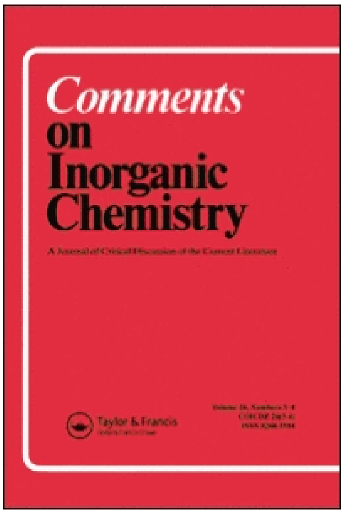

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Pentadienyl Ligands: Their Properties, Potential, and Contributions to Inorganic and Organometallic Chemistry

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Pentadienyl Ligands: Their Properties, Potential, and Contributions to Inorganic and Organometallic Chemistry

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Pentadienyl ligands have been found to possess many unique and potentially useful characteristics, including the ability to adopt a wide variety of η^1, η^3, and η^5 bonding modes, a propensity for bonding to metals in low oxidation states, a tendency toward forming sterically crowded complexes, and the ability to engage in a wide variety of coupling reactions, even while being more strongly bound to a metal center than the ubiquitous cyclopentadienyl ligand. The combination of these properties has led to a rich body of chemistry for these ligands, and the promise that much more remains to be gained.

Keywords: *Pentadienyl; Metallocene; Open metallocene*

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* Correspondence author.

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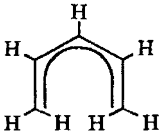
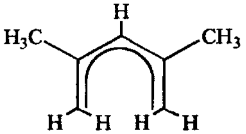
Abbreviations used:



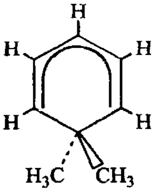
C_5H_7

pentadienyl



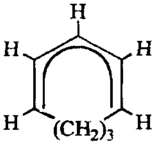
2,4-C_7H_{11}

2,4-dimethyl-pentadienyl



6,6-dmch

6,6-dimethyl-cyclohexadienyl



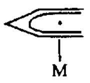
C_8H_{11}

cyclooctadienyl

In 1979 we came to the conclusion that the chemistry of metal pentadienyl complexes had been severely neglected, and we initiated a broad range of studies in this area, beginning with bis(pentadienyl)metal compounds, the open metallocenes.[1] Not surprisingly, other groups had reached conclusions similar to ours,[2] and we subsequently learned that at least two of these groups had also considered, if not actually attempted, the preparation of open ferrocenes. Ultimately, these and other groups have contributed a great deal to the understanding of the chemistry of metal pentadienyl compounds.[2,3] Herein will be presented a summary of what has been learned concerning the fundamental nature of pentadienyl ligands, and their relationships to similar species such as the allyl and cyclopentadienyl ligands, as has been gained both from studies of the physical properties of, and the reactivity patterns exhibited by, their metal complexes. Included as well will be some unique contributions and insight resulting from these studies.

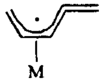
Before discussing individual facets of pentadienyl ligands, it is worthwhile to provide an overview of the key aspects of these ligands which contribute to their uniqueness. Briefly, these may be summarized as follows:

1. They may bond to metals in a variety of η^1, η^3, and η^5 modes (e.g., below):



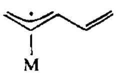
η^5-U

1



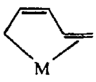
η^5-S

2



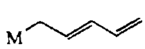
η^3

3



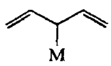
$\eta^{3'}$

4



η^1

5



$\eta^{1'}$

6

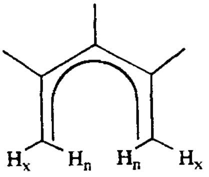
2. The usual η^5-U-Pdl (Pdl = various pentadienyl ligands) form is even more sterically demanding than C_5Me_5 as a result of the former's shorter M-ligand plane separations.
3. η^5-U ligands are often much better acceptors than C_5H_5, due to enhanced δ–backbonding.
4. At least the η^5-U ligands favor bonding to metals in low oxidation states. Thus, Hf(IV) is spontaneously reduced to Hf(II), and even M^{III} (η^5-U-dienyl) complexes are not very common.
5. η^5-U-Pdl ligands may be both more strongly bound, and more reactive, than C_5H_5.

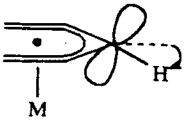
The above are interrelated. Thus 2 may contribute to 3, while 3 may contribute to 4 and 5, and 2–5 may lead to the stabilization of very electron deficient species, e.g., a 14 electron open zirconocene.[4] Each of these aspects will be considered in turn.

IA. AVAILABILITY OF VARIOUS η^1, η^3, AND η^5 BONDING MODES

As can be seen above, there are at least two well-defined bonding modes each for η^1, η^3, and η^5 coordination. Other minor variations in η^1 and η^3 coordination are also known, in which the dienyl fragment may adopt **S** (sickle) or **U** geometries, but these do not involve any alteration of the geometry of the metal-bound carbon atoms.[5]

The η^5 coordination mode occurs almost exclusively with a **U** shaped dienyl ligand (**η^5-U, 1**, above). In this mode, the five carbon atoms lie nearly in a planar arrangement, although significant deviations from the plane are typical for the attached substituents.[6] All but the H(1,5-endo) (internal) substituents are tilted toward the metal atom, to a generally greater extent than observed for cyclopentadienyl ligands. This has been attributed to greater difficulties in achieving good metal-ligand overlap for the open ligand, which can be overcome to some extent through the substituent tilting, which leads to an accompanying tilt by the carbon atoms′ p(π) orbitals (**7**).[6,7] Another means by which the metal-ligand overlap may be enhanced is through a decrease in the separation between the open edge carbon atoms (C1, C5), which has been observed for η^5-bound complexes involving smaller metal centers (vide infra).[6] In contrast to the downward tilts observed for most dienyl substituents, H(1,5-endo) substituents (below) tilt significantly away from the metal. This has been attributed to a partial sp^3 rehybridization of their attached carbon atoms, again to improve metal-ligand overlap,[8] and as well to an attempt to relieve repulsions generated between the two H(1,5-endo) substituents.[9] One final effect of a substituent X has to do with the accompanying delocalized dienyl C-C(X)-C angle. In general, such an angle will decrease in the presence of a non-hydrogen substituent,[6,10] although in the case of at least a siloxy substituent, the angle can increase.[11]





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The alternative η^5-S coordination mode (**2**) is very uncommon, and may be regarded as akin to η^4-trans-diene coordination.[12] However, whereas η^4-trans-diene coordination has been observed for both early and late metal complexes, to date the η^5-S dienyl coordination is generally observed only for metal centers possessing d^4 configurations,[13] at least in the absence of overriding steric effects.[14] It has been concluded that electronic effects specific to the d^4 configuration are responsible for this circumstance.[13] An interesting example of this coordination is found in the M(2,4-C_7H_{11})$_2$ (PEt_3) complexes (M = Mo, W), in which one η^5-S and one η^5-U ligand are each present (Fig. 1).[13a,b]

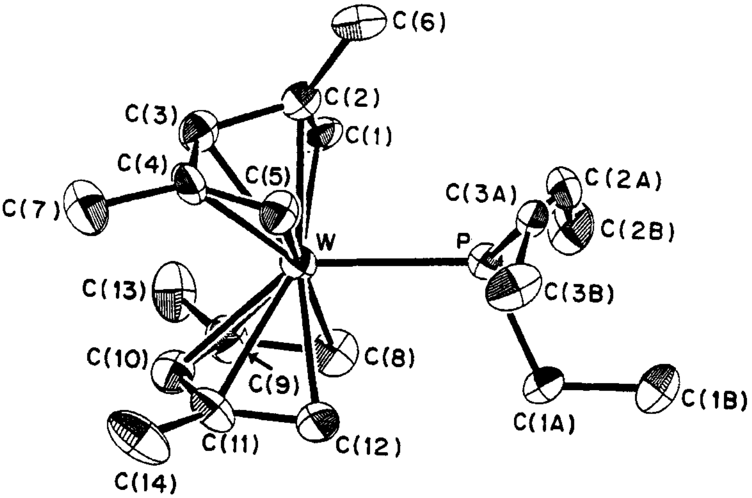
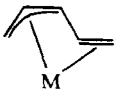


FIGURE 1 Solid state structure of W(η^5-U-2,4-C_7H_{11})(η^5-S-2,4-C_7H_{11})(PEt_3)[13b]

Not surprisingly, substantial difficulties are encountered in bringing about effective bonding for this coordination mode. One can readily see that the η^5-S-dienyl fragment is decidedly nonplanar, with a C(1–2–3–4) torsion angle of 125.6° for the tungsten complex.[13b] This tilt likely leads to a loss in π overlap between the two sides of the ligand, such that a relatively long C2-C3 bond (1.486(17) Å) results, suggesting a significant contribution from an η^5-allyl-ene resonance form (**8**). Furthermore, other difficulties for this coordination mode are evident from the delocalized C-C-C angles, which range from 109.9(12)°-119.3(13)°. Their very low values reflect an attempt to optimize simultaneous coordination of the two dienyl ends, which are 3.81 Å apart, by bringing the ends closer together. Given the problems in bringing about effective η^5-S coordination, one would not expect η^5-W coordination to be at all realistic. Nonetheless, something of this sort has been encountered in a couple thiopentadienyl complexes of tungsten.[15] In these species the torsion angles, beginning for each at the sulfur end, are 129.1 and −119.0 vs. 121.0 and −122.3 degrees, respectively, not unlike the value of 125.6° cited above for $W(2,4\text{-}C_7H_{11})_2(PEt_3)$.



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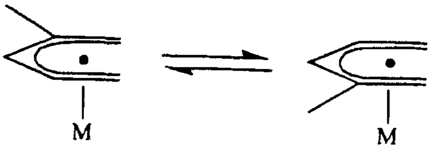
For η^3-pentadienyl coordination there are two possibilities. The first and by far most common mode (**3**) is directly analogous to that of a normal π (η^3) allyl complex, and will therefore not be considered here. The second mode of η^3 coordination is that described by **4**, involving localization of the dienyl fragment, and formation of formal metal-alkyl and metal-olefin interactions. This mode of coordination was first observed in $Ta(C_5H_5)_2(\eta^3\text{-Pdl})$ complexes (Pdl = $2,3\text{-}C_7H_{11}$; $2,4\text{-}C_7H_{11}$) (Fig. 2), and for the latter species, variable temperature ^1H NMR spectra revealed a facile ($\Delta G^{\neq} = 10.2 \pm 0.2$ kcal/mole) fluctional process by which the two ends of the dienyl ligand were rendered equivalent.[16] Notably for Pdl = $1,5\text{-}(Me_3Si)_2C_5H_5$, the steric effects of the two silyl substituents led to adoption of a more normal η^3-allyl coordination mode.[17] The localized η^3 coordination has also been observed in some iridium complexes.[18]

It is interesting to note that in the fluctional rearrangement of $Ta(C_5H_5)_2(\eta^3\text{-}2,4\text{-}C_7H_{11})$, opposite sides of the dienyl fragment take turns being coordinated to the metal center. This circumstance suggested the possibility that such a species could participate as a low energy intermediate in the formal racemization of a planar chiral pentadienyl complex, e.g.,



Indeed, it has now been observed that the two diastereomeric forms of $Fe(2,3\text{-}C_7H_{11})_2$, depicted as **9** and **10** (rather than in their actual

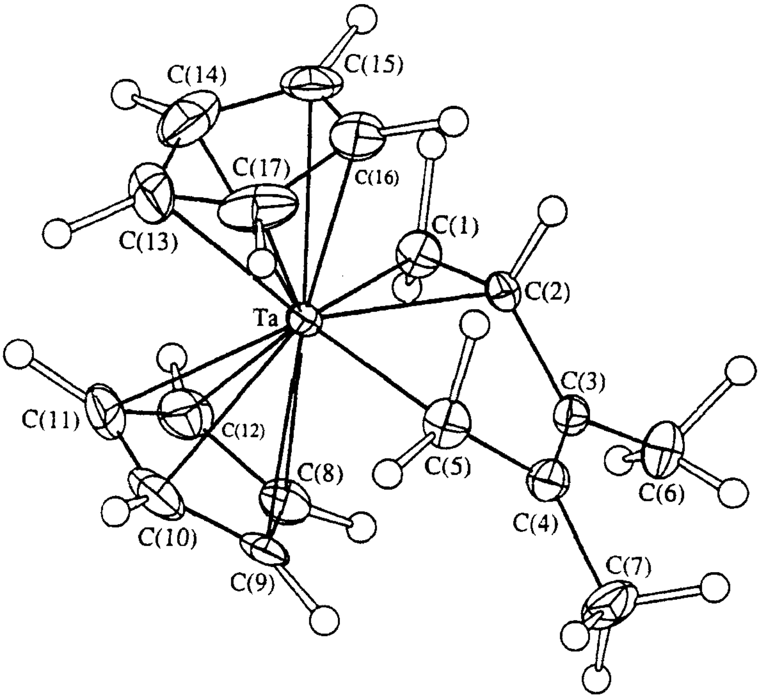
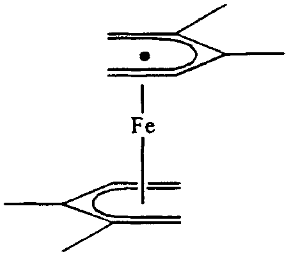


FIGURE 2 Structure of $Ta(C_5H_5)_2(\eta^3\text{-}2,3\text{-}C_7H_{11})$[17]

gauche-eclipsed forms[1,6,7]), can be separately isolated, and that the reequilibration process can be detected in solution within a few hours.[19] The barrier ($\Delta H^{\neq}$) to the process is approximately 22 kcal/mole, very similar to thermochemical estimates of Fe-olefin interactions,[20] which then is nicely consistent with the intervention of a localized η^3-pentadienyl intermediate (Scheme 1). Notably, the approximate geometries of the above-mentioned tantalum and iridium complexes match the structures of intermediates **11** and **12**, respectively. As would be expected, complexes such as $Ru(2,3\text{-}C_7H_{11})_2$ and $Ru(2\text{-}CH_3\text{-}4\text{-}C_6H_5C_5H_5)_2$ exhibit much higher barriers to the isomerization process.[19] The only rational alternative to this process would be to go through a 14 electron η^1 complex, which should be energetically prohibitive. For comparison, intramolecular flips (as opposed to flips via intermolecular ligand transfer) for a C_5H_5 ligand encounter very high barriers,[21] although an interesting "flip" via C-Si bond breakage has been demonstrated.[22]



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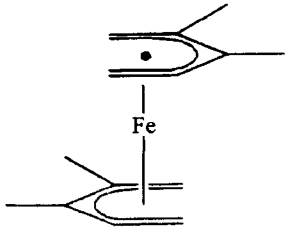

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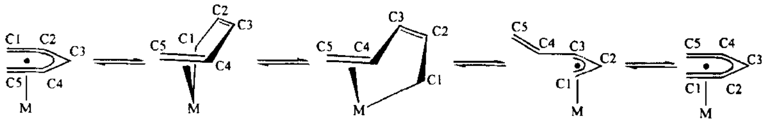


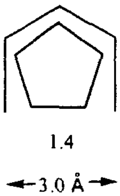
12 11

SCHEME 1

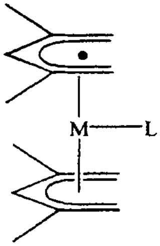
The usual η^1 coordination mode, **5**, is electronically not substantially different from σ-allyl or σ-alkyl complexes, which are quite abundant species. Hence, such complexes will not be considered here. However, the alternative η^1 coordination mode, **6**, in which the central dienyl carbon atom interacts with the metal center, would not have been expected to be a likely coordination mode, both due to the obviously greater congestion that should result near the metal center, and due to the loss of a conjugated diene unit. Nonetheless, just this sort of bonding has been found in $Re(C_5H_7)(CO)_3(Et_2PC_2H_4PEt_2)$,[23] generated photochemically as a metastable intermediate between two terminally coordinated η^1 isomers.

B. STERIC DEMANDS OF PENTADIENYL LIGANDS

One of the most dramatic features of the pentadienyl ligand is the severe degree of steric crowding that can be found in a variety of its complexes. The origin of this effect can be traced to the long separation between the terminal carbon atoms of the pentadienyl ligand. The separation is actually substantially variable, taking on a value of 2.785(5) Å for $Fe(2,4\text{-}C_7H_{11})_2$[24] vs. 3.05(1) Å for $V(2,4\text{-}C_7H_{11})_2$.[6,25] The difference has been attributed to an attempt by the relatively wide ligand in the former complex to enhance overlap with the relatively small iron center.[6] In any event, these lengths are significantly longer than the ca. 1.40 Å bonded edge length of a cyclopentadienyl ligand (below), and as a direct geometric consequence, the open dienyl plane must make a closer approach to the metal center in order to have comparable M-C bond distances. Thus, in $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$,[26] the Fe-ligand plane distances are 1.686 and 1.420 Å, whereas for $V(C_5H_5)(C_5H_7)(PEt_3)$,[27] the V-ligand plane distances are 1.967 and 1.554 Å, respectively. The greater difference for the vanadium complex is not only a result of the wider open edge separation relative to $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$, but also due in part to the much shorter V-C distances for the open vs. closed ligand (*vide infra*), whereas for the iron complex the Fe-C distances for the two ligands are comparable.



There are numerous situations in which the dramatic steric properties of the pentadienyl ligands are evident. Related to the discussion above, the M-C distances in the $M(2,4\text{-}C_7H_{11})_2$ complexes of chromium[28] and iron[24] are significantly longer than those for the $2,4\text{-}C_7H_{11}$ ligand in the $M(C_5H_5)(2,4\text{-}C_7H_{11})$ complexes,[29] although a part of the difference could be attributed to a lengthening of the M-C(Pdl) distances in the open metallocenes as a result of greater competition between the two strongly accepting pentadienyl ligands for bonding to the metal center. Even more dramatic evidence of steric crowding may be seen in the behavior of the electron deficient open metallocene complexes and their ligand adducts. An early example came from the report of a stable 14 electron open titanocene, $Ti(2,4\text{-}C_7H_{11})_2$,[30] and subsequently, of the 14 electron $Zr[1,5-(Me_3Si)_2C_5H_5]_2$.[4] Neither of these forms an adduct with N_2. A thermally unstable, 16 electron mono(carbonyl) adduct could be formed from $Ti(2,4-C_7H_{11})_2$, however, whereas with the C_5Me_5 ligand, the 18 electron $Ti(C_5Me_5)_2(CO)_2$ results.[31] Again, the short M-Pdl plane separations may be implicated. Thus, even in the $M(2,4-C_7H_{11})_2$ complexes a number of interligand C--C contacts are within a van der Waals separation, so that the only way an additional ligand may generally be added is for the two dienyl ligands to twist to the syn-eclipsed conformation, leading to the additional ligand being incorporated by the open dienyl edges (**13**, Fig. 3).[32] However, since even the starting $Ti(2,4-C_7H_{11})_2$ complex is sterically crowded, the 16 electron $Ti(2,4-C_7H_{11})_2(L)$ (L = phosphine or phosphite ligand) complexes are formed reversibly, with binding energies typically in the range of 10–18 kcal/mole.[33]



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While it has proven possible to isolate the 18 electron $Zr(2,4-C_7H_{11})_2(CO)_2$[13a] (Fig. 4), this species is stable only under CO, and otherwise rapidly reverts to $Zr(2,4-C_7H_{11})_2(CO)$. Very analogous behavior is exhibited by the thermally unstable $Ti(C_5H_5)(2,4-C_7H_{11})(CO)_{1,2}$ complexes.[34] Again, the primary cause of such behavior is clearly steric, although the more strongly accepting nature of pentadienyl vs. cyclopentadienyl ligands (*vide infra*) may also contribute. One other notable example relates to the kinetics of CO exchange reactions for 17 electron $V(C_5H_5)(Pdl)(CO)$ and $V(Pdl)_2(CO)$ complexes,[35] as well as 18 electron $Cr(C_5H_5)(Pdl)(CO)$[29] complexes. Whereas all other 17 electron carbonyl complexes undergo rapid, associative CO exchange, the vanadium pentadienyl carbonyl species undergo very slow exchange, primarily through a dissociative process,

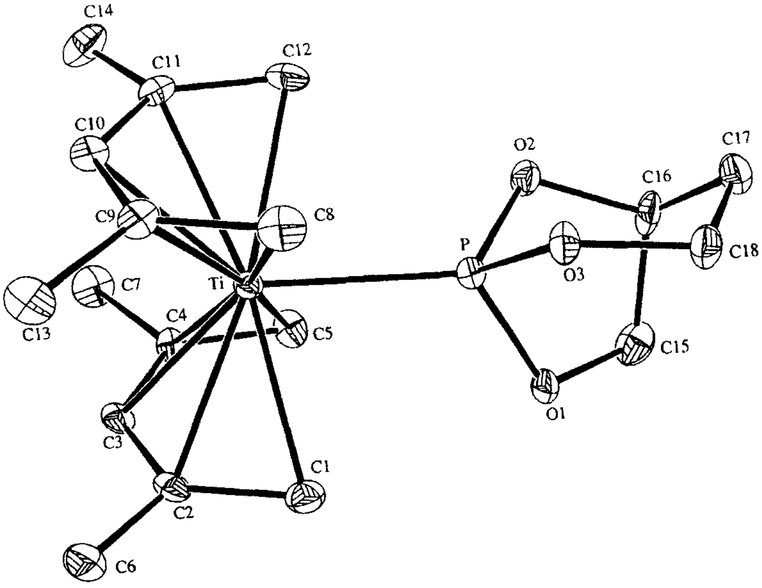


FIGURE 3 Structure of one form of the chiral Ti(2,4-C_7H_{11})$_2$($PO_3C_4H_7$) in the solid state[32b]. The other form differs by a rotation around the Ti-P bond

which may be attributed to steric inhibition of associative processes. Finally, significant crowding is also evident in [Fe(2,4-C_7H_{11})$(CO)_2]_2$, for which an ESR spectrum of the 17 electron monomer is readily observable under ambient conditions.[36]

C. DONOR/ACCEPTOR ABILITIES OF PENTADIENYL LIGANDS

Although the relative ionization potentials and electron affinities for C_5H_5 and C_5H_7 would suggest that cyclopentadienyl should be the better accepting ligand,[37] in large part due to the formation of an (aromatic) anion with greater resonance delocalization energy, it has become quite evident that pentadienyl ligands are significantly better acceptors than cyclopentadienyl. This is evidenced first of all by the formation of alkyl

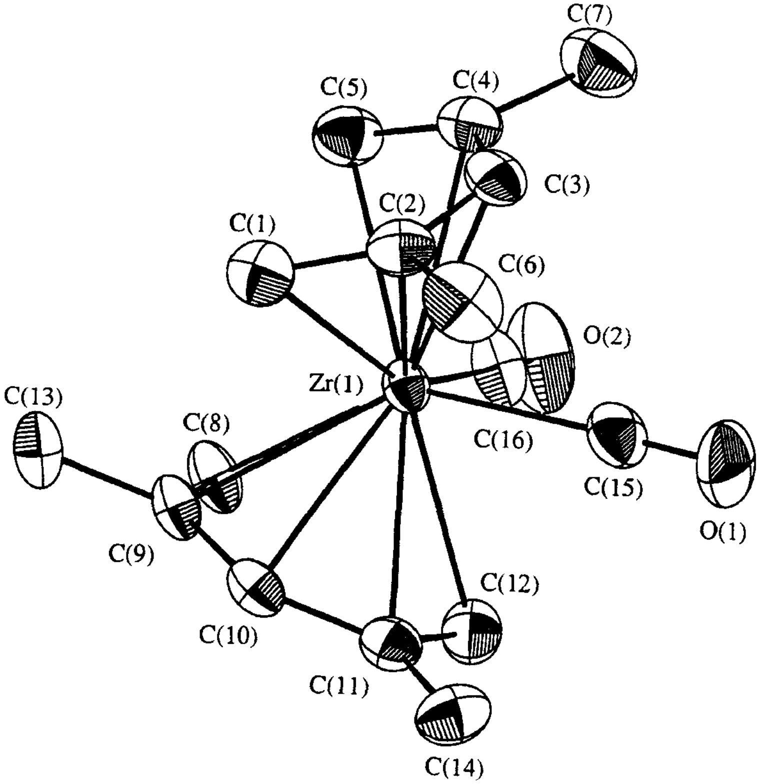
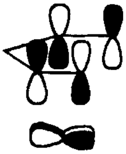


FIGURE 4 Perspective view of the solid state structure of $Zr(2,4\text{-}C_7H_{11})_2(CO)_2$ [13a]

phosphine adducts of $Ti(2,4\text{-}C_7H_{11})_2$,[33] whereas the sterically less crowded $Ti(C_5Me_5)_2$ fragment forms none. In addition, however, the behavior of these 14 electron fragments with N_2 is just the opposite.[38] More detailed information in this regard has been obtained through IR spectral studies of carbonyl complexes. Thus, the C-O stretching frequencies for $V(C_5H_5)_2CO$,[39] $V(C_5H_5)(C_5H_7)CO$,[27] and $V(C_5H_7)_2CO$[40] are 1881, 1938, and 1962 cm^{-1}, respectively, and this trend is fairly general for many other (pentadienyl)metal carbonyl complexes. Nonetheless, there are a few cases in which analogous pentadienyl and cyclopentadienyl metal carbonyl complexes exhibit similar C-O stretching frequencies.[41] However, in these cases the presence of additional ligands complicated the situation by preferentially occupying poorer backbonding locations, allowing the carbonyl ligands to accept more electron density than they could have had they been equally distributed through all sites. In addition to the IR spectral studies, ESR[27,40,42] and Mössbauer[43] data have also been interpreted on the basis of stronger pentadienyl backbonding.

Given the greater accepting ability of pentadienyl vs. cyclopentadienyl, the question naturally arises as to what mechanism leads to this difference. As will be discussed subsequently, in analogous compounds, pentadienyl ligands appear generally to be more strongly bound than C_5H_5 and could be functioning as both better donors and acceptors than C_5H_5. It would seem, therefore, that the greater electron accepting properties of pentadienyl must arise from an enhancement of the δ backbonding interaction (e.g., **14**), usually regarded as negligible for C_5H_5.[44] This enhancement could occur for both energetic and geometric reasons, the latter reflecting the much shorter metal to ligand plane separation. MO calculations have indeed provided support for significantly enhanced δ backbonding interactions,[34] although quantitative comparisons are not readily made due to the lower symmetry of the pentadienyl ligand and its complexes, which leads to much more complex MO diagrams,[45] and even mixing of donor/acceptor behavior (e.g., σ/δ) in some of the orbitals.



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Nonetheless, the MO calculations do indicate that the pentadienyl ligands acquire substantially more negative charge in their complexes. In $Ti(C_5H_5)(C_5H_7)(PH_3)$,[34] for example, the net charge on C_5H_7 is calculated to be −0.39, whereas for C_5H_5 it is only −0.18. Given these and other data (*vida infra*), it becomes appropriate in at least some circumstances to regard pentadienyl as a strong δ acid, much as CO is regarded as a strong π acid.

D. INFLUENCES OF METAL OXIDATION STATE

Perhaps the feature of pentadienyl ligands which has proven to be most of a surprise has been the great preference these species have shown for bonding to metals in low oxidation states. To date, there seem to be no (η^5-U) pentadienyl complexes of transition metals in the +4 oxidation state, and relatively few in even the +3 oxidation state. Thus, analogs to the ubiquitous $M(C_5H_5)_2Cl_2$ complexes are unknown, although some might be stable at low temperatures.[46] Even, reactions of even Zr(IV) and Hf(IV) chlorides with pentadienyl anions lead to facile, spontaneous reduction to divalent complexes, such as $M(2,4\text{-}C_7H_{11})_2(PEt_3)$[13a] and $Zr[1,5\text{-}(Me_3Si)_2C_5H_5]_2$.[4] What is a tremendously rich area of C_5H_5 chemistry thus seems (as yet, anyway) to have no analog for the pentadienyl ligands. There are a number of factors that can be considered to lead to such a dramatic difference. To begin with, it might be of value to include allyl ligands in our comparisons. One can note that C_5R_5 complexes are known in which the transition metal is in the formal oxidation state of +7 (e.g., $Re(C_5Me_5)O_3$),[47] while for allyl ligands, at least the +4 state has been reached (e.g., $Mo(C_3H_5)_4$, $W(C_3H_5)_4$,[48] and η^3-pentadienyl complexes such as $Ru(C_5Me_5)(\eta^3\text{-}2,4\text{-}C_7H_{11})Cl_2$[49]), and as noted above, pentadienyl complexes of transition metals in the +3 oxidation state are known (e.g., $Co(C_5H_5)(2,4\text{-}C_7H_{11})^+$, $Cr(C_5H_5)(Pdl)(L)^+$, and $Re(2,4\text{-}C_7H_{11})(H)_2[P(C_6H_5)_3]_2$[29,50,51]). To explain the difference between C_5H_5 and the two open ligands, one can first recognize that for a metal in a relatively high oxidation state, one can expect any δ backbonding interaction to be weak, and perhaps completely negligible. This should not prove detrimental for C_5H_5, for which such interactions rarely if ever are sizeable. For pentadienyl, if not allyl, however, the lack of the δ backbonding interaction would lead to less negative charge on the open ligand relative to C_5H_5, consistent with the HOMO of C_5H_5 being bonding vs. nonbonding for C_3H_5 and C_5H_7.[52] With higher radical character for the open ligands, one could then expect it to become much easier to lose them, whether through spontaneous dissociation or via inter- or intramolecular coupling reactions, which are quite common.[53] For C_5H_5, any coupling reaction would be less likely as much more resonance delocalization energy would be lost due to its aromaticity.[54] The apparent difference between C_3H_5 and C_5H_7 may also be understood on the basis of radical stabilities. For the allyl group, radical or charge character is delocalized over the two terminal positions, whereas for C_5H_7, delocalization occurs over the 1, 3, and 5 positions. The pentadienyl radical is thereby stabilized relative to the allyl radical, thus promoting the former's release, at least when considering complexes with comparable hapticities.[55] It should be noted that U(IV) pentadienyl complexes are known, $U(2,4\text{-}C_7H_{11})(BH_4)_3$ and $U(2,4\text{-}C_7H_{11})_2(BH_4)_2$,[56] and their stabilities could be attributed to the greater ionic character generally found for actinide complexes, which then renders it more difficult to release the pentadienyl fragment as a radical species.

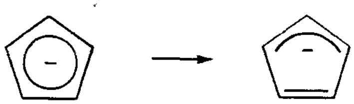
Perhaps a simpler way to account for the preference of pentadienyl ligands for metals in low oxidation states would be to recall these ligands′ tendency toward functioning as strong δ acids, so that like the normally strong π acid CO, bonding to metals in low oxidation states would generally be favored.[57] One could also imagine that the large girth of the pentadienyl ligand may lead to problems in achieving effective overlap with metals in higher oxidation states, for which the valence orbitals are significantly contracted.

Despite the above discussion, it seems inevitable that some higher oxidation state transition metal pentadienyl complexes will ultimately be synthesized. In such efforts it may be advantageous to focus on mono(pentadienyl)metal complexes, in order to avoid at least intramolecular coupling reactions, and to alleviate steric crowding. Furthermore, steric blocking of the 1, 3, and 5 positions could be used to hinder coupling reactions in general. This has been achieved with the $3\text{-}CH_3\text{-}1,5\text{-}(Me_3Si)_2C_5H_4$ ligand, which allowed for the isolation of the first purely Mn(II) pentadienyl complex,[58] although in at least some other attempts at preparing metal complexes with this ligand, crystalline products did not appear isolable. Alternatively, perhaps the presence of strong π donor ligands such as amides or alkoxides would add sufficient electron density to the metal center that strong δ backbonding would still be feasible even for a metal center in a formally high oxidation state.[59] Or, perhaps for the appropriate late, presumably 2nd or 3rd row, metal center, for which the d orbitals are fairly low in energy anyway, rendering backbonding interactions less important, the lower oxidation state species might not achieve their special stabilization. On the other hand, perhaps for the large early metals, their electropositive natures might in the right case lead to sufficient negative charge on a pentadienyl ligand that reductive processes involving pentadienyl radical contributions may be retarded. Possibly even all of the above will be found feasible, and the current lack of higher oxidation state complexes will simply have been a consequence of the approaches used for their preparations. These unresolved questions appear to represent one of the most interesting fundamental challenges remaining in metal pentadienyl chemistry.

E. BINDING AND REACTIVITY COMPARISONS FOR PENTADIENYL AND CYCLOPENTADIENYL

While many of the features of the pentadienyl ligands described in sections B-D were unrecognized early on, at least some indications could be had from the outset that these ligands should have significant promise in inorganic and organometallic chemistry. As was the case with cyclobutadiene[60] and allyl ligands,[61] as well as uranocene,[62] many of these indications were derived from an examination of the π molecular orbitals of the organic fragment. Thus the fact that the filled π molecular orbitals (and the HOMO in particular) of the C_5H_7 anion are on the average significantly higher in energy than those of the C_5H_5 anion should render the pentadienyl anion a better donor.[1,6,52] The fact that the empty C_5H_7 molecular orbitals (and the LUMO in particular) are on the average lower in energy than those for the C_5H_5 anion should likewise render pentadienyl a better acceptor. Clearly this indicates that pentadienyl could be a much more strongly bound ligand than even the "stabilizing" C_5H_5. In essence, the high resonance stabilization (and aromaticity) of C_5H_5 leads to a lesser tendency for it to engage in bonding interactions with other species. Indeed, PES and Mössbauer data have provided clear evidence for much greater metal-ligand orbital mixing in the pentadienyl complexes[43,45]. On the other hand, subsequent insight into the pentadienyl ligand has revealed an offsetting factor for smaller (later) metal centers, for which there may be poorer overlap with the relatively large pentadienyl ligand, as well as enhanced steric crowding.[6,7]

In terms of reactivity comparisons, it proved helpful that the higher reactivity of the allyl ligand relative to C_5H_5 had been correlated with the much lower loss in resonance stabilization energy for the conversion of a delocalized allyl anion to a localized anion (0.83 β) as compared to the loss which resulted for conversion of a fully delocalized C_5H_5 anion to a partially delocalized anion (1.64 β, below).[61] As the conversion of a fully delocalized pentadienyl anion to a partially delocalized anion is accompanied by a loss of only 0.64 β units of resonance stabilization energy, one would therefore anticipate $\eta^5 \rightleftarrows \eta^3$ (and $\eta^3 \rightleftarrows \eta^1$) interconversions to be far more common than what is observed for the C_5H_5 ligand.[1,6,52] Such has proven to be the case. Likewise, since far less stabilization energy could be lost during coupling of a pentadienyl (vs. the aromatic C_5H_5) ligand, pentadienyl ligands were expected to be quite prone to "allyl-like" reactivity, particularly coupling reactions. This has indeed been demonstrated to a very high degree for naked metal reactions,[63] metal film depositions,[64] preparations of inorganic materials through oxidations of pentadienyl complexes,[65] coupling reactions with unsaturated organic molecules,[34,66] nucleophilic additions,[7,13i,67] dehydrogenations, including conversions to metallabenzenes,[68] and polymerization catalysis.[69]



While the π molecular orbital comparisons provided great initial impetus to the notion that pentadienyl ligands had perhaps been overlooked, other helpful hints were also gleaned from the literature. For example, it had been reported that methyl substitution in allyl complexes could lead to significant thermal stabilization,[70] and this certainly was responsible in large part for early successes in the metal pentadienyl field. Likewise, the fact that the U conformation of a pentadienyl anion may be preferentially stabilized through 2,4-substitution has appeared to be important for the successful preparations of at least some η^5-U dienyl complexes,[71] although in other cases, the mode of substitution may seem unimportant.

In any event, the early expectations that pentadienyl could be both more strongly bound and more reactive than cyclopentadienyl have been realized. Good examples of this are provided by the half-open titanocenes,[34] such as $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$, for which a structural study has revealed much shorter average Ti-C bond distances for the open vs. closed dienyl ligands (2.240(3) vs. 2.346(4) Å, Fig. 5). Supporting MO calculations revealed a correspondingly higher average Ti-C bond index for the open vs. closed dienyl ligand (0.35 vs. 0.11). Nonetheless, the more strongly bound open dienyl ligand is still more reactive, preferentially undergoing coupling reactions with a wide variety of unsaturated organic molecules.[34a,66] It is the high stabilization of the aromatic C_5H_5 ligand which leads to its reluctance to undergo change – whether by engaging in bonding interactions with a metal, or through coupling reactions which would remove its aromaticity.

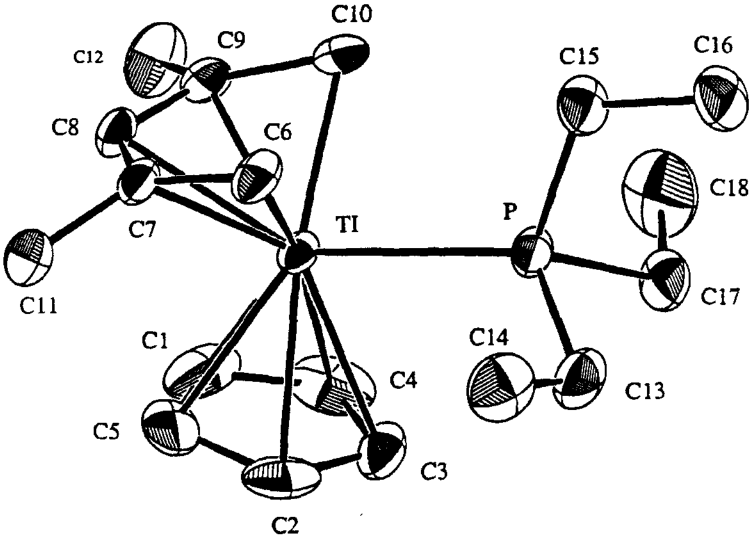
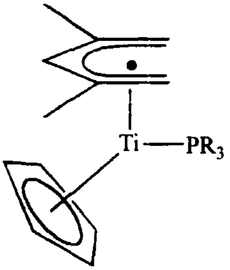


FIGURE 5 Solid State structure of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$[34a]

II. MODIFIED PENTADIENYL LIGANDS AND BONDING MODES

While this article has as its primary focus the properties of simple pentadienyl ligands, it is of interest to at least draw some attention to closely related ligands, as well as to additional bonding modes observed for pentadienyl ligands. Historically, edge-bridged pentadienyl complexes must be considered of principal importance, some like $Fe(C_6H_7)(CO)_3^+$ and $Mn(C_6H_7)(CO)_3$[72] having been prepared years before $Fe(C_5H_7(CO)_3^+$, the first simple pentadienyl complex.[73] Prior to 1980, in fact, most pentadienyl studies focussed on these edge-bridged species, and notable utility has even been found in synthetic organic applications.[74] Since that time, however, there has been a significant turnaround in the emphasis on dienyl chemistry, so that species such as open or half-open metallocenes were often first prepared for non-bridged pentadienyl ligands. As the data suggest that the edge-bridged ligands may be surprisingly different from the non-bridged species, it is important to gain some insight into the origins of these differences. As indicated above, some of the earliest edge-bridged complexes predated their open metallocene analogs. The "pseudo-ferrocenes"[75] and $M(C_8H_{11})_2$[76] (C_8H_{11} = cyclooctadienyl; M = Cr, Ru) are just such species. However, their general properties are not such as to suggest significant differences relative to their younger $M(2,4\text{-}C_7H_{11})_2$ analogs. However, a wider variety of $M(6,6\text{-dmch})_2$ (dmch = dimethylcyclohexadienyl; M = Ti, V, Cr, Fe) complexes has been prepared, along with some mono(ligand) adducts for the titanium and vanadium complexes.[77] What has been especially intriguing is the fact that the C-O stretching frequency of $V(6,6\text{-dmch})_2(CO)$ is intermediate between those of $V(C_5H_5)_2(CO)$[39] and $V(C_5H_7)_2(CO)$[40] (1912 vs. 1881 and 1962 cm^{-1}). Thus, it may be that the 6,6-dmch ligand has electronic properties intermediate between those of C_5H_7 and C_5H_5. It is tempting to attribute this to geometric factors, particularly the shorter open edge separation (C1--C5) for the 6,6-dmch ligand relative to C_5H_7, which could then lead to a reduction in the δ backbonding interaction, perhaps as a consequence of the fact that the ligand would need to back away for geometrical reasons in order to maintain similar M-C distances. The red $Cr(6,6\text{-dmch})_2$ also bears more similarity to the scarlet chromocene than to the green $Cr(2,4\text{-}C_7H_{11})_2$. Subsequently, a fuller series of $M(C_8H_{11})_2$ complexes has been prepared (M = Ti, V, Fe),[78] and along with the previously reported $Cr(C_8H_{11})_2$, structurally and spectroscopically characterized. Many of the structural features are quite similar to those of the $M(2,4\text{-}C_7H_{11})_2$ complexes, and will therefore not be described here. Interestingly, spectroscopic data reveal some significant differences between the seemingly similar edge-bridged dienyl ligands. Thus, the green $Cr(C_8H_{11})_2$ seems more similar to $Cr(2,4\text{-}C_7H_{11})_2$, rather than to the red $Cr(6,6\text{-dmch})_2$. On the other hand, the edge bridges for both the $M(6,6\text{-dmch})_2$ and the $M(C_8H_{11})_2$ (M = Ti, V) complexes lead to significant retardation of their tendencies to incorporate additional 2 electron donor ligands.[77,78] In fact, structural studies of $Ti(C_5H_5)(6,6\text{-dmch})(PMe_3)$ and $Ti(C_5H_4CH_3)(C_8H_{11})(PEt_3)$[79] reveal that in contrast to $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$[34] **(15)**

and related species (*vide supra*), the phosphine ligands in the edge-bridged complexes reside near the central dienyl position, as in **16** (Fig. 6), clearly reflecting the greater steric influence of the edge-bridges. However, in M(6,6-dmch)$_2$(L) (Fig. 7) and M(C_8H_{11})$_2$(L) complexes, the 2 electron donors are again found by the electronically open edges; presumably, were these ligands to reside by the central carbon atoms, even worse repulsions would be generated as the two edge bridges were forced together. Notably, the isolations of Zr(C_5H_5)(6,6-dmch)(PMe_3)$_2$ and Zr(C_5H_5)(C_8H_{11})(PMe_3) indicate that the C_8H_{11} ligand is sterically more demanding than 6,6-dmch.[80]



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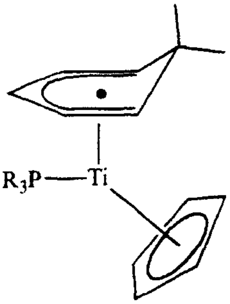

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Although there are clearly very substantial differences between edge-bridged and non-bridged pentadienyl ligands, there is at least one further regard in which their complexes are similar. Thus, the half-open metallocenes for titanium and zirconium, whether edge-bridged or not, all possess much shorter M-C bonds for the electronically open dienyl ligands as compared to their cyclopentadienyl ligands.

One final example of an edge-bridged complex merits attention. Some edge-bridged dienyl analogs of a constrained geometry olefin polymerization catalyst (e.g., **17**) have recently been reported.[81] Notably, with the proper cocatalyst this species becomes a very active polymerization catalyst. Furthermore, it is an example of a higher oxidation state metal dienyl complex, although given the aforementioned intermediacy of the edge-bridged dienyl ligands′ electronic properties between those of C_5H_5 and C_5H_7, it would seem that higher oxidation states should be more accessible for the edge-bridged complexes. However, it can also

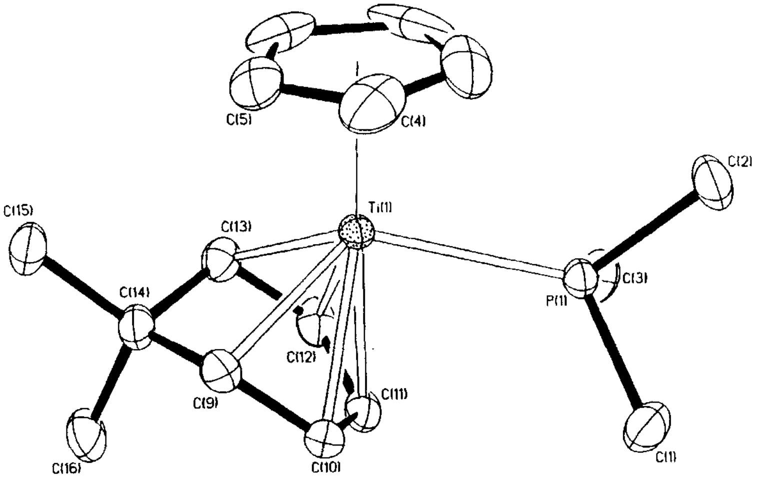
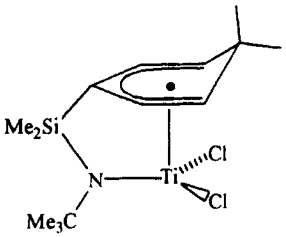


FIGURE 6 Perspective view of Ti(C_5H_5)(6,6-dmch)(PMe_3)

be noted that the complex contains a π donating amide group along with some steric blocking of the 1, 3, and 5 positions, and both of these circumstances could aid in stabilizing the higher oxidation state (*vide supra*).



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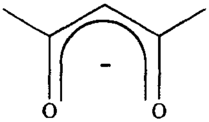
Another potentially rich modification to a dienyl ligand involves the formal replacement of skeletal carbon atoms by heteroatoms. Such alterations have led to very profound effects in cyclopentadienyl chemistry, one example being some chromium pyrollyl complexes which are extremely active catalysts for the selective trimerization of ethylene to 1-hexene.[82] In fact, one heteroatom analog of the 2,4-C_7H_{11} ligand is already quite familiar – the acac ligand (**18**). Of course the acac ligands almost always bond solely through oxygen atom lone pairs, although a few exceptions involving soft metal centers are known.[83] Conceivably, the replacement of CH_3 groups in acac by CF_3 could lead to π coordination, as CF_3 substituents have already been observed to bring about significant effects in regular pentadienyl complexes.[84] However, η^5 (π) coordination has been observed for a variety of complexes in which one terminal CH_2 group of a pentadienyl ligand has been replaced by O, S, or an NR group.[85] Included in this group is the 2,4-dimethyloxopentadienyl ligand, the hybrid between acac and 2,4-C_7H_{11}. A mixed (η^4) σ/π mode of coordination has been demonstrated for an azapentadienyl complex, in which a combination of lone pair and π allyl coordination leads to a net 5 electron donation.[86] Consideration of spectral data for a species formulated as an η^5-azadienyl complex [851] has led to the suggestion that it too may actually involve the mixed σ/π coordination.[87]



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One final aspect of interest relates to the ability pentadienyl ligands have shown to bridge two or more metal centers. In some cases linked bis(pentadienyl) ligands have been used either to chelate a single metal center, or to bridge two metals,[88] while conjugated "open fulvalene" ligands have also been used to bond to two metal centers.[89] In other cases, a single dienyl ligand has been used to coordinate to two or even three (through $\eta^1,\eta^{2'},\eta^{2''}$ coordination) metal centers.[90]

Besides discussing what has been learned about pentadienyl ligands, it is also advantageous to examine some cases in which studies of metal pentadienyl compounds have provided interesting insight into other areas of inorganic and organometallic chemistry. The first example involves the cone angles of phosphite ligands. As has been noted earlier, the 14 electron open titanocene, Ti(2,4-$C_7H_{11})_2$, is sterically crowded even prior to the coordination of any additional ligand. As a result, only

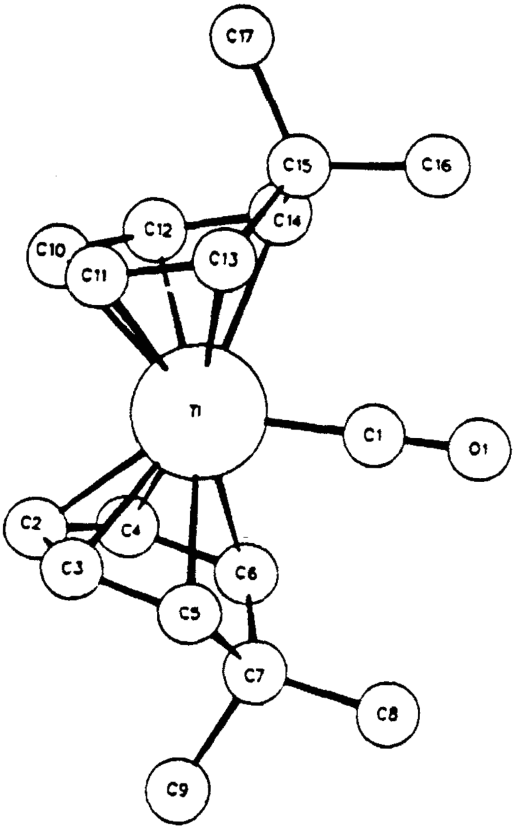
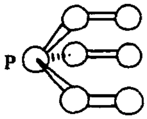


FIGURE 7 Solid state structure of Ti(6,6-dmch)$_2$(CO)[11]

one additional ligand can be tolerated in the coordination sphere, and even its coordination is typically highly reversible. Given the generally expected dominance that phosphine steric effects seem to have in determining their strength of binding to a metal complex, one would have to expect these effects to be especially important when dealing with a sterically crowded metal complex. Hence, the coordination of phosphine and phosphite ligands to Ti(2,4-C_7H_{11})$_2$ was expected to correlate predictably with the cone angles of these ligands. For alkyl phosphines and PF_3 this expectation was realized; however, the coordination by phosphites such as $P(OMe)_3$ and $P(OEt)_3$ was anomalously weak (Table I)[33]. Both phosphites supposedly had cone angles only slightly greater than PF_3, and much smaller than PMe_3,[91] yet their binding was quite poor. This could not arise from an electronic effect, as the comparably or larger-sized strongly donating (PMe_3) and strongly accepting (PF_3) ligands bound well. Ultimately it was recognized that the cone angles originally estimated for phosphites were based on a conformation in which the three alkoxy arms were bent back away from the metal center, as in **19**, and while that was a reasonable assumption at the time, a large number of subsequent structural studies has demonstrated that that conformation is, at least to date, nonexistent. Such an arrangement would place the oxygen-bound carbon atoms well within a van der Waals separation, so that the smallest attainable conformation is actually that of **20**,[92] in which only one arm is bent back, the other two being bent to the side. Significantly, a cone angle for structure **20** could be estimated to be 128° for $P(OMe)_3$, or 134° for $P(OEt)_3$. As can be seen in Table I, one now does achieve a strong correlation between the strength of binding and the cone angles of these ligands. As a test of the above conclusion, the strength of binding for a cage phosphite, $P(OCH_2)_3CEt$, was measured, and found to be 16.3 ± 0.9 kcal/mole. Obviously, such a ligand is constrained to adopt a structure analogous to **19**, so that its originally estimated cone angle of 101° must be considered accurate. That the binding of an obviously small phosphite is now substantially increased can be taken as confirmation of the conclusion that phosphite cone angles are not so small as had been assumed. Furthermore, the observation that the binding of the cage phosphite is 1.1 ± 0.4 kcal/mole less than that of the slightly larger PF_3 indicates that there is at least a small electronic effect operative in favor of π accepting ligands. Given this observation, one could not hope to explain the weak binding of $P(OMe)_3$ and $P(OEt)_3$, compared to that of the supposedly larger PMe_3, using the original cone angles.



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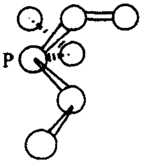

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TABLE I Bonding and Binding Parameters for $Ti(2,4\text{-}C_7H_{11})_2\text{-}PX_3$ Complexes

PX_3	*-ΔH, kcal/mole*	*Cone angle*[a]	*d(Ti – P), Å*
PF_3	17.4(8)	104°	2.324(1)
$P(OCH_2)_3CEt$	16.3(9)	101°	2.437(2)
PMe_3	14.5(8)	118°	2.550(2)
PMe_2Ph	12.9(5)	122°	
$P(OMe)_3$	11.4(9)	107° (128°)	
$P(OEt)_3$	10.6(6)	109° (134°)	2.472(4)
PEt_3	10.0(1)	132° (137°)	

a. Values in parentheses are revised cone angles.

Additional insight into metal-phosphine binding was obtained from structural studies on the ligand adducts of $Ti(2,4\text{-}C_7H_{11})_2$.[93] As can be seen in Table I, the Ti-P bond lengths are clearly not related to the Ti-P bond strengths, although the most strongly bound ligand, PF_3, does lead to the shortest Ti-P distance. In particular, while the Ti-PMe_3 bond is longer than the Ti-$P(OEt)_3$ bond, it is nonetheless stronger. In fact, numerous times the observation has been made that stronger π-acid ligands lead to shorter M-P distances compared to stronger donors.[94] Several explanations have been offered for this trend, a fairly common one being that the M-P bonding becomes enhanced through additional π bonding.[95] Alternatively, it has been proposed that as the substituents attached to phosphorus become more electronegative, the s character of the phosphorus atom's lone pair will increase, leading to a shorter extension, and hence a shorter M-P distance.[96] There is, however, one other mechanism by which substituents on phosphorus could affect the M-P bond distance. As the substituents become more electronegative, the net charge on the phosphorus center would increase, leading to a contraction of its orbitals, again leading to a shorter M-P separation.[97] From the data in Table I, the first of the three explanations may be discounted. Thus, given the significantly weaker binding of the phosphites relative to PMe_3, it is clear that there is no additional bonding to account for the shortening of the Ti-$P(OR)_3$ bond. Furthermore, the significantly stronger bonding of the cage phosphite can be observed to have relatively little effect on the Ti-P bond distance, relative to the non-cage phosphite complexes. As a result, one must conclude that the shortening occurring in M-P bond distances is not so much related to bond strengths, but to shortening of the extension of the phosphorus center's lone pair, due either to an increase in s orbital character and/or to an increase in atomic charge. Similar observations have also been made for complexes with boranes or the $Fe(CO)_4$ fragment.[98]

One final example of insight that has been provided by pentadienyl complexes to a peripheral area arose from studies of various coupling reactions between unsaturated organic compounds and titanium or zirconium pentadienyl complexes. In some of these reactions, one finds the metal center in close proximity to saturated carbon atoms, at separations that may be comparable to, or even significantly shorter than, distances to unsaturated, metal-bound carbon atoms. The data that have been obtained establish that the metal centers in these complexes actually interact with C-C or C-N single bonds.

The first such complex was isolated from the reaction of $Ti(C_5H_5)(C_8H_{11})(PEt_3)$ with $C_6H_5C_2SiMe_3$.[99] As opposed to the analogous reaction for $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$,[100] in which two equivalents of alkyne were incorporated, three equivalents were incorporated for the edge-bridge complex, leading to complex **21** (Fig. 8), which formally has a 14 electron count. However, a saturated carbon atom, C7, is only 2.293(7) Å away from the metal center – closer than C4, C5, or any of the Cp carbon atoms. An adjacent saturated atom, C2, is also only 2.579(7) Å from the metal center. This can be compared to a value of 2.52 Å for a complex with a (C-Si)→Ti agostic interaction,[101] and raised the possibility that there could be a (C2-C7)→Ti agostic interaction in complex **21**. A subsequent theoretical study indicated that there was indeed a significant (C2-C7)→Ti agostic interaction,[99] but surprisingly at first, even stronger interactions were indicated for the C2-C3, C6-C7, and C7-C8 single bonds. In retrospect, this seems reasonable, however, given that C3, C6, and C8 are all closer to the metal than either C2 or C7, so that the latter three bonds are likewise closer than is the C2-C7 bond. These three interactions may therefore be considered to be analogous to an α (C-H)→M agostic interaction arising from a bound alkyl group.[102] Notably, the Ti-C7 bond index was found to be 0.168, compared to values of 0.182–0.209 for C4, C5, and the Cp carbon atoms, whereas for C2, a value of 0.082 was found. The calculated stabilizations for the four C-C bonds were found to total a remarkable, but not quantitative, 57 kcal/mole. A very nice correlation was observed between the individual stabilization energies and the ^{13}C-^{13}C coupling constants determined through INADEQUATE NMR methods (Table II). Values for normal C-C single bonds generally fall in the range of 30–39 Hz, as was the case for all other single bonds here. As can be seen in the Table, the ^{13}C-^{13}C couplings for the four agostic C-C bonds range from 17.9–29.8 Hz, the largest coupling corresponding to the weakest interaction, and the weakest coupling to the strongest interaction, involving the significantly lengthened (to 1.596(8) Å) C6-C7 bond. One other notable indication of the interactions was provided by the ^{13}C-H coupling constant of 149 Hz for C7-H (135 Hz for C2-H), compared to a value of ca. 125–130 Hz which would have been expected.

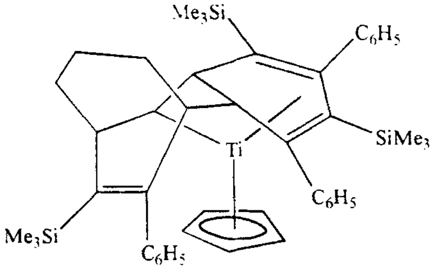

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TABLE II Comparison of ^{13}C-^{13}C Coupling Constants with Theoretical Estimates of Agostic (C-C)→Ti Interaction Energies

Interacting Bond	*Interaction Energy, kcal/mole*	*$J(^{13}C$-$^{13}C)$, Hz*
C6-C7	20.2	17.9
C2-C3	14.3	24.8
C7-C8	12.2	21.4
C2-C7	10.3	29.6

From the relatively similar reaction of $Ti(C_5H_5)(C_8H_{11})(PMe_3)$ with $C_6H_5C_2SiMe_3$, a much different product (**22**) was isolated, in which only two equivalents of alkyne were incorporated (Fig. 9).[79] In this case the complex again formally possessed a 14 electron count. Given the

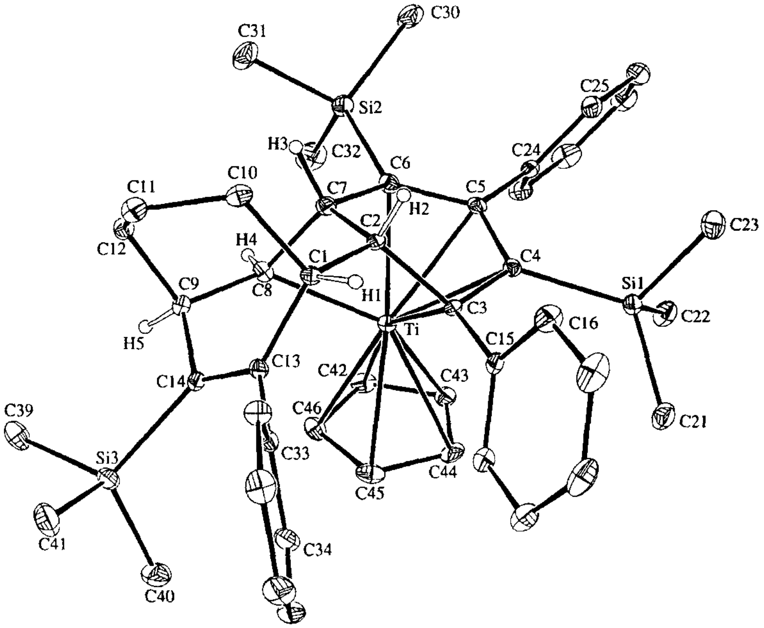


FIGURE 8 Perspective view of the structure of the coupling product of the $Ti(C_5H_5)(C_8H_{11})$ fragment with three equivalents of $C_6H_5C_2SiMe_3$[99]

significant electron deficiency, it seems surprising that the metal center would settle for σ-allyl coordination. Indeed, both manganese and iron complexes are known in which a similar bicyclic species achieves η^3-allyl and η^2-olefin coordination (the η^2-olefin coordination in **22** has been represented as a metallocyclopropane for clarity).[103] However, several telling features indicate that once again an agostic interaction is present, in this case involving the C5-C10 bond. Thus, this bond is anomalously long (1.593(11) Å, cf., 1.596(8) Å above) and the titanium center is only 2.541(8) Å from the saturated carbon atom C5. Although one might consider the possibility of a (C5-H)→Ti agostic interaction, this should be accompanied by a dramatic drop in the ^{13}C-H coupling constant, whereas instead it is essentially the same as that of the other bridgehead CH group (123–124 Hz). One therefore observes an unusual situation in which the apparent (C5-C10)→Ti agostic interaction is

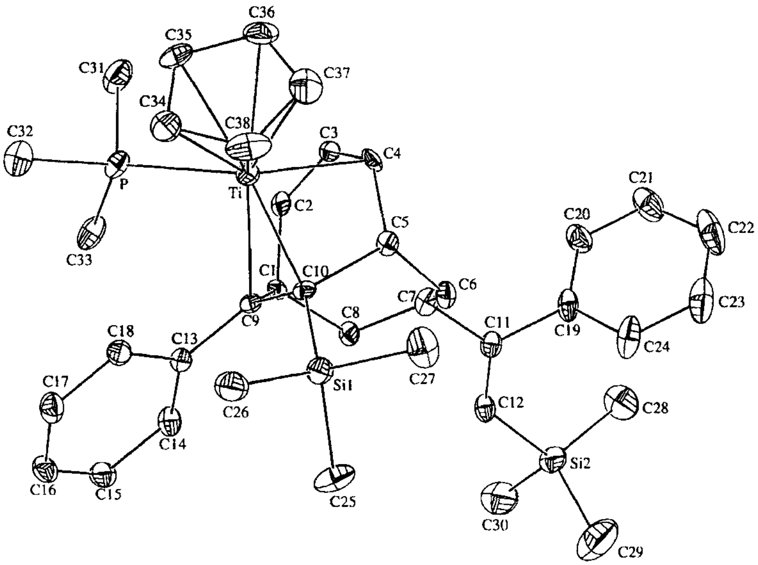
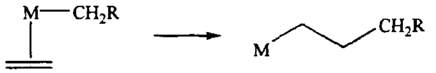


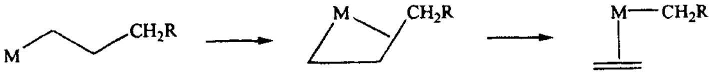
FIGURE 9 Perspective view of the structure of the coupling product of $Ti(C_5H_5)(C_8H_{11})(PMe_3)$ with two equivalents of $C_6H_5C_2SiMe_3$

favored relative to the seemingly more normal olefin→M coordination. It seems likely that geometric constraints imposed by the bicyclic system could play some role in disfavoring the π-allyl coordination; nonetheless, the fact that such coordination is possible for both manganese and iron complexes indicates that even in an unstrained situation the agostic interaction with titanium must be unexpectedly competitive with the olefin coordination. In retrospect this is not too surprising, since no bis(olefin) complexes of titanium are known. This observation may well have implications concerning the mechanism of Ziegler-Natta and related polymerizations. If one considers a typical (migratory) insertion process, e.g., eq. (1), it is generally depicted as a



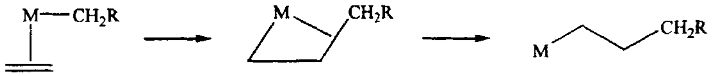
(1)

single step process, although intervening (C-H)→M interactions might be included in the mechanism.[104] However, if one considers the microscopic reverse, a C-C activation process (eq. (2)), it is obvious that a (C-C)→M



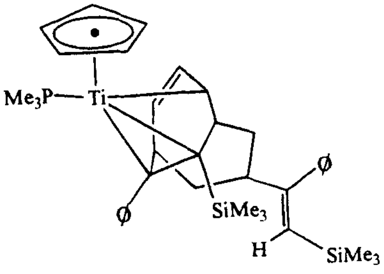
(2)

intermediate needs to be included. Thus, by microscopic reversibility, such an intermediate will occur in the migratory insertion process (eq. (3)). That



(3)

this intermediate could be of importance in the polymerization process derives from the observation that a (C-C)→Ti agostic interaction can be surprisingly competitive with olefin coordination. One can see that in the first step of the above process, olefin→M coordination is replaced by an agostic (C-C)→M interaction. Thus, if the latter interaction is relatively competitive with the olefin coordination, it could play an important role in promoting the reaction, by reducing the overall energy of activation. Of course, subsequent rearrangement of the product to a species with a presumably stronger (C-H)→M interaction may occur.



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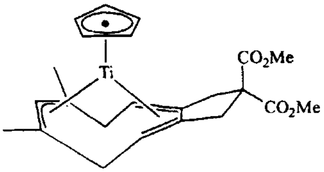
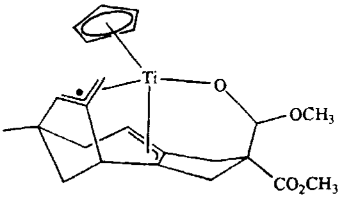
The above cage-like titanium complexes bear some resemblance to carboranes, in which the presence of an electrophilic boron center leads to electron deficient bridge bonding interactions with C-C bonds, even leading to C-C bond cleavage.[105] In fact, in other cage-like coupling products, such as **23**, in this case derived from the $Ti(C_5H_5)(2,4\text{-}C_7H_{11})$ unit and a diyne, one again observes short Ti-saturated carbon atom distances, and even slow but selective and quantitative C-C bond cleavage,[100] yielding **24**. Complex **22** also appears to undergo a rearrangement, although the product's constitution has not yet been determined.

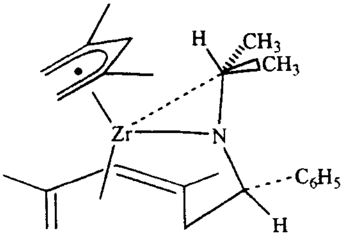


23



24

It would naturally be of interest to try to increase the extent of the (C-C)→M interaction, and thereby at least approach, if not promote, C-C activation. An obvious strategy, then, would be to replace titanium by zirconium, which forms stronger bonds and fewer electron deficient complexes, and should thus lead to stabilization of both (C-C)→M agostic species, as well as the oxidatively added (bond activated) extreme.[106] In fact, in a complex containing what may be considered to be a (B-C)→Zr interaction, an elongation by ca. 0.11 Å of two B-C bonds was observed (cf., ca. 0.04–0.05 Å above for the C-C bonds in **21** and **22**),[107] compared to a B-C bond distance in a similar compound.[106a] Indeed, a coupling product of the $Zr(2,4\text{-}C_7H_{11})_2$ unit with $C_6H_5C(H){=}N(i\text{-}C_3H_7)$ demonstrates the reasonableness of this approach.[80] Thus, in the formally 16 electron complex (**25**, Fig. 10), the zirconium center makes a very close approach to the N-bound carbon atom of the isopropyl group (2.772(4) Å, only ca. 0.14 Å longer than one of the bonded carbon atoms). Such a close contact was not present in a related titanium complex (cf., ∢Ti-N-C = 130.4(5)° vs. ∢Zr-N-C = 103.5(2)°), in which the remaining $2,4\text{-}C_7H_{11}$ ligand was replaced by a $C_5H_3(t\text{-}C_4H_9)_2$ ligand.[79] Although at first it was suspected that a (C-H)→Zr interaction was present, the ^{13}C-H coupling constant was not found to be low, indicating that the actual agostic interaction involves the N-C(i-propyl) bond. The complex does seem to undergo a slow rearrangement, but the nature of the product is not known.



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Concerning the goal of generating stronger (C-C)→M agostic interactions, and of more examples of C-C bond activation reactions, several half-open zirconocenes have been synthesized, including $Zr(C_5H_5)(2,4\text{-}C_7H_{11})(dmpe)$, $Zr(C_5H_5)(C_8H_{11})(PR_3)$ (R = Me, Et), $Zr(C_5H_5)(dmch)(PMe_3)_2$, and $Zr(C_5H_5)(tmch)(PMe_3)_2$ (dmch = 6,6-dimethylcyclohexadienyl; tmch = 2,6,6-trimethylcyclohexadienyl).[80] Structural studies have been carried out for one complex of each ring size, and reveal the expected shorter distances for the electronically open dienyl ligands. These species should then be ideal for generating new complexes which display either (C-C)→Zr interactions or C-C bond activation chemistry. It is important to note that C-C activations by zirconium complexes have been demonstrated, even in polymerization processes.[108]

It is also important to recognize there could be a variety of complexes already reported in which fairly short M--C nonbonded contacts are also present, but their extent and type (attractive vs. repulsive) may either not have been established,[100,109] or perhaps the contacts have been overlooked altogether. Given that there actually appears to be a "fuzzy" interface between bonding and nonbonding regimes,[110] it is certainly important that data bearing on these points be obtained. One can expect that greater attention will be given to such species in the future.

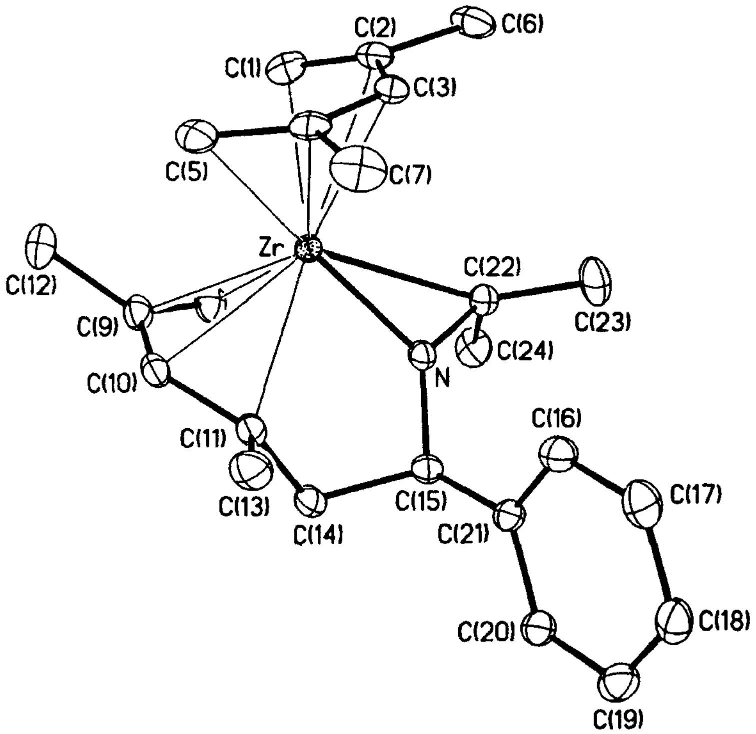

FIGURE 10 Structure of the coupling product of the $Zr(2,4\text{-}C_7H_{11})_2$ fragment with $C_6H_5C(H){=}N(i\text{-}C_3H_7)$

III. CONCLUSIONS

The chemistry and bonding of metal pentadienyl complexes have proven to be remarkably rich. The pentadienyl ligand may bond even more strongly to a metal center than does the cyclopentadienyl ligand, while still retaining much higher chemical reactivity. Pentadienyl ligands are particularly sterically demanding, which could prove important in the preparation of new, selective polymerization catalysts.[111] While these ligands have been found to serve as stronger (δ) accepting ligands than C_5H_5, this can be tempered somewhat through the inclusion of edge bridges, which, however, also greatly increase steric demands. Of course, the pentadienyl ligands display a rich variety of η^1, η^3, and η^5 bonding modes (plus others for the heteroatom analogs). While an understanding of many of the fundamentals about pentadienyl ligands has now been gained, many frontiers remain to be explored, such as higher oxidation state species. Clearly, many opportunities for both fundamental and applied contributions remain, and it is hoped that these will receive appropriate attention.

Acknowledgements

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