkyl, SiR_3, GeR_3, acyl, C(O)I, C(O)CN),[139,144] $[M(\eta^5\text{-cyclo-dienyl})(CO)_2]_2$,[138,144] $M(\eta^5\text{-cyclo-dienyl})(CH_3)(CO)(P(OC_6H_5)_3)$,[144] and $M(\eta^5\text{-cyclo-dienyl})(X)(phosphine)_2$ (X = I, Br, CH_3, C_6H_5).[145]

A number of observations from the above η^5-cyclo-dienyl reports deserve mention. Of course, $Fe(\eta^5\text{-cyclo-dienyl})(CO)_3^+$ complexes have found many useful applications in organic synthesis.[10] It is also notable that a number of the $M(\eta^5\text{-cyclo-dienyl})(L_3)$ complexes contain potentially versatile hydride (e.g., $Ru(\eta^5\text{-}C_6H_5O)(H)(P(C_6H_5)_3)_2\cdot 2C_6H_5OH$, $Fe(\eta^5\text{-cyclohexadienyl})(H)(P(OMe)_3)_2)$,[143] alkyl (e.g., $Ru(\eta^5\text{-6-methylcycloheptadienyl})(CH_3)(PMe_3)_2$, $Ru(\eta^5\text{-6-phenylcyclohexadienyl})(C_6H_5)(PMe_3)_2$,[145] unusual $(\eta^5\text{-cyclo-dienyl})(R)(CO)_2$ complexes,[144e,l,m] and $Fe(\eta^5\text{-cycloheptadienyl})(CH_3)(CO)(P(OC_6H_5)_3))$,[144f] silyl or germyl[139,144g] (e.g., $Os(\eta^5\text{-cycloheptadienyl})(SiR_3)(CO)_2$ for SiR_3 = $SiMe_3$ or $SiMe_2(C_6H_5)$, a ruthenium analogue, and $Os(\eta^5\text{-cycloheptadienyl})(GeMe_3)(CO)_2)$, or acyl ligands.[144h]

Most of these complexes demonstrate quite clear conformational preferences. In the $M(\eta^5\text{-}C_6H_7)(CO)_x(P(OCH_2)_3CEt)_{3-x}^+$ and $M(\eta^5\text{-}C_7H_9)(CO)_x(P(OCH_2)_3CEt)_{3-x}^+$ (M = Fe, Ru; x = 1, 2) complexes,[124] mixtures were observed which always favored the unsymmetric isomer. Thus, 99% of the $Fe(\eta^5\text{-cyclo-dienyl})(CO)_2(P(OCH_2)_3CEt)^+$ complexes existed in the unsymmetric form, analogous to 22, while for the ruthenium analogues, the unsymmetric population dropped to ca. 60%. For the $Fe(\eta^5\text{-cyclo-dienyl})(CO)(P(OCH_2)_3CEt)_2^+$ complexes, the symmetric form reached respective populations of 13% and 28% for the six- and seven-membered rings, while for ruthenium, these values were only 5%. The barriers to dienyl ligand oscillation in these complexes were reported for the interconversion of the two unsymmetric forms, as well as for the interconversion of the symmetric and unsymmetric forms, yet all fall in the relatively narrow range of 9.8–13.4 kcal/mol, similar to values for $Fe(\eta^5\text{-cyclo-dienyl})(CO)_3^+$ species.[146]

The unusual acyl complex 24 has been found by a structural study to exist in the unsymmetric form shown; however, this orientation is required by geometric constraints.[144h] The cycloheptadienyl complexes $Fe(C_7H_9)(CH_3)(CO)(L)$ (L = CO, $P(OC_6H_5)_3$) each exist in unsymmetric conformations having a carbonyl group located by the open dienyl edge, and the methyl group



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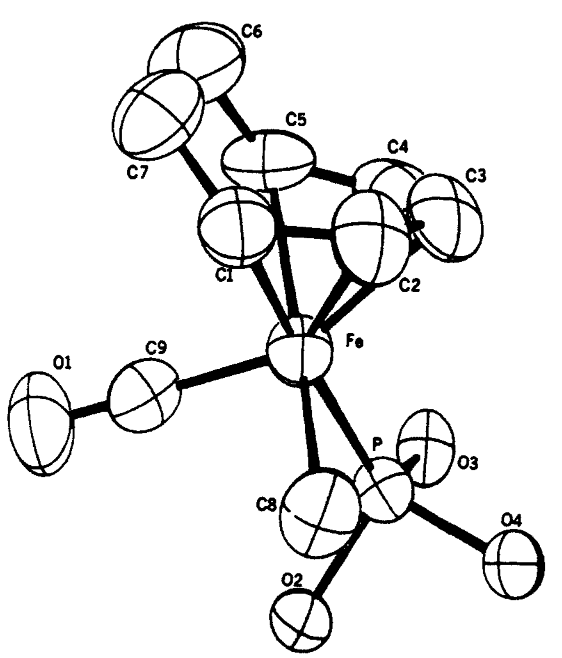


Figure 32. Structure of $Fe(C_7H_9)(CH_3)(CO)(P(OC_6H_5)_3)$ (reprinted from ref 144f; copyright 1986 American Chemical Society).

located under a formally uncharged pentadienyl carbon atom, as in Figure 32.[144f] Similarly, a diffraction study on the cycloheptadienyl complex $Ru(\eta^5\text{-}6\text{-}SiMe_3\text{-}1\text{-}C_6H_5C_7H_7)(SiMe_3)(CO)_2$ also revealed an unsymmetric structure.[144i] In contrast, related osmium silyl and germyl complexes $Os(C_7H_9)(MR_3)(CO)_2$ (MR_3 = $SiMe_3$, $SiMe_2(C_6H_5)$, $GeMe_3$) seem to exist in an equilibrium involving both the symmetric and unsymmetric forms, with the former appearing to dominate.[144g,i,j] However, $Os(\eta^5\text{-}C_7H_7)(CO)(P(OMe)_3)_2^+$ appeared to exist primarily in the unsymmetric form,[139] as do various Ru(cyclohexadienyl)$(PMe_3)_2(L)^+$ (L = $P(C_6H_5)_3$, $P(NMe_2)_3$, or CH_3CN)[137a] and Os(cyclohexadienyl)(I)$(PMe_3)_2$ complexes.[145] In contrast, $Fe(C_6H_7)(H)(P(OMe)_3)_2$ and the structurally characterized $Ru(C_6H_5O)(H)(P(C_6H_5)_3)_2\cdot 2C_6H_5OH$ appear to prefer symmetric orientations.[143d]

The species $Fe(C_5H_7)(CO)_3^+$ and $Fe(1\text{-}CH_3C_5H_6)(CO)_3^+$, prepared by protonation of η^4-bound pentadienyl alcohols, were actually the first metal pentadienyl complexes to be reported.[11] While these species are generally isolated with **U**-shaped pentadienyl ligands, a number of studies have demonstrated that it is possible to prepare **S**-shaped analogues, which generally rearrange to the more stable **U** forms on warming.[71] However, for the 1,1,5-trimethylpentadienyl ligand, significant $CH_3\cdots H$ repulsions destabilize the **U** form, so that an equilibrium between η^5-**U**- and η^5-**S**-bound pentadienyl complexes results. Structural studies on the **U** complex forms, e.g., $Fe(2,4\text{-}C_7H_{11})(CO)_3^+BF_4^-$, reveal the expected coordination geometries.[119b]

A series of $Fe(2,4\text{-}C_7H_{11})(X)(L)_2$ complexes has been prepared from $Fe(2,4\text{-}C_7H_{11})(CO)_3^+$. Thus, reaction with KI in acetone leads to the crystallographically characterized, unsymmetric ($\Delta G^\ddagger$ = 11.45 kcal/mol) $Fe(2,4\text{-}C_7H_{11})(I)(CO)_2$.[110b] Interestingly, similar attempts to prepare analogous species for other pentadienyl ligands do not succeed; apparently, the success for the $2,4\text{-}C_7H_{11}$ ligand is due to its inherent preference for the **U** conformation.[147] Reduction of $Fe(2,4\text{-}C_7H_{11})(I)(CO)_2$ with sodium amalgam leads either to $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$ or $Fe(2,4\text{-}C_7H_{11})(CO)_2^-$, depending on stoichiometry. The dimer has been found to exist in the solid state in a form very similar to that of the cis isomer of $[Fe(C_5H_5)(CO)_2]_2$, except that it is a much more crowded molecule.[111] Probably for this reason, $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$ exhibits a strong ESR signal, presumably due to Fe–Fe bond homolysis.[110b] An unsymmetric analogue, $Fe(2,4\text{-}C_7H_{11})(CO)_2Fe(C_5H_5)(CO)_2$, prepared from the reaction of $Fe(2,4\text{-}C_7H_{11})(I)(CO)_2$ with $Fe(C_5H_5)(CO)_2^-$, also seems to possess a weak Fe–Fe bond, as on prolonged standing in solution, significant disproportionation occurs. Treatment of $Fe(2,4\text{-}C_7H_{11})(CO)_2^-$ with CH_3I leads to the unsymmetric ($\Delta G^\ddagger$ = 12.75 kcal/mol), thermally unstable liquid, $Fe(2,4\text{-}C_7H_{11})(CH_3)(CO)_2$. However, the methyl complex reacts readily with $PMe_2(C_6H_5)$ to yield a solid compound, which has been spectroscopically identified as an acyl complex, $Fe(2,4\text{-}C_7H_{11})(C(O)CH_3)(CO)(PMe_2(C_6H_5))$. It is noteworthy that acyl formation here and for η^5-cyclo-dienyl analogues is much more facile than for the related C_5H_5 analogues. However, ^{31}P NMR spectroscopy indicates that on standing this material slowly converts to two other species (85:15 ratio), which appear to involve acyl–pentadienyl coupling.

Electron-rich analogues of the above, such as $Fe(2,4\text{-}C_7H_{11})(PMe_3)_3^+$ and $Fe(C_5H_7)(PMe_3)_3^+$, have also been reported. Thus, reaction of $FeCl_2(PMe_3)_2$ with 2 equiv of $K(2,4\text{-}C_7H_{11})$ leads to $Fe(\eta^5\text{-}2,4\text{-}C_7H_{11})(\eta^3\text{-}2,4\text{-}C_7H_{11})(PMe_3)$, for which the $\eta^3\text{-}2,4\text{-}C_7H_{11}$ ligand was proposed to adopt the **W** conformation.[148] Protonation of this compound leads to $Fe(2,4\text{-}C_7H_{11})(PMe_3)_3^+$, which could also be isolated from the reaction of $K(2,4\text{-}C_7H_{11})$ with 2 equiv of $FeCl_2(PMe_3)_2$. The pentadienyl ligand in solution was found to undergo hindered rotation, with $\Delta G^\ddagger$ = 11.5 ± 0.5 kcal/mol. The solid-state structure of $Fe(2,4\text{-}C_7H_{11})(PMe_3)_3^+$ was determined as the $FeCl_3(PMe_3)^-$ salt and was found to be quite similar to that of $Re(2,4\text{-}C_7H_{11})(PMe_2(C_6H_5))_3$ (Figure 31). The Fe–P distance for the unique phosphine ligand was found to be shorter than those for the other two (2.232 (1) vs 2.274 (1) Å), while the Fe–C bonds to the formally uncharged 2,4-positions, 2.187 (3) Å, were found to be longer than those to the formally charged 1,5- (2.175 (3) Å) or 3- (2.161 (4) Å) positions. The similar complex $Fe(C_5H_7)(PMe_3)_3^+$ could be prepared by the reaction of $Fe(\eta^3\text{-}C_5H_7)_2(PMe_3)_2$ with $HPMe_3^+$ (vide infra). An unusual result was obtained from the reaction of $FeCl_2(PMe_3)_2$ with 1 equiv of $K(2,4\text{-}C_7H_{11})$. In this case, an (η^4-isopropenyltrimethylenemethane)$Fe(PMe_3)_3$ complex was isolated, whose formation was postulated to occur by disproportionation of an intermediate such as $Fe(2,4\text{-}C_7H_{11})(Cl)(PMe_3)_2$, and in support of this claim it was noted that 2,4-dimethyl-1,3-pentadiene was a product of the reaction and that never more than a 50% yield of product (based on iron) was obtained.

Related ruthenium complexes have been isolated from the treatment of the protonated open ruthenocene $Ru(2,4\text{-}C_7H_{11})_2(H)^+$ (vide infra) with CO and/or phosphine ligands.[81] Thus, exposure to CO or $P(OMe)_3$ leads to rapid incorporation of one ligand and addition of the hydride ligand to one of the $2,4\text{-}C_7H_{11}$ ligands, yielding an η^4-2,4-dimethyl-1,3-pentadiene ligand, as in $Ru(2,4\text{-}C_7H_{11})(\eta^4\text{-}2,4\text{-}C_7H_{12})(CO)^+$, which has been crystallographically characterized (Figure 33). As can be seen, the CO ligand resides by the open edges of both

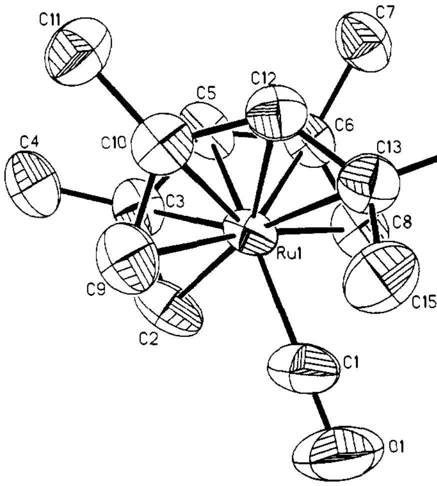


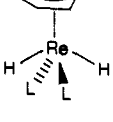
Figure 33. Solid-state structure of the cation in Ru(2,4-C_7H_{11})(η^4-2,4-Me_2-1,3-C_5H_6)(CO)$^+BF_4^-$.[81b]

acyclic organic ligands. Subsequent ligand additions proceed more slowly allowing the selective preparations of unsymmetric Ru(2,4-C_7H_{11})(CO)(phosphine)$_2^+$ and symmetric Ru(2,4-C_7H_{11})$(CO)_2$(phosphine)$^+$ complexes, examples of which have been crystallographically characterized. An Ir(η^5-cyclo-dienyl)(H)(phosphine)$_2^+$ complex has also been reported.[149]

3. *M(η^5-pentadienyl)(L)$_4$ and M(η^5-pentadienyl)(L)$_5$*

The compounds in this category tend to fit the expected structural patterns. Exceptions, however, seem to include the reported compounds "Cr(η^5-cyclohexadienyl)(H)$(PF_3)_3$" and the structurally characterized "Cr(η^5-cyclooctadienyl)(H)$(PF_3)_3$", both of which were prepared by metal atom reactions, utilizing PF_3 and cyclo-dienes.[150] While these compounds were formulated originally as hydrides, recent reports have suggested that they actually are "agostic" complexes,[1e,137b,151] in which the "hydride" ligands serve to bridge their metal centers and a terminal pentadienyl carbon atom. In fact, the orientation of the three PF_3 ligands in the cyclooctadienyl structure does not match that expected for a M(η^5-pentadienyl)(L)$_4$ complex[98b] but rather seems to match the orientation of the additional ligands in the known agostic complex Cr(2,4-C_7H_{12})$(CO)_2(P(OMe)_3)$,[152] in which the L_3 unit twists somewhat away from the "agostically" bound hydrogen atom. Mo(η^5-cyclo-dienyl)$(CO)_3$Cl and Mo(η^5-cyclo-dienyl)$(CO)_2$(phosphine)I complexes have also been reported.[114g,153]

The complex Re(C_6H_7)$(H)_2(P(C_6H_5)_3)_2$ has been prepared from the reaction of $ReH_7(P(C_6H_5)_3)_2$ with benzene and 3,3-dimethylbutene.[154] A structural study was undertaken, but the hydride ligands could not be located directly. However, based on the placement of the $P(C_6H_5)_3$ ligands, one of the hydride ligands must be located at the open edge of the pentadienyl fragment, and the other opposite to it, under the central carbon atom



Notably, an open analogue, Re(2,4-C_7H_{11})$(H)_2(P(C_6H_5)_3)_2$, has been prepared, and spectroscopic studies indicate the opposite orientation of H and $P(C_6H_5)_3$ ligands.[155] A related complex, Re(2,4-C_7H_{11})(H)$(PMe_2(C_6H_5))_3^+$, has been prepared by protonation of Re(2,4-C_7H_{11})$(PMe_2(C_6H_5))_3$.[136] Deuteriation studies suggested that protonation initially takes place by the open edge of the pentadienyl ligand, as exchange with the hydrogen atoms on the terminal CH_2 groups readily occurs. From variable-temperature ^1H NMR spectroscopy, the barrier to this process was estimated to be 17.3 ± 0.3 kcal/mol, while variable-temperature ^{31}P NMR spectroscopy revealed a barrier of 16.9 ± 0.3 kcal/mol for the interconversion of the two phosphorus environments. A structural study of the complex was undertaken. The hydride ligand was located and found to occupy the position beneath the central pentadienyl carbon atom (Figure 34). The unique Re–P bond was found to be longer than the other two (2.502 (3) Å vs an average of 2.422 (6) Å), while the Re–C bonds to the terminal pentadienyl carbon atoms (2.255 (10) Å) appeared shorter than those to the other three atoms (2.29 (1) Å).

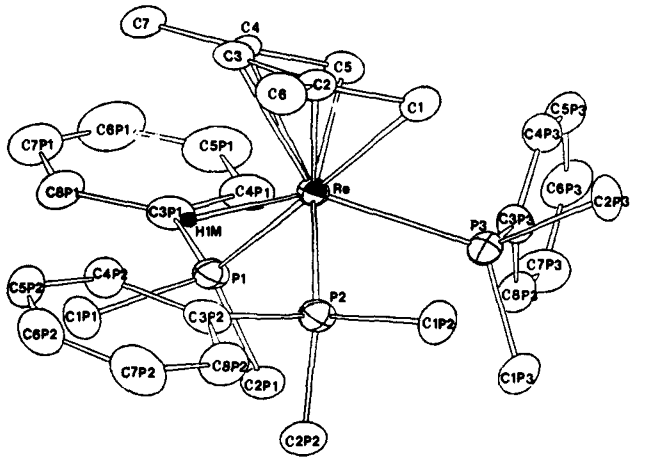


Figure 34. Structure of the Re(2,4-C_7H_{11})(H)$(PMe_2(C_6H_5))_3^+$ ion (reprinted from ref 136b; copyright 1987 American Chemical Society).

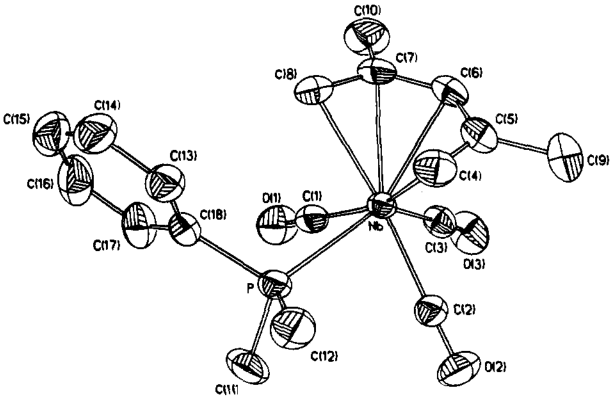


Figure 35. Perspective view of Nb(2,4-C_7H_{11})$(CO)_3$($PMe_2(C_6H_5)$).[155]

Related niobium compounds may be prepared from the paramagnetic Nb(2,4-C_7H_{11})$_2$(L) complexes (L = PEt_3, $PMe_2(C_6H_5)$).[155] These compounds react with CO to yield the diamagnetic Nb(2,4-C_7H_{11})$(CO)_3$(L) complexes, for which ^1H NMR spectroscopy and a structural study of the L = $PMe_2(C_6H_5)$ complex demonstrate that the phosphine ligand is located by the open edge of the pentadienyl ligand (Figure 35). Addition of excess $PMe_2(C_6H_5)$ to this compound results in replacement of one CO ligand and isolation of $Nb(2,4\text{-}C_7H_{11})(CO)_2(PMe_2(C_6H_5))_2$. Spectroscopic data and a structural determination revealed that one of the phosphine ligands is located at the open edge of the pentadienyl ligand, while the other one is located opposite to it, being underneath the central pentadienyl carbon atom. The related complex $V(C_6H_7)(CO)_4$ has been prepared by the reaction of $V(C_6H_6)(CO)_4^+$ with $NaBH_4$.[156]

Two examples of $M(\eta^5\text{-pentadienyl})(L)_5$ complexes are $Zr(C_6H_7)(H)(dmpe)_2$ and $Zr(C_8H_{11})(H)(dmpe)_2$, prepared by the Na/Hg reduction of $ZrCl_4(dmpe)_2$ in the presence of 1,3-cyclohexadiene or 1,3-cyclooctadiene, respectively.[157] An X-ray structural study of the cyclooctadienyl complex revealed a coordination geometry which may be regarded as highly distorted octahedral, with the dienyl and hydride ligands opposite to one another. The phosphorus atoms are naturally bent significantly away from the dienyl ligand plane, as can be seen from the H–Zr–P angles, which range from 58 to 81°, averaging 68.5°. The shortest Zr–P distance (2.730 (4) Å) involves the phosphine ligand by the open pentadienyl edge while the next shortest (2.758 (4) Å) involves the opposite phosphorus atom, and the longest involves the two formally (not crystallographically) equivalent phosphorus atoms (average 2.796 (3) Å). Additionally, a portion of a metallabenzene complex, $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$ (section II.H.3), also contains a formal $M(\eta^5\text{-pentadienyl})(L)_5$ complement, as do $Re_3(\eta^5\text{-}C_7H_9)(H)_2(CO)_{10}$, $Os_3(\eta^5\text{-}C_6H_7)(H)(CO)_9$, and $Os_3(\eta^6\text{-}C_7H_5O)(H)(CO)_9$, the latter two containing bridging ($\eta^{1,2',2''}$- and $\eta^{2,3'}$-) dienyl coordination.[158] However, due to the cluster nature of these compounds, their geometric arrangements are likely not very meaningful in this context.

F. Metal Complexes Containing η^3- and η^1-Bound Pentadienyl Ligands

Just as η^5-cyclo-dienyl metal complexes often preceded their acyclic analogues, η^3-cyclo-dienyl complexes have often set the stage for later observations on η^3-pentadienyl complexes. As noted earlier, the facile reaction of $Co(\eta^5\text{-}C_7H_9)(P(C_6H_5)_3)_2$ with CO to produce $Co(\eta^3\text{-}C_7H_9)(CO)_2(P(C_6H_5)_3)$ provided an indication that η^5–η^3 dienyl transformations should be readily induced,[16] and for the η^3 complex, variable-temperature NMR spectroscopic data revealed that an $\eta^3 \rightarrow \eta^3$ interchange process, perhaps involving an η^1-bound intermediate, could take place ($\Delta G^{\ddagger} = 17.6 \pm 1.5$ kcal/mol), making the two sides of the ligand equivalent.[159] Similarly, variable-temperature NMR spectroscopy of a variety of 16-electron $Pd(\eta^3\text{-}C_7H_9)(L)_2^+$ complexes (L_2 = various acac anions, tmeda, dienes, bipyridine; or L = $AsEt_3$, PEt_3, or $P(OMe)_3$, etc.) demonstrated facile $\eta^3 \rightarrow \eta^5 \rightarrow \eta^3$ interconversions.[17] Other pertinent examples of η^3-cyclo-dienyl complexes include species of the general types $Cr(C_5H_5)(\eta^3\text{-cyclo-dienyl})(CO)_2$,[160] $Pd(C_5H_5)(\eta^3\text{-cyclo-dienyl})$, $[Pd(\eta^3\text{-cyclodienyl})X]_2$ (X = acac, Cl, Br), $Pd(\eta^3\text{-cyclo-dienyl})(Cl)(P(C_6H_5)_3)$,[161] $Ru(\eta^3\text{-cyclo-dienyl})(H)(cyclohexene)(PC_6H_5)_3)_2$,[143d] $Ni(\eta^3\text{-cyclo-dienyl})_2$,[162] and $[Ni(\eta^3\text{-cyclo-dienyl})(Cl)(phosphine)]_2$.[162] Examples of the latter five complexes, as well as $Pd(\eta^3\text{-}C_8H_{11})(acac)$ (Figure 2),[14c] have been structurally characterized.

Early η^3-pentadienyl reports have often dealt with related species,[14] such as $Pd(\eta^3\text{-dienyl})(acac)$, $Pd(\eta^3\text{-dienyl})(1,5\text{-COD})^+$, or $[Pd(\eta^3\text{-dienyl})(Br)]_n$ (for η^3-dienyl = $\eta^3\text{-1-}(C_6H_5)\text{-3-}(OC(O)CH_3)\text{-5-}(C_6H_5)C_5H_4)$ or $Ni(C_5H_5)(\eta^3\text{-dienyl})$ for dienyl = $1,1,5,5\text{-}C_9H_{15}$ or $2,4\text{-}C_7H_{11}$). For the latter complex, two isomers were observed and assigned as containing the U- and **W**-pentadienyl conformers.[163] $[Ni(\eta^3\text{-}C_5H_7)Br]_2$ has also been reported,[164] and its reaction chemistry will be described in section II.H.2.

By 1983, interest in η^3-bound metal pentadienyl complexes seemed to increase greatly. Thus, treatment of $Rh(C_5H_5)(\eta^4\text{-1-}C_6H_5C(O)\text{-6-}C_6H_5\text{-1,3,5-hexatriene})$ with HCl or HBr was found to lead to the respective $Rh(C_5H_5)(\eta^3\text{-1-}C_6H_5C(O)CH_2\text{-5-}C_6H_5\text{-pentadienyl})(X)$ complexes, whereas HBF_4 led to an analogous but cationic species in which the halide ion coordination was replaced by intramolecular coordination of the benzoyl group.[86] Another η^3-pentadienyl complex, $Mn(\eta^3\text{-}C_5H_7)(CO)_4$, was isolated from the photochemical reaction of $Mn_2(CO)_{10}$ with 1,3-pentadiene, and subsequent work led also to the identification of 2-methyl, 4-methyl, 5-methyl, and 2,4-dimethyl derivatives, as well as $Mn(\eta^5\text{-dienyl})(CO)_3$ analogues which were postulated to arise through η^3–η^1–η^3–η^5 interconversions.[128,165] An entirely different route, the reaction of $Sn(C_4H_9)_3(C_5H_7)$ with a metal halide complex, $RuCl_2(CO)(PMe_2(C_6H_5))$, was utilized to prepare $Ru(\eta^3\text{-}C_5H_7)(Cl)(CO)(PMe_2(C_6H_5))_2$.[166]

Numerous other reports of η^3-pentadienyl complexes followed thereafter, including various cobalt and rhodium compounds whose preparations have been described in sections II.C and II.E.1. Related carbonyl complexes have also been obtained, such as $Co(\eta^3\text{-}\mathbf{W}\text{-}C_5H_7)(CO)_3$, utilizing the reaction of $NaCo(CO)_4$ with *trans*-1-bromo-2,4-pentadiene.[167] On treatment of this oily complex with $P(C_6H_5)_3$, the solid product $Co(\eta^3\text{-}\mathbf{W}\text{-}C_5H_7)(CO)_2(P(C_6H_5)_3)$ could be isolated. A structural determination confirmed the presence of the η^3-**W**-pentadienyl unit.

Various η^3-pentadienyl complexes of iron have also been reported. Thus, reaction of $FeCl_2(PMe_3)_2$ with KC_5H_7 leads to the formation of $Fe(\eta^3\text{-}\mathbf{W}\text{-}C_5H_7)_2(PMe_3)_2$, which was crystallographically characterized and found to possess the structure presented in Figure 19.[75a] Subsequently allyl analogues $Fe(2\text{-}CH_3C_3H_4)_2(L)_2$ (L = PMe_3, $PMe_2(C_6H_5)$, $P(OMe)_3$) have been reported.[168] The reaction of $Fe_2(CO)_9$ with *trans*-1-bromo-2,4-pentadiene was found to lead to $Fe(\eta^3\text{-}C_5H_7)(Br)(CO)_3$, for which spectroscopic data suggested the presence of the **W**-shaped pentadienyl ligand.[169] An alternative route to such species has also been developed, utilizing the reaction of cationic species such as $Fe(\eta^5\text{-1-}CH_3\text{-5-}C_6H_5C_5H_5)(CO)_3^+$ with halide ions (X = Cl, Br, I), through which $Fe(\eta^3\text{-}\mathbf{W}\text{-1-}CH_3\text{-5-}C_6H_5C_5H_5)(X)(CO)_3$ complexes are isolated, in addition to some η^4-diene complexes that arise from the addition of X^- to the 5-position of the pentadienyl ligand.[147] A structural study of $Fe(\eta^3\text{-1-}CH_3\text{-5-}C_6H_5C_5H_5)(Br)(CO)_3$ confirmed the conformational assignment of the pentadienyl ligand. Other iron carbonyl complexes have been isolated from the reaction of $NaFe(C_5H_5)(CO)_2$ with *trans*-1-chloro-2,4-pentadiene or with 1-chloro-2,4-hexadiene, which yielded $Fe(C_5H_5)(\eta^1\text{-}C_5H_7)(CO)_2$ or $Fe(\eta^1\text{-5-}CH_3C_5H_6)(CO)_2$, and upon photolysis or

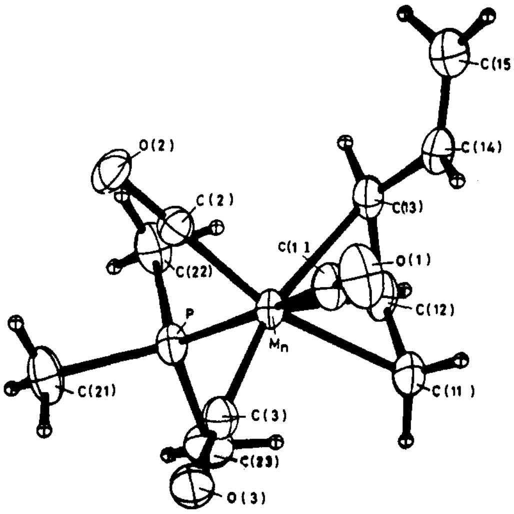


Figure 36. Structure of $Mn(\eta^3-C_5H_7)(CO)_3(PMe_3)$ (reprinted from ref 132; copyright 1984 American Chemical Society).

treatment with Me_3NO, these could be converted to the respective $Fe(C_5H_5)(\eta^3$-**W**-dienyl)(CO) compounds.[82] A structural study on the η^3-hexadienyl complex confirmed the conformational assignment and revealed that the methyl substituent was present on the 5-position, away from the metal atom. Both the mono- and dicarbonyl complexes could be selectively protonated. Thus, reaction of the appropriate monocarbonyls with HPF_6 led to $Fe(C_5H_5)(\eta^4$-diene)(CO)$^+$ complexes, for diene = 1,3-pentadiene or 2,4-hexadiene. Protonation of the monocarbonyls, however, led to $Fe(C_5H_5)(\eta^2$-diene)$(CO)_2^+$ complexes, containing both 1,3- and 1,4-dienes. Photolysis of the monocarbonyl complexes leads to the formation of half-open ferrocenes $Fe(C_5H_5)(C_5H_7)$ and $Fe(C_5H_5)(1-C_6H_9)$.

Additional manganese compounds containing η^3-pentadienyl ligands have also been obtained through several different routes. Thus, $Mn(C_5H_7)(CO)_3$ has been found to react at room temperature with good σ-donor phosphine ligands to produce $Mn(\eta^3-C_5H_7)(CO)_3(L)$ complexes (L = PMe_3, $PMe_2(C_6H_5)$, $P(n-C_4H_9)_3$).[132] A structural determination for the PMe_3 complex revealed the presence of an η^3-*syn*-**S**-pentadienyl ligand[109] (Figure 36). Various $Mn(\eta^3$-pentadienyl)$(CO)_4$ complexes (pentadienyl = C_5H_7, 1-C_6H_9, 2-C_6H_9, 2,4-C_7H_{11}) have been prepared through photolysis of $Mn_2(CO)_{10}$ with appropriate dienes[128] or, for pentadienyl = C_5H_7, from photolysis of $Mn(\eta^1-C_5H_7)(CO)_5$, prepared from the reaction of $NaMn(CO)_5$ with *trans*-1-bromo-2,4-pentadiene.[129] Thermolysis of the η^3-bound complexes leads to loss of CO and the adoption of η^5-pentadienyl bonding modes. In another report, the reaction of $MnBr_2$ with 2 equiv each of KC_5H_7 and dmpe was found to lead to a reduction to the Mn(I) complex $Mn(\eta^3$-**W**-$C_5H_7)(dmpe)_2$.[170] The conformational nature of the pentadienyl ligand was revealed by an X-ray structural study, although it was observed that at least one other isomer was also present in solution.

A high degree of versatility has also been observed for $NaMo(C_5H_5)(CO)_3$. Thus, reaction with *trans*-1-chloro-2,4-pentadiene yields $Mo(C_5H_5)(\eta^1-C_5H_7)(CO)_3$, which was found to decompose slowly at room temperature. Spectroscopic data were in accord with the expected **W** conformation. Photolysis of this compound led to the formation of $Mo(C_5H_5)(\eta^3$-**W**-$C_5H_7)(CO)_2$ and $Mo(C_5H_5)(C_5H_7)(CO)$.[171] The former compound was observed to exist as two isomers, analogous to the situation for related $Mo(C_5H_5)$(allyl)$(CO)_2$ complexes. The $Mo(C_5H_5)(C_5H_7)(CO)$ species exhibited very unsymmetric NMR spectra, and the complex was therefore proposed to contain an unusual η^5-**S**-pentadienyl ligand by analogy to related chromium and iron compounds. Subsequently, similar results were obtained for 1-chloro-2,4-hexadiene, and several phosphine-substituted relatives were isolated, including $Mo(C_5H_5)(\eta^1-C_5H_7)(CO)_2(L)$ and $Mo(C_5H_5)(\eta^3-C_5H_7)(CO)(L)$ (L = PMe_3, PEt_3, $PMe_2(C_6H_5)$).[172] Some Diels–Alder reactions of these species are described in section II.H.2. For chromium, essentially the reverse strategy may be employed to isolate some of these species. Thus, half-open chromocenes react rapidly with CO to yield monocarbonyl complexes containing unusual η^5-**S**-bound pentadienyl ligands (section II.C), and prolonged exposure of these to CO leads reversibly to $Cr(C_5H_5)(\eta^3$-pentadienyl)$(CO)_2$ compounds, crystallographically characterized for pentadienyl = **W**-C_5H_7.[44] An unusual complex of platinum, $Pt[\eta^3-B(CH_3)_2C(CH_3)CHCHC(CH_3)(B(CH_3)_2)](PEt_3)_2$, has also been reported.[173]

A variety of other η^1-bound pentadienyl complexes has been reported. The earliest examples of η^1 coordination involve main-group complexes, e.g., pentadienylsilanes,[53,174] -stannanes,[29c,175] and -boranes,[19,176] and various complexes of beryllium, magnesium, and zinc.[19,176,177] Structural characterizations have been carried out for both $Zn(\eta^1$-**W**-$C_5H_7)(Cl)$(tmeda) and $Mg(\eta^1$-**U**-2,4-$C_7H_{11})_2$(tmeda).[19] Subsequently, $Cu(\eta^1$-pentadienyl)$(P(n-C_4H_9)_3)$ complexes have been identified (pentadienyl = C_5H_7, 1-$Me_3SiC_5H_6$, 1,5-$(SiMe_3)_2C_5H_5$), and spectroscopic data have demonstrated the presence of the expected **W**-pentadienyl conformations, as well as rapid 1,3 rearrangements.[177] A bis(η^1-pentadienyl) complex of zirconium has also been reported.[178] Thus, reaction of $Zr(C_5H_5)_2Cl_2$ with 2 equivalents of $K(2-C_6H_9)$ leads to the formation of $Zr(C_5H_5)_2(\eta^1$-**W**-4-$C_6H_9)_2$, in which spectroscopic data indicate that the methyl group is positioned away from the metal (i.e., in the 4- rather than 2-position).

Recently it has also been reported that $Re(C_5H_7)(CO)_3$ will react with 2 equiv of phosphine (PMe_3 or PEt_3) to yield *fac*-$Re(\eta^1$-syn-**S**-$C_5H_7)(CO)_3$(phosphine)$_2$ complexes,[109,179] quite analogous to earlier and surprising reports of the reaction of $Re(C_5H_5)(CO)_3$ with PMe_3, which yielded $Re(\eta^1-C_5H_5)(CO)_3(PMe_3)_2$.[180] The η^1-**S**-C_5H_7 compounds have been observed to isomerize slowly to the respective η^1-**W**-C_5H_7 complexes. Further exposure of the $Re(\eta^1-C_5H_7)(CO)_3(PMe_3)_2$ isomers to PMe_3 in refluxing THF leads to *mer*-$Re(\eta^1$-**W**-$C_5H_7)(CO)_2(PMe_3)_3$. Structural determinations have been carried out for $Re(\eta^1$-**S**-$C_5H_7)(CO)_3(PEt_3)_2$ and $Re(\eta^1$-**W**-$C_5H_7)(CO)_2(PMe_3)_3$ and are presented in Figure 37 along with that of $Mg(\eta^1$-2,4-$C_7H_{11})_2$(tmeda) for comparison.

From the oxidative additions of 1-halo-2,4-pentadienes to $MCl(CO)(L)_2$ complexes (M = Rh, Ir; L = $PMe_2(C_6H_5)$, $P(C_6H_5)_3$), additional η^1-pentadienyl complexes have been isolated, including $Ir(\eta^1-C_5H_7)(Cl)_2(CO)(L)_2$, $Ir(\eta^1-C_5H_7)(Cl)(Br)(CO)(L)_2$, and $Rh(\eta^1-C_5H_7)(Cl)(X)(CO)(PMe_2(C_6H_5))_2$ (X = Cl, Br).[181] The formations of the iridium complexes are actually re-

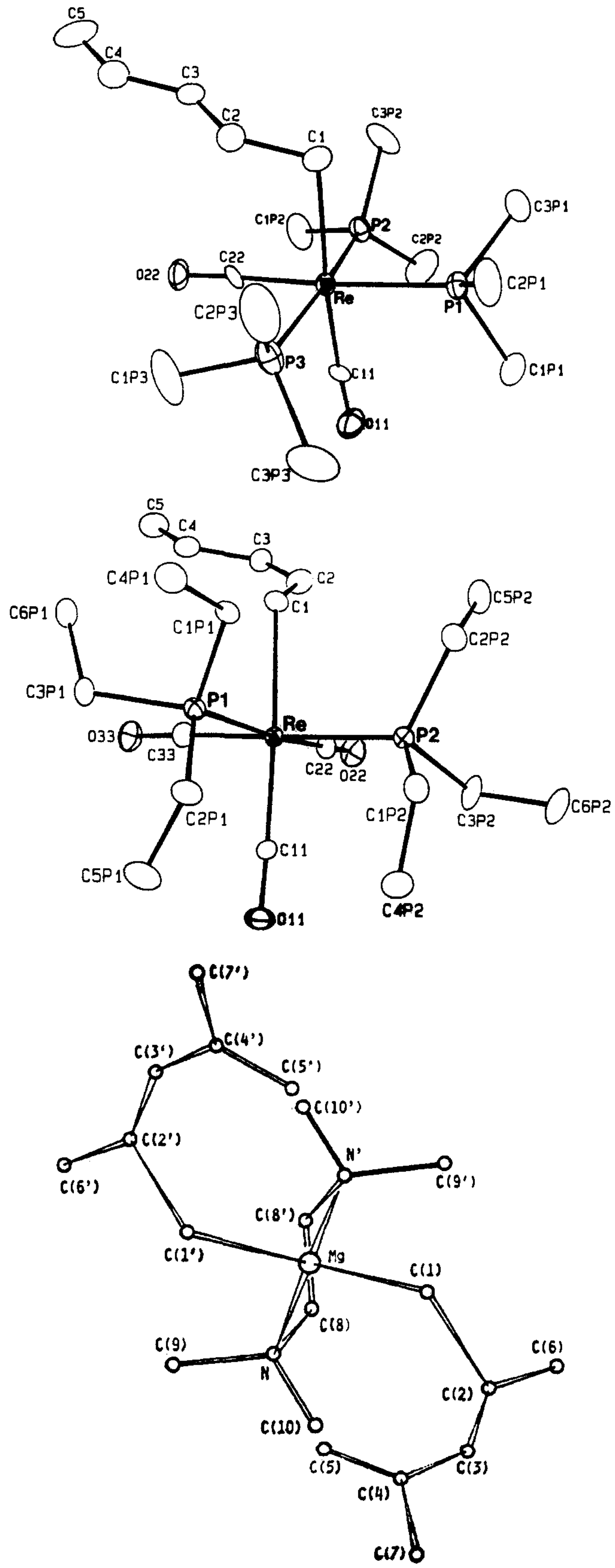


Figure 37. Structures of the representative η^1-bound pentadienyl compounds $Re(\eta^1\text{-W-}C_5H_7)(CO)_2(PMe_3)_3$ and $Re(\eta^1\text{-S-}C_5H_7)(CO)_3(PMe_3)_2$ (reprinted from ref 179; copyright 1987 American Chemical Society) and $Mg(\eta^1\text{-U-}2,4\text{-}C_7H_{11})_2$(tmeda) (reprinted from ref 19b; copyright 1980 Nippon Kagakkai).

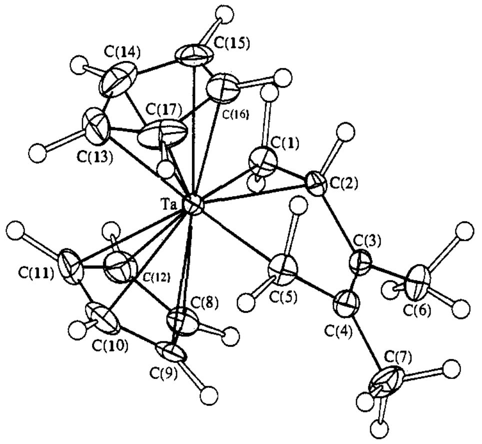


Figure 38. Perspective view of $Ta(C_5H_5)_2(\eta^3\text{-}2,3\text{-}C_7H_{11})$.[182]

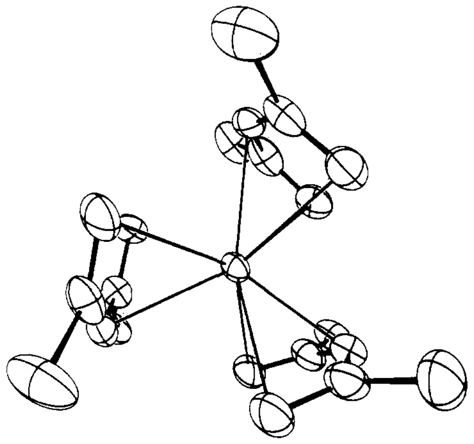
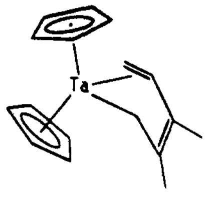


Figure 39. Solid-state structure of $Nd(2,4\text{-}C_7H_{11})_3$ (reprinted from ref 183; copyright 1982 American Chemical Society).

versible. In each case, structures are proposed in which the two phosphine ligands are trans to one another, with the two halides cis to one another. For at least the mixed halide complex of rhodium, the presence of two isomers was evident spectroscopically.

A very new mode of η^3-pentadienyl bonding has been revealed in $Ta(C_5H_5)_2(\eta^3\text{-}2,3\text{-}C_7H_{11})$.[182] The complex was prepared by the reaction of $Ta(C_5H_5)Cl_4$ with 4 equivalents of $K(2,3\text{-}C_7H_{11})$, suggesting that a disproportionation took place. As can be seen in Figure 38, the bonding involves localized Ta–alkyl and Ta–olefin coordination, through the 1-, 4-, and 5-positions of the C_7H_{11} ligand



Interestingly, for the analogous $2,4\text{-}C_7H_{11}$ complex, variable-temperature ^1H NMR spectroscopy indicated that the two C_5H_5 ligands could become equivalent, as could the two ends of the $2,4\text{-}C_7H_{11}$ ligand, with $\Delta G^\ddagger = 10.4 \pm 0.2$ and 10.7 ± 0.2 kcal/mol, respectively.

G. Lanthanide and Actinide Complexes

Reactions of $NdCl_3$ or "$UCl_3 \cdot n$THF" with 3 equiv of $K(2,4\text{-}C_7H_{11})$ have led to the paramagnetic, f^3 complexes $Nd(2,4\text{-}C_7H_{11})_3$[183] and $U(2,4\text{-}C_7H_{11})_3$,[184] which exhibited the expected broadening of peaks in their ^1H NMR spectra. A structural study of $Nd(2,4\text{-}C_7H_{11})_3$ revealed that all five dienyl carbon atoms were η^5-bound (Figure

39), providing the first structural evidence for the interaction of a highly ionic lanthanide ion with formally uncharged carbon atoms. Not surprisingly, however, the Nd-C(2,4) distances were longest, averaging 2.855 (8) Å, compared to 2.801 (9) Å for the 1- and 5-positions and 2.749 (10) Å for the 3-position, which should bear the greatest negative charge. Due to its thermal instability, U(2,4-C_7H_{11})$_3$ has only recently been subjected to structural studies.

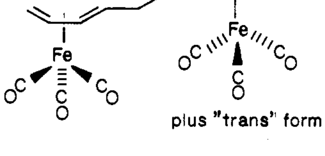
H. Reaction Chemistry Involving Pentadienyl Ligands

As the neutral pentadienyl fragment may donate five electrons to a metal center and possesses molecular orbitals quite similar in nodal properties to the cyclopentadienyl fragment, it is natural that there should be some relationships between their analogous compounds with respect to stoichiometry, structure, and bonding. However, such similarities should not be expected to carry over to reaction chemistry given the aromatic nature of the cyclopentadienyl anion and the much different π-orbital energies of the two dienyl fragments. In this key respect, the pentadienyl unit is much more similar to the allyl group, as both are nonaromatic, but have odd alternant delocalized π systems, resulting in a SOMO (S = singly) for the radical which is nonbonding. Of course, metal-allyl complexes have found a tremendous number of applications in catalysis and organic synthesis, including coupling reactions, "naked metal" reactions, and catalytic polymerizations.[3] It can therefore be expected that while metal-pentadienyl compounds may resemble metal-cyclopentadienyl compounds in the aspects of stoichiometry, structure, and bonding (and even be more strongly bound), the chemistry of metal-pentadienyl complexes should be more closely related to that of the versatile metal-allyl complexes and hence should prove of some value.

1. Pentadienyl Dimerizations and "Naked Metal" Reactions

In metal-allyl chemistry, the dimerization of two allyl ligands generally leads to 1,5-hexadiene, which often is readily removed from the metal center(s). In contrast, pentadienyl dimerizations would generally give rise to 1,3,7,9-decatetraenes, and as each end of these molecules is a 1,3-butadiene moiety, these dimers should prove far more potent in their coordinating ability relative to 1,5-hexadiene and hence should display a greater tendency to remain attached to the metal centers rather than coming off completely, as in "naked metal" reactions.[19d]

Indeed, such considerations seem to be borne out. The earliest examples of pentadienyl dimerization reactions were brought about by the reduction of Fe(pentadienyl)(CO)$_3^+$ complexes with appropriate reagents such as zinc.[185] A typical example of an isolated product from such a reaction is shown below.



plus "trans" form

It is notable that the pentadienyl fragments in the dimer have assumed the sickle shape. This can readily be understood by considering the likely intermediate in these reactions, Fe(C_5H_7)(CO)$_3$. In all probability, this should exist primarily as a 17-electron complex, Fe(η^3-C_5H_7)(CO)$_3$ (**25**), for which rotation of the C-C single bond would lead to the generally observed sickle geometry **26**. A contribution of the type **27** then may be considered to bring about the subsequent dimerization. Of course, the dimerizations observed on reduction of Fe(η^5-cyclo-dienyl)(CO)$_3^+$ complexes would not be accompanied by a conversion to the sickle geometry. One interesting application of such dimerizations involves the syntheses of polycyclic hydrocarbons, which may be accomplished through a two-electron reduction of two linked Fe(η^5-cyclo-dienyl)(CO)$_3^+$ species, leading to further coupling between the two units.[186]

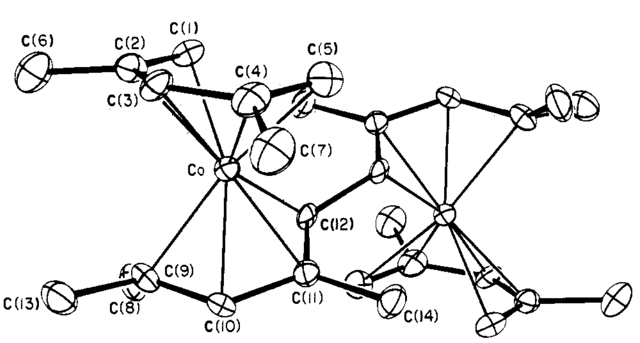
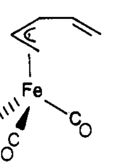


Figure 40. Structure of the open cobaltocene dimer [Co(2,4-C_7H_{11})]$_2$[μ_2-η^4,$\eta^{4'}$-2,4,7,9-Me_4-2,4,6,8-$C_{10}H_{10}$] (reprinted from ref 104; copyright 1984 American Chemical Society).



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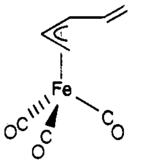

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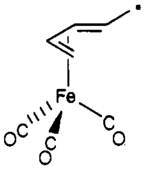

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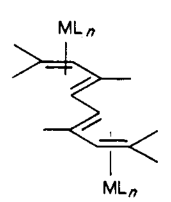
A particularly interesting dimerization product was observed from the reaction of $CoCl_2$ with 2 equiv of K(2,4-C_7H_{11}).[104] As the initial product of such a reaction would likely be an open cobaltocene (having probably one η^3-bound and one η^5-bound 2,4-C_7H_{11} ligand, thereby leading to a 17-electron complex), a dimerization would appear quite reasonable. However, the actual product (Figure 40), while a dimer, was found to have undergone an unusual isomerization, which led to a more conjugated 2,4,6,8-decatetraene complex (**28**, ML_n = Co(2,4-C_7H_{11})) rather than to a 1,3,7,9-decatetraene complex (**29**, ML_n = Co(2,4-C_7H_{11})). Several considerations suggested quite strongly that this isomerization must have been brought about by η^5-η^3 transformations of the unaltered 2,4-C_7H_{11} ligands, as in Scheme I, which could explain in part why such isomerizations had not been observed in previous di-



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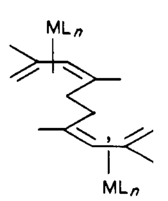

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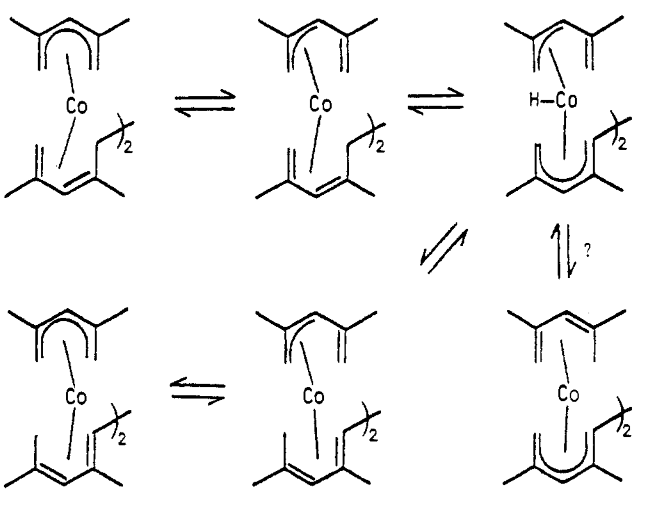
SCHEME I



mers, which did not possess unaltered pentadienyl ligands. However, there is also a geometric barrier to such a process in most of the other systems. This arises from the fact that sickle-shaped pentadienyl fragments are present in most final dimers, and formation of a 2,4,6,8-decatetraene would lead to *trans*-diene units, which should not favor η^4 coordination. The geometric barrier is avoided in the $Co(2,4\text{-}C_7H_{11})_2$ dimerization due to the presence of the $2,4\text{-}C_7H_{11}$ ligands, which actually prefer the **U** conformation and hence do not rearrange to the **S** form upon reduction. Therefore, to test the possibility that other systems might also undergo isomerizations (perhaps through η^4–η^2 transformations of the coordinated diene fragments) if the geometric barrier were removed, the reductions of both $Fe(2,4\text{-}C_7H_{11})(CO)_3^+$ and $Co(C_5H_5)(2,4\text{-}C_7H_{11})^+$ were carried out, and in each case, dimers of the sort **29** (ML_n = $Fe(CO)_3$[187] or $Co(C_5H_5)$,[87] respectively) were isolated. In fact, similar results, i.e., a lack of isomerization, have been obtained for related dimers formed through the coupling of two $M(\eta^5$-cyclo-dienyl) fragments.[185c,186] Hence, it becomes clear that the observed isomerization of the open cobaltocene dimer was initiated through an η^5–η^3 conversion of the $2,4\text{-}C_7H_{11}$ ligand.

Another unusual pentadienyl dimerization has been observed in a chromium complex.[188] While open titanocenes and open vanadocenes readily undergo Lewis base coordination by a variety of ligands, this is not the case for open chromocenes. An attempt to make such a species was therefore carried out by introducing a ligand, PEt_3, to the metal center prior to the addition of pentadienyl ligands. The appropriate reaction (eq 23) did lead to a product having the designated stoichiometry; however, the product was paramagnetic and exhibited a strong ESR signal. An X-ray diffraction study (Figure 41) revealed that a dimeric complex had been formed through pentadienyl dimerization, leading to 17-electron Cr(I) centers (there was no evidence for butenediyl coordination to Cr(III)). Of course, Cr(I) is an unusual oxidation state, and the dimerization reaction represents a striking example of a spontaneous reduction of Cr(II) to Cr(I). Interestingly, $Cr(C_5H_7)_2$ has been reported to react with CO to yield $Cr(CO)_6$ and the *diamagnetic* $[Cr(C_5H_7)_2(CO)]_2$, which yields various pentadienes on hydrolysis.[24] However, this carbonyl dimer exhibits a strong ESR signal[188] and may therefore be similar in structure to the related PEt_3 dimer.

$$CrCl_2(PEt_3)_n + 2K(C_5H_7) \rightarrow \text{“}Cr(C_5H_7)_2(PEt_3)\text{”} \quad (23)$$

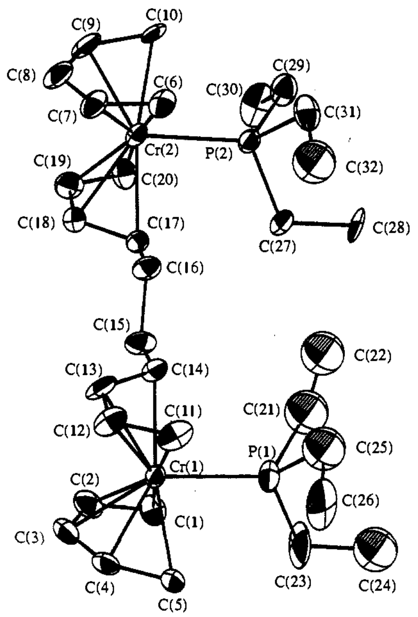


Figure 41. Molecular structure of the Cr(I) dimer $[Cr(C_5H_7)(PEt_3)]_2[\mu_2\text{-}\eta^4,\eta^{4'}\text{-}1,3,7,9\text{-}C_{10}H_{14}]$.

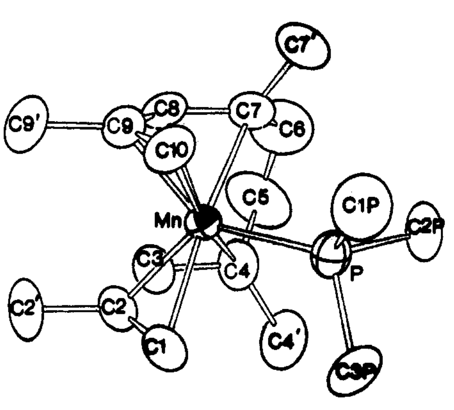


Figure 42. Structure of $Mn(\eta^8\text{-}2,4,7,9\text{-}Me_4\text{-}1,3,7,9\text{-}C_{10}H_{10})(PMe_3)$ (reprinted from ref 189; copyright 1983 American Chemical Society).

In contrast to the common nature of intermolecular pentadienyl dimerizations, their intramolecular analogues have been observed only more recently. The unusual reaction leading to $Mn_3(3\text{-}C_6H_9)_4$[84a] (section II.D) might involve such a dimerization, but other possibilities exist as well. A clear-cut example of such a process was observed, however, in the related reaction of $MnBr_2$ with PMe_3 and 2 equiv of $K(2,4\text{-}C_7H_{11})$.[189] The isolated product (Figure 42) is a paramagnetic, 17-electron complex, proposed to form via an open manganocene complex, which becomes coordinated by PMe_3, leading to a $Mn(\eta^3\text{-}\mathbf{S}\text{-}2,4\text{-}C_7H_{11})_2(PMe_3)_2$ intermediate, which then undergoes intramolecular coupling. Pertinent to these open manganocene systems are some results obtained for isoelectronic open ferrocene and half-open ferrocene cations.[41] The 17-electron cations may be generated electrochemically from $Fe(2,4\text{-}C_7H_{11})_2$ and $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$. The oxidation may be reversed for $Fe(2,4\text{-}C_7H_{11})_2^+$ only at low temperatures (e.g., −45 °C), however, while that for $Fe(C_5H_5)(2,4\text{-}C_7H_{11})^+$ may be reversed even at room temperature. This trend is consistent with the occurrence of an intramolecular coupling reaction for $Fe(2,4\text{-}C_7H_{11})_2^+$ and

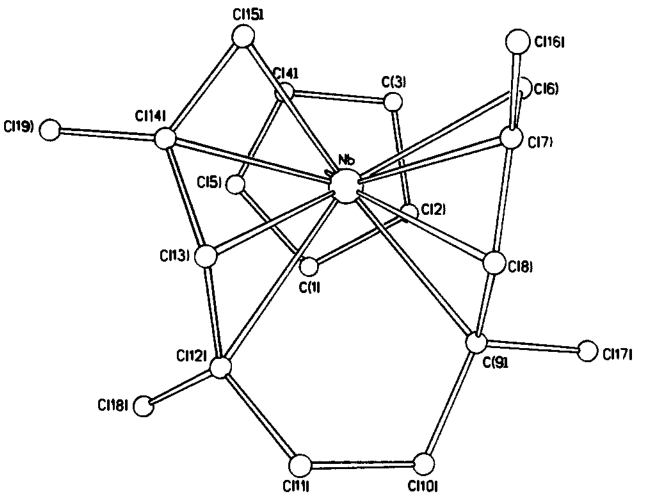


Figure 43. Structure of $Nb(C_5H_5)(\eta^8\text{-}2,4,7,9\text{-}Me_4\text{-}1,3,7,9\text{-}C_{10}H_{10})$.[182]

an intermolecular coupling reaction for $Fe(C_5H_5)(2,4\text{-}C_7H_{11})^+$. In fact, recent kinetic studies of the electrochemical processes have revealed the loss of $Fe(2,4\text{-}C_7H_{11})_2{}^+$ to be a first-order process, while that of $Fe(C_5H_5)(2,4\text{-}C_7H_{11})^+$ is second-order.[85] In both cases, dipentadienyl units are isolated as products. Crossover experiments for $Fe(2,4\text{-}C_7H_{11})_2$ and $Fe(2,4\text{-}C_7D_{11})_2$ mixtures demonstrated that the coupling process is essentially completely intramolecular.[85] These data clearly point to an intramolecular coupling reaction for $Fe(2,4\text{-}C_7H_{11})_2{}^+$, and perhaps as well for the isoelectronic $Mn(3\text{-}C_6H_9)_2$.

A rather unusual intramolecular coupling reaction has been observed for a Nb(III) complex.[182] Thus, the reaction of $Nb(C_5H_5)Cl_4$ with 4 equiv of $K(2,4\text{-}C_7H_{11})$ leads to an initial product which spectroscopically appears to be a Nb(III) complex, $Nb(C_5H_5)(2,4\text{-}C_7H_{11})_2$. On warming to room temperature, however, this material slowly transforms itself to a $Nb(C_5H_5)(\eta^8\text{-}$2,4,7,9-tetramethyl-1,3,7,9-decatetraene) complex (Figure 43). Particularly notable about this molecule is the fact that one coordinated butadiene unit is present in the usual cis arrangement, while the other is trans, unlike other $Nb(C_5H_5)(\eta^4\text{-diene})_2$ complexes.[58b,190] The coordination of the *cis*-diene fragment resembles that of a butenediyl complex, so that the product may still be considered to be a Nb(III) compound.

In addition to the "naked metal" reactions given above, several other reports have appeared that constitute potentially useful applications for the open metallocenes. Thus, $Cr(C_5H_7)_2$ and $Cr(2,4\text{-}C_7H_{11})_2$ have been observed to react with CO, leading to a high yield of $Cr(CO)_6$.[24,42] Similar reactions involving $t\text{-}C_4H_9NC$ or dmpe lead respectively to $Cr(CN(t\text{-}C_4H_9))_6$ and $Cr(dmpe)_3$, in yields of ca. 60% or better. The result for $Cr(dmpe)_3$ is notable in that only relatively mild conditions were required, whereas other methods require more forcing (even metal atom) conditions, provide much lower yields, and often waste large amounts of dmpe.[191] Similarly, $Fe(C_5H_7)_2$ has been found to react with PF_3 under mild conditions to yield $Fe(PF_3)_5$.[192]

2. Coupling Reactions and Nucleophilic Additions

As metal complexes of η^1-bound pentadienyl ligands may be regarded as substituted butadienes, it seems reasonable that they should be capable of undergoing Diels–Alder reactions with dienophiles. In fact, such reactions have been observed for pentadienylsilanes, pentadienylstannanes, $Mn(\eta^1\text{-}C_5H_7)(CO)_5$, and $Mo(C_5H_5)(\eta^1\text{-}C_5H_7)(CO)_3$. Thus, the reactions of $Sn(\eta^1\text{-}C_5H_7)(CH_3)_3$ or $Mo(C_5H_5)(dienyl)(CO)_3$ (dienyl = $\eta^1\text{-}C_5H_7$, $\eta^1\text{-}1\text{-}C_6H_9$) with maleic anhydride, of $Si(\eta^1\text{-}C_5H_7)(CH_3)_3$ with crotonaldehyde or mesityl oxide,[29c,172] and of $Mn(\eta^1\text{-}C_5H_7)(CO)_5$ or $Mo(C_5H_5)(dienyl)(CO)_3$ with TCNE[129,172] all have led to the expected Diels–Alder adducts, although in the mesityl oxide reaction, a 1,4-addition product was also observed. Furthermore, it was noted that the mesityl oxide and crotonaldehyde reactions might actually be polar, stepwise processes rather than concerted Diels–Alder reactions. $Mn(\eta^1\text{-}C_5H_7)(CO)_5$ was also found to undergo an insertion reaction with SO_2, yielding an S-bound $Mn(\eta^1\text{-}S(O)_2C_5H_7)(CO)_5$ complex.

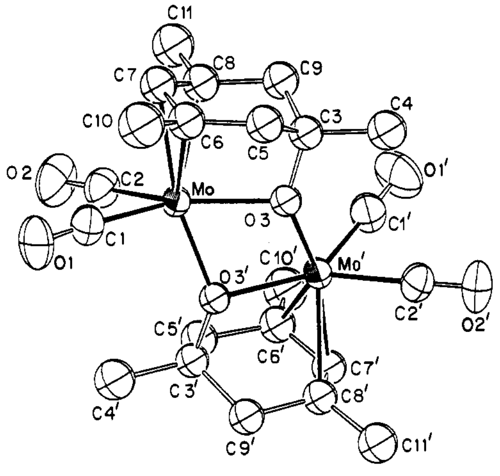
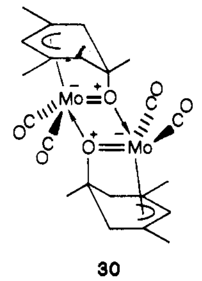


Figure 44. Perspective view of the unusual, dimeric coupling product formed from the attempted preparation of $Mo(2,4\text{-}C_7H_{11})(CH_3)(CO)_3$ (reprinted from ref 119a; copyright 1985 American Chemical Society).

Coupling reactions have also been observed for η^3-bound pentadienyl complexes. Thus, $[Ni(\eta^3\text{-}C_5H_7)(Br)]_2$ and $[Ni(\eta^3\text{-}1\text{-}C_6H_9)(Br)]_2$ have been found to react with C_6H_5I, $C_6H_5CHCHBr$, and $C_6H_5CHCHCH_2Br$, in general leading to attachment of the organic group onto a terminal pentadienyl position (for the $1\text{-}C_6H_9$ ligand, on the side opposite to the methyl group).[164] However, in the reaction of $[Ni(\eta^3\text{-}C_5H_7)(Br)]_2$ with $C_6H_5CHCHCH_2Br$, attack at the pentadienyl 3-position was also noted, and a 1:1 mixture of trienes was obtained.

An unusual coupling reaction was observed on the attempted preparation of $Mo(2,4\text{-}C_7H_{11})(CH_3)(CO)_3$ from $Mo(2,4\text{-}C_7H_{11})(CO)_3{}^-$ and CH_3I.[119a] The product **30** (Figure 44) is essentially a $[Mo(allyl)(OR)(CO)_2]_2$ complex which was apparently formed by three successive coupling reactions (Scheme II), which led to trialkylation of CO, converting it to an alkoxide, and in the process a 5 + 1 ring construction was accom-



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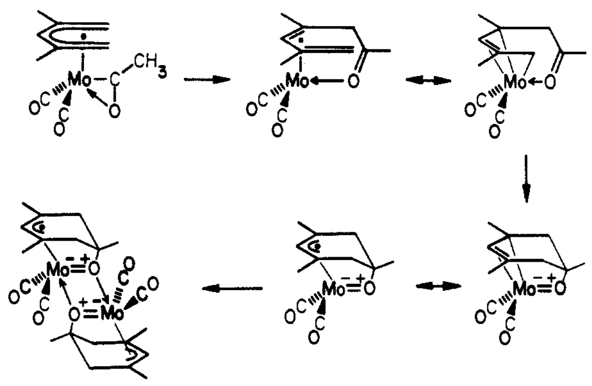
SCHEME II



plished. Given the fact that pentadienyl anions may be prepared with a wide variety of substituents and the possibility that related (η^5-cyclo-dienyl) complexes might be converted to bicyclic compounds, there would seem to be a possibility of developing useful applications from this type of reaction. It must be noted that methylation of some $Cr(\eta^5\text{-cyclo-dienyl})(CO)_3^-$ complexes has been observed to produce 5-acetyl-1,3-cyclohexadienes,[193] and the possibility of highly modified $Cr(\eta^5\text{-cyclo-dienyl})(alkyl)(CO)_3$ complexes being intermediates in other transformations has been mentioned,[112c] while various (acetyl-1,3-cycloheptadiene)iron complexes have been isolated from the reaction of $Fe(\eta^5\text{-}C_7H_9)(CO)_2^-$ with acetyl chloride and CO.[110a] Acetyl–pentadienyl coupling also appeared to take place for $Fe(2,4\text{-}C_7H_{11})(C(O)CH_3)(CO)(PMe_2(C_6H_5))$[110b] on standing, but the oily nature of the product did not allow complete characterization. Interestingly, couplings involving both the 1- and 5-positions of cyclo-dienyl anions and cations have been reported.[194]

Pentadienyl ligands may also undergo coupling reactions with neutral unsaturated molecules such as nitriles. Thus, an instantaneous reaction occurs on mixing the half-open titanocene $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$ with CH_3CN, leading to a dimeric product in which coupling between the pentadienyl and acetonitrile ligands has taken place, as indicated earlier (Figure 25).[90] Related coupling reactions have been observed for $Zr(\eta^4\text{-diene})$ complexes,[195] but it is noteworthy here that the pentadienyl ligand has undergone a coupling reaction even though it is more strongly bound than the cyclopentadienyl ligand (vide supra). Other coupling reactions also seem to take place with acetylenes and isonitriles, but presently the nature of the products is not completely clear.[57,88b]

Cationic pentadienyl and cyclo-dienyl complexes are very susceptible to nucleophilic attack, and such reactions have developed into a number of useful applications. Particularly notable have been the applications involving the $Fe(\eta^5\text{-cyclohexadienyl})(CO)_3^+$ complexes, for which a wide variety of substituents may initially be placed in various positions of the η^5-dienyl fragment.[10] In at least some cases, such as the reaction of $Ru(C_6H_7)(CO)_3^+$ with methoxide, attack usually occurs first on a CO ligand, leading to observable or isolable intermediates, after which transfer to the dienyl ligand occurs.[196] Attack at the terminal carbon atom positions is most common, but attack at the 2-position is not uncommon either, especially as one descends the iron triad.[197] Various studies have been carried out to understand the factors determining the favored site of attack in some of these systems, and ring size, the nature of metal, and hardness of the attacking nucleophiles have all been found to be important.[9a,198] For open pentadienyl complexes, similar trends have been observed, and typical nucleophiles such as hydroxide, amide, or alkoxide tend to add at a terminal site.[199] However, $NaBH_4$ reduction of $Rh(C_5H_5)(1\text{-}C_6H_9)^+$ leads to addition of H^- to the 3-position, leading to a neutral 1,4-diene complex.[200] Similar attack by methoxide is observed on both $Rh(C_5H_5)(1\text{-}C_6H_9)^+$ and $Ir(C_5H_5)(1\text{-}C_6H_9)^+$.

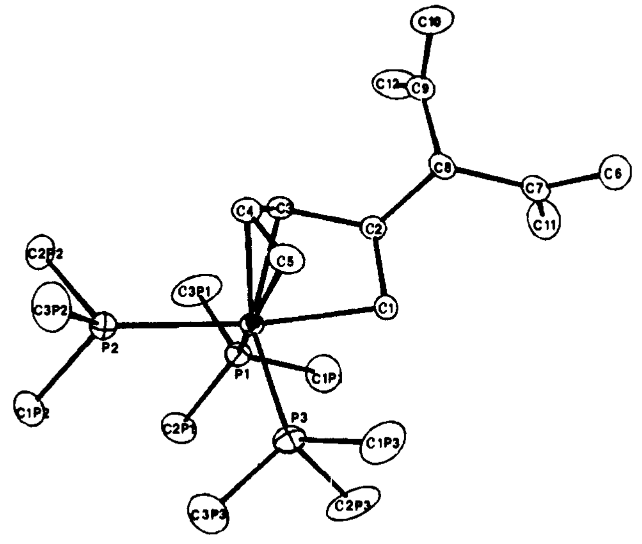
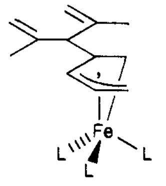


Figure 45. Molecular structure of $Fe(1,2,3,5\text{-}\eta^4\text{-}4\text{-}(C_7H_{11})C_5H_7)(PMe_3)_3$ (reprinted from ref 201; copyright 1987 American Chemical Society).

The reaction of $Fe(C_5H_7)(PMe_3)_3^+$ with $K(2,4\text{-}C_7H_{11})$ also involves nucleophilic addition, and leads to C-C bond formation.[201] The product 31 (Figure 45) demonstrates that the 3-position of the $2,4\text{-}C_7H_{11}$ anion has attacked the bound pentadienyl ligand at its 2-position, leading to an $Fe(allyl)(alkyl)(PR_3)_3$ complex. The general structural features are similar to those observed in a compound formed by hydride ion transfer to a $Cr(\eta^5\text{-cyclo-dienyl})(CO)_2(NO)^+$ complex.[202] As noted before, the 3-position of a pentadienyl anion tends to bear greater negative charge than either the 1- or 5-position and for this reason might be expected to be more reactive than the terminal sites, although it is possible that initial attack through a terminal position may have occurred at the metal.[198] Interestingly, similar carbon–carbon bond-forming processes have been observed in reactions of $Fe(\eta^5\text{-cyclo-dienyl})(CO)_3^+$ complexes with enolate anions and β-diketones.[203]



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3. Protonations and Other Hydrogen Atom Transfer Reactions

A number of metal pentadienyl compounds are known in which formal hydride ligands have been incorporated by protonation. Of course, M(pentadienyl)(hydride) species such as Zr(η^5-cyclo-dienyl)(H)(dmpe)$_2$,[157] Re(η^5-C_6H_7)(H)$_2$(P(C_6H_5)$_3$)$_2$,[154] Re$_3$(η^5-C_7H_9)(H)$_2$(CO)$_{10}$,[158] Fe(η^5-C_6H_7)(H)(P(OMe)$_3$)$_2$,[143c] and Ru(η^5-cyclo-dienyl)(H)(P(C_6H_5)$_3$)$_2$[143a,b,d] have already been mentioned, as have protonation reactions in which η^3- or η^1-dienyl groups become converted to η^4- or η^2-diene ligands[82] or in which bound dienyl ligands are removed as dienes and in the process are replaced by other ligands.[81,148] In a related report, the reaction of Zr(C_5H_5)$_2$(H)(Cl) with various pentadienyl anions has been found to lead to Zr(C_5H_5)$_2$(η^4-diene) compounds, presumably via Zr(C_5H_5)$_2$(η^1-pentadienyl)(H) intermediates.[178] The complex Mn$_3$(3-C_6H_9)$_4$ has also been mentioned (section II.D) and had earlier been described as demonstrating both metal- and ligand-centered basicities.[84a] In other situations, metal dienyl hydride compounds may be isolated by protonation reactions. Thus, Os(η^5-cyclo-dienyl)(I)(PMe$_3$)$_2$ complexes undergo protonation to yield Os(η^5-cyclo-dienyl)(H)(I)(PMe$_3$)$_2^+$ species, in which the metal-bound hydride ligands were found to undergo exchange with hydrogen atoms of the η^5-cyclo-dienyl ligands.[204] In the process, alkyl substituents initially on the 6-position become transferred to the various cyclo-dienyl positions, analogous to the exchange mentioned previously for Mn(η^5-cyclo-dienyl)(CO)$_3$ complexes (section II.E.2). Similarly, protonation of Re(η^5-cyclooctadienyl)(C_6H_6) was found to lead to the expected cationic metal hydride complex.[121b] From indirect protonation reactions, the cationic ruthenium hydride species Ru(C_5Me_5)(η^5-C_8H_{11})(H)$^+$ and Ru(η^5-C_8H_{11})$_2$(H)$^+$ have been prepared.[205]

Related complexes incorporating open pentadienyl ligands may be similarly prepared. Thus protonation of Re(2,4-C_7H_{11})(PMe$_2$(C_6H_5))$_3$ leads to Re(2,4-C_7H_{11})(H)(PMe$_2$(C_6H_5))$_3^+$, whose structure, previously described, is presented in Figure 34.[136b] As noted before, the protonation initially occurs by the open edge of the pentadienyl ligand, and exchange occurs between the hydride ligand and the four hydrogen atoms on the terminal carbon atoms. Similarly, both Ru(2,4-C_7H_{11})$_2$ and Ru(C_5H_5)(2,4-C_7H_{11}) are readily protonated by HBF$_4$,[81] yielding Ru(2,4-C_7H_{11})$_2$(H)$^+$ and Ru(C_5H_5)(2,4-C_7H_{11})(H)$^+$. In each case, variable temperature ^{1}H NMR spectroscopy reveals at low temperatures a well-defined hydride resonance which is split by the two or four endo hydrogen atoms on the terminal pentadienyl carbon atoms, and hence the resonances appear as a triplet or quintet. At higher temperatures, exchange between the hydride ligands and the hydrogen atoms on the terminal carbon atoms takes place, and ultimately a single resonance is observed for the five or nine exchanging atoms. Ru(2,4-C_7H_{11})$_2$(H)$^+$ has been found to exist in an unsymmetric conformation by variable-temperature NMR spectroscopy and by X-ray diffraction. Although some disorder appeared to complicate the structural study, it was clear that the nearly gauche-elipsed orientation was retained.[206] Exposure of Ru(2,4-C_7H_{11})$_2$(H)$^+$ to CO leads to rapid incorporation of one CO ligand, yielding Ru(2,4-C_7H_{11})(η^4-2,4-C_7H_{12})(CO)$^+$, which has been crystallographically characterized.[81b] Exposure to PR$_3$ (R = Me, Et) then leads to Ru(2,4-C_7H_{11})(CO)(PR$_3$)$_2^+$ complexes, which by NMR spectroscopy and X-ray diffraction are unsymmetric. An inverse approach has also been applied to allow isolation of symmetric, structurally characterized Ru(2,4-C_7H_{11})(CO)(PR$_3$)$_2^+$ complexes. For first-row transition metals, "agostic" complexes are more common. Thus, Cr(2,4-C_7H_{12})(CO)$_2$(L)[152] (L = P(OMe)$_3$ or PMe$_3$) and Mn(C_5H_8)[(PCH$_2$)$_3$CCH$_3$]$^+$ possess structures in which a η^5-pentadienyl metal unit is formally protonated, the proton bridging a terminal carbon atom and the metal center (Figure 46). Variable-temperature ^{1}H NMR spectroscopy for the pentadienyl complexes demonstrates two hydride exchange processes, one involving rotation of the terminal CH$_3$ group, followed by an exchange of all five terminal hydrogen atoms.

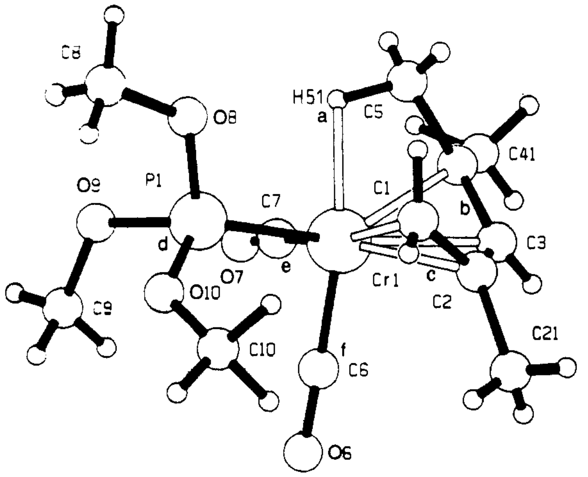


Figure 46. Perspective view of the "agostic" complex Cr(2,4-C_7H_{12})(CO)$_2$(P(OMe)$_3$) (reprinted from ref 152; copyright 1985 VCH (Weinheim)).

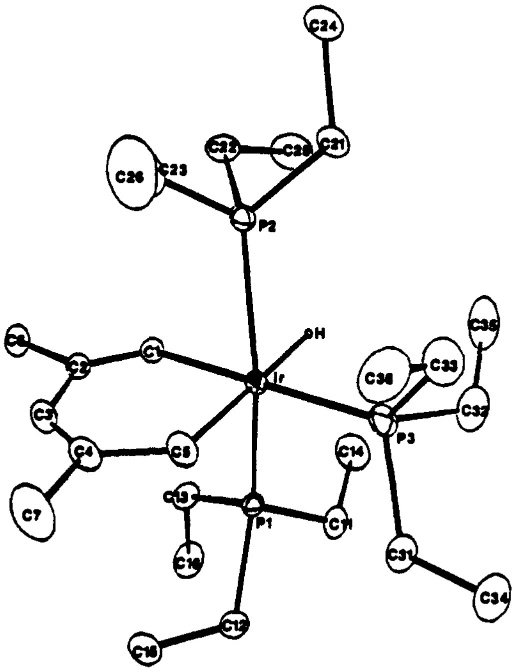
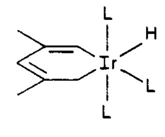


Figure 47. Structure of Ir(η^2-2,4-C_7H_{10})(H)(PEt$_3$)$_3$ (reprinted from ref 207; copyright 1987 American Chemical Society).

In a few cases, transformations have been observed in which hydrogen atoms are abstracted from the terminal carbon atoms of a pentadienyl ligand. In one example, the reaction of Ir(Cl)(PEt$_3$)$_3$ with K(2,4-C_7H_{11}) did not yield a pentadienyl complex, but rather the iridacyclohexadiene complex Ir(η^2-2,4-C_7H_{10})(H)(PEt$_3$)$_3$ (32) (Figure 47), presumably via an η^1-2,4-C_7H_{11} inter-



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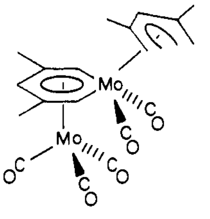
mediate.[207] Reaction of 32 with CH_3I leads to replacement of the hydride ligand by iodide, whereas reaction with $CH_3OSO_2CF_3$ leads to formal removal of H^- (the hydride ligand), and this loss is compensated for by coordination of the internal olefinic bond to the metal (Figure 48). Interestingly, heating this complex in solution results in its conversion to a cyclopentadienyl complex, $Ir(\eta^5\text{-}1,3\text{-}(CH_3)_2C_5H_3)(H)(PEt_3)_2^+$. Similarly, the reaction of 1,4-pentadiene with $Ru(H)(Cl)(P(C_6H_5)_3)_3$ yields an intermediate allyl complex proposed to be $Ru(\eta^3\text{-}C_5H_9)(Cl)(P(C_6H_5)_3)_2$, which transforms on standing to $Ru(\eta^5\text{-}C_5H_7)(Cl)(P(C_6H_5)_3)_2$.[208] Upon reflux in methyl ethyl ketone, this complex is converted in high yield to $Ru(C_5H_5)(Cl)(P(C_6H_5)_3)_2$. This latter conversion was proposed to occur through a $Ru(\eta^3$-cyclopentenyl$)(Cl)(P(C_6H_5)_3)_2$ intermediate.

A somewhat different transformation has been observed in a molybdenum carbonyl system. While reaction of $Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ with CH_3I led to an unusual coupling reaction, reaction with 0.5 equiv of IC_2H_4I followed an entirely different course, producing $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$ (Figure 49).[120] Examination of the structural parameters suggested that this compound is best considered as an (η^6-molybdenabenzene)molybdenum complex, 33. In particular, the molybdenabenzene Mo–C bond distances average 2.156 (3) Å, vs the single Mo–C bond distance of 2.38 Å in $Mo(C_5H_5)(C_2H_5)(CO)_3$.[209] Complex 33 reacts with phosphine and phosphite ligands, during which simple replacement of the CO ligands occurs.



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4. Catalytic Applications

As many catalytic applications have arisen for metal–allyl compounds, related activity should be demonstrated by metal–pentadienyl analogues. In fact, just as $Fe(C_5H_7)_2$ readily participates in "naked iron" reactions,[192] yielding $Fe(PF_3)_5$ from PF_3, so too will it catalyze the oligomerization of butadiene, producing a product mixture quite similar to those reported from other iron-based catalysts.[210]

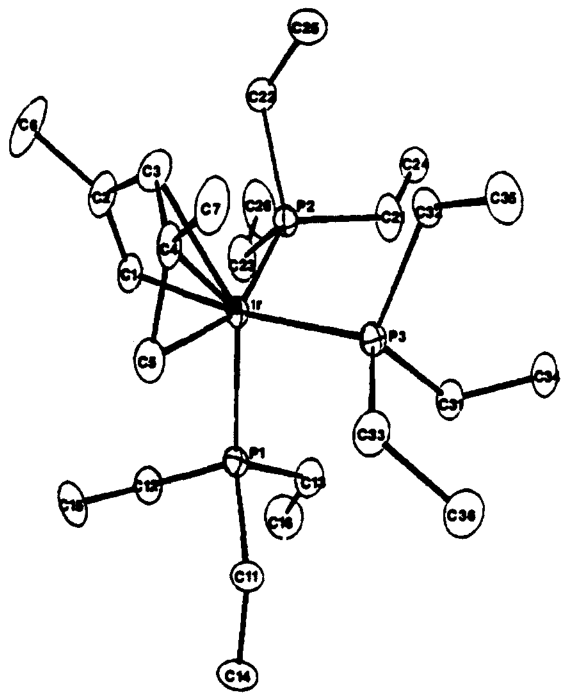


Figure 48. Perspective view of $Ir(\eta^4\text{-}2,4\text{-}C_7H_{10})(PEt_3)_3^+$ (reprinted from ref 207; copyright 1987 American Chemical Society).

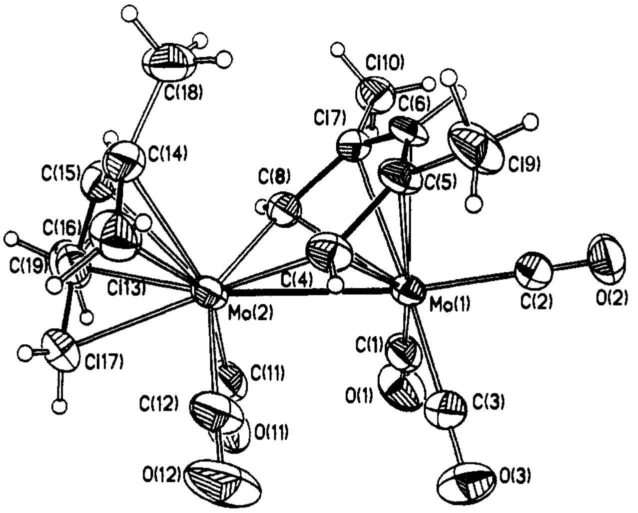
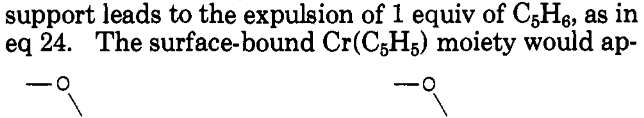


Figure 49. Structure of $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$ (reprinted from ref 120; copyright 1987 American Chemical Society).

The early metal open metallocenes will also catalyze ethylene polymerization, once they are attached to a silica or aluminophosphate surface.[88,211] The situation for chromium is most interesting, as supported chromocene has proven very useful, yielding products with high average molecular weights, whereas other organochromium compounds (e.g., alkyls and allyls) yield products with much less desirable properties, e.g., high 1-butene and 1-hexene contents and rather broad molecular weight distributions. The vast difference in behavior between supported chromocene and other organochromium compounds may readily be related to the kinetic stability of metal–C_5H_5 linkages. Thus, exposure of $Cr(C_5H_5)_2$ to a silica or aluminophosphate support leads to the expulsion of 1 equiv of C_5H_6, as in eq 24. The surface-bound $Cr(C_5H_5)$ moiety would appear to be the active catalyst for the polymerization. The presence of the one relatively unreactive C_5H_5 ligand thus seems to exert an extremely powerful influence on subequent polymerizations. To serve as a test for this model of supported chromocene polymerization and to allow further comparisons of the relative reactivities of metal–C_5H_5 and metal–pentadienyl



$$(\text{—O})_3\text{Si-OH} + Cr(C_5H_5)_2 \longrightarrow (\text{—O})_3\text{Si-OCr}(C_5H_5) \quad (24)$$

linkages, the behaviors of supported $Cr(2,4\text{-}C_7H_{11})_2$ and of the supported half-open chromocene $Cr(C_5H_5)(2,4\text{-}C_7H_{11})$ as ethylene polymerization catalysts were examined. Not surprisingly, $Cr(2,4\text{-}C_7H_{11})_2$ proved to be very active once supported, but the products were typical of those from other organochromium complexes (e.g., low molecular weights etc.). For the half-open chromocene, one should expect the pentadienyl ligand to be more reactive than the C_5H_5 ligand, and hence it should be the former which is removed upon interaction with a surface hydroxyl unit, leaving $Cr(C_5H_5)$ attached to the surface. As this is exactly the species proposed to result for supported chromocene polymerizations, a similar polymer should result. Indeed, the observed polymer is virtually identical with that produced by supported chromocene and entirely different from those made from other supported organochromium complexes, including $Cr(2,4\text{-}C_7H_{11})_2$.[88]

III. Summary

It is now abundantly clear that metal–pentadienyl chemistry is an area with much to offer. Early proposals that pentadienyl ligands could bond even more strongly than the ubiquitous, "stabilizing" C_5H_5 ligand, and yet still impart high chemical and catalytic reactivities to their metal complexes, have now been substantiated. Thus, metal–pentadienyl bonds may be much shorter than metal–cyclopentadienyl bonds, as in $M(C_5H_5)(\text{pentadienyl})(PEt_3)$ (M = Ti, V) complexes, yet the open ligand still retains its much higher reactivity toward coupling reactions, some of which offer a real possibility of developing into useful applications. In addition, a wide variety of η^5–η^3–η^1 transformations have been observed, and complexes in each category are relatively common—obviously much more so than for cyclopentadienyl ligands. It is also clear that pentadienyl ligands exert profound electronic influences, as can be seen from the conformational natures of bis- and mono(pentadienyl) complexes, and in the fact that low oxidation states are greatly favored. Thus, spontaneous Cr(II)–Cr(I) and Zr(IV)–Zr(II) reductions are brought about, and it is notable that while neither titanocene nor any second- or third-row metallocene is known which violates the 18-electron rule,[59i] both open titanocenes and open zirconocenes have already been isolated, and other unusual species will likely follow. Certainly, many more intriguing developments may be expected in this field.

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(2) One common observation is that methylation at a C(X) (X = 2, 3, or 4) position leads to a contraction of the C–C(X)–C angle. In addition, substituents at the 2-, 3-, or 4-position generally bend down toward the metal atom, although this is not necessarily observed in cases in which the methyl group eclipses another species. The tendency for the 3-substituents to bend is less than that of the 2- or 4-position substituents. For the 1- and 5-positions, the substituents directed away from one another ("exo") bend significantly down toward the metal atom (15–20°), while those directed toward each other ("endo") bend ca. 45–50° away from the metal atom.[1a]

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