distances are on the average only ca. 0.025 Å longer than the corresponding distances in $Fe(2,4-C_7H_{11})_2$, it can be concluded that the "electron imbalances"[16] of the two systems are essentially equal at zero.[25] Thus, the terminal $Mn(3-C_6H_9)_2$ fragments must obtain the noble gas configuration by either forming formal single bonds to the central manganese atom or by each abstracting a single electron from the central manganese atom. The latter scheme seems more appropriate, and the valence designations for the complex would then involve Mn^+ for the terminal manganese atoms and Mn^{2+} for the central manganese atoms. In essence, the complex may then be regarded as the associated salt of Mn^{2+} and $Mn(3-C_6H_9)_2^-$. The ability of high spin Mn^{2+} to adopt such ionic configurations is, of course, well exemplified in manganocene itself. The formal positive valences of all three manganese atoms explains their mutual attractions to the pentadienyl ligands as well as the shorter metal–metal separation than that observed in the linear $Mn_3(CO)_{14}^-$ ion [2.895 (5) Å].[26] The coordination geometry of the central Mn^{2+} ion is particularly unusual in that it closely approximates an *edge*-bicapped tetrahedral geometry [the C(5)–Mn–C(5)′ angles ranging from 103.6 (3) to 118.4 (3)° with Mn–C(bridge) = 2.334 (4) Å]. An alternative description is that there are two nearly perpendicular trigonal planar sets of bonds surrounding Mn(2) for which the appropriate Mn(1 or 3)–Mn(2)–C(bridge) angles average 127.3 (1)° while the C(bridge)–Mn(2)–C(bridge) angles average 105.3 (2)°. The interaction of the apparent electrophile Mn^{2+} with both the terminal manganese atoms and the bridging C(5) atoms can be taken as evidence of both ligand and metal basicities in our systems. Such basicities have been proposed for ferrocene,[27] and the present structural result may even serve as a model for electrophilic substitution reactions of ferrocene and ferrocene-like molecules. Also of interest are the carbon–carbon bond distances, averaging 1.410 (3) Å for all but the C(4)–C(5) bonds, which averaged 1.441 (6) Å. The central C(2)–C(3)–C(4) angles average 121.1(4)°—significantly smaller than the C(1)–C(2)–C(3) or the C(3)–C(4)–C(5) angles at 125.2 (4) and 127.5 (3)°, respectively. Interestingly, the reverse order was observed in $Fe(2,4-C_7H_{11})_2$ with the C(2)–C(3)–C(4) angles averaging 125.5 (3)° while the others averaged 122.4 (2)°. In both cases, then, the methyl substituents serve to contract the C–C–C bond angles to ca. 122° from the value of ca. 126° when no methyl substituent is present. This contraction upon methylation may be responsible for the apparent stabilizing effect of methylation observed in the iron series by bringing about an increase in the metal–ligand overlap and perhaps also by allowing for increased separation between ligands as longer metal–ligand plane distances can still give rise to shorter metal–carbon distances.

Naturally of interest is the origin of this unusual complex. Obviously, at this early stage only some speculation may be offered. One possibility is that during an initial formation of $Mn(3-C_6H_9)_2$, some of the complex may either function as, or become converted to, some source of "bare manganese" complex, analogous to Wilke's fascinating "bare nickel" chemistry.[28] Other molecules of (perhaps somewhat ionic) $Mn(3-C_6H_9)_2$ may function as ligands which then coordinate sequentially to the bare manganese source. Such a process could then involve an intermediate $Mn_2(3-C_6H_9)_2$ complex, perhaps akin to the known $Ni_2(C_5H_7)_2$ compound.[29] If this were the case, the formation of these two polynuclear complexes could well proceed along related mechanistic paths. Indeed, there is good precedent for the interaction of carbanions with zero-valent metals. One pertinent example is the unusual complex $[[(LiC_6H_5)_3Ni]_2N_2\cdot(ether)_2]_2$ which results from the interaction of LiC_6H_5 with a "bare nickel" complex.[30] A second possible mechanism could involve an association process in solution of $Mn(3-C_6H_9)_2$ molecules, such as must take place in the crystallization or condensation of the manganocene polymer. Methylpentadienyl fragments or dimers may then be homolytically lost from these associated species, ultimately leading to the observed product. Whether or not this or a similar process takes place for other manganese complexes of varying degrees of substitution remains to be determined. However, the formation of bis(3-methylpentadienyl)manganese anions can be compared to the recent characterization of the decamethylmanganocene anion.[31]

The present report demonstrates that pentadienyl groups should indeed find broad application as useful and interesting ligands. In this regard we have, in fact, already observed high catalytic activity for some such complexes.[32] It is clear in some cases (such as iron and perhaps chromium) that a great deal of similarity exists with metallocene or metal allyl chemistry, while in other cases (such as manganese and perhaps vanadium) completely new facets of behavior seem to be emerging. We are continuing to explore this new ligand system.

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Supplementary Material Available: A listing of positional coordinates for $Mn_3(3-C_6H_9)_4$ (2 pages). Ordering information is given on any current masthead page.

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[25] As noted later, the 3-methylpentadienyl ligand is larger in size than the 2,4-dimethylpentadienyl ligand, and hence slightly longer M–C distances might be expected due to a slight loss of orbital overlap.

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[30] (a) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 997. (b) Krüger, C.; Tsay, Y.-H. *Ibid.* **1973**, *12*, 998.

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[32] Wilson, D. R.; Liu, J.-Z.; Cymbaluk, T. H.; Ernst, R. D., experiments in progress.

Direct Observation of Metal-Centered Radicals in an Oxidative-Addition Reaction

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Oxidative addition of organic halides by free-radical mechanisms is a widely accepted pathway in organometallic chemistry.[1-4] A variety of methods, including racemization of chiral substrates,[1,3] radical cyclizations,[1,2] observation of CIDNP effects,[1,2] and "spin trapping",[4] have been used to ascertain the existence of free *organic* radicals in these processes. While these techniques presuppose intermediary paramagnetic transition-metal counterparts, the *direct* observation of such species in radical-chain oxidative-addition processes has not been noted.[5] We now report that if the reaction between alkyl halides and $Cp_2Zr(PPh_2Me)_2$ (where Cp is cyclopentadienyl) is continuoulsy monitored by EPR spectroscopy, *direct* evidence for the presence of these previously

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[1] Williams, G. M.; Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3660.

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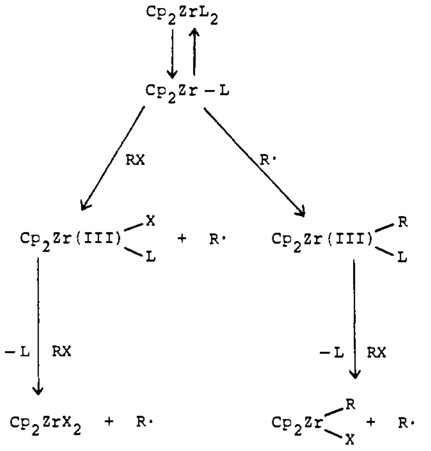
[5] The EPR spectrum of a Mo(I) radical cation was reported in a non-chain oxidation: Connor, J. A.; Riley, P. I. *J. Chem. Soc., Chem. Commun.* **1976**, 634.

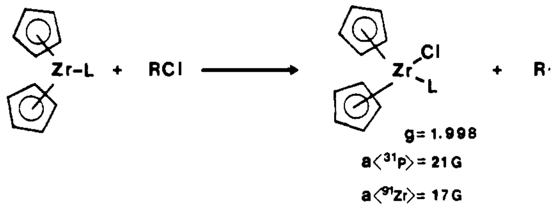
Scheme I



postulated odd-electron metal-complex intermediates can be obtained.

We have proposed a mechanism (Scheme I) for the oxidation of Cp$_2$Zr(phosphine)$_2$ by alkyl halides;[1] these reactions produce both the oxidative adduct, Cp$_2$ZrRX, and the dihalide, Cp$_2$ZrX$_2$. Primary alkyl halides strongly favor formation of Cp$_2$ZrRX while tertiary alkyl halides yield Cp$_2$ZrX$_2$; secondary halides give product mixtures. Initiation of either pathway occurs by halogen atom abstraction and should produce Cp$_2$Zr^{III}XL. This species leads only to Cp$_2$ZrX$_2$, while competing radical capture by Zr(II) should give Cp$_2$Zr^{III}RL and, eventually, the oxidative adduct.

We have monitored these oxidation reactions by EPR spectroscopy[6] and have noted the presence of paramagnetic species. Lifetimes of these species, observed by EPR spectroscopy, correlate with the growth of the reaction products as monitored independently by ^{1}H NMR spectrometry. In the course of the reactions, in which Cp$_2$Zr(PPh$_2$Me)$_2$ is treated with either *n*-, *sec*-, or *tert*-butyl chloride, a doublet (g = 1.998, 21 G; see Figure 1) is observed. This is consistent with a monophosphine Zr(III) species (see reaction 1) and is in agreement with data for other



(1)

phosphine-substituted metal-centered radicals.[7] Hyperfine splitting by ^{91}Zr (11.3% natural abundance, $I = {}^5/_2$) is also observed (17 G). Similarly, oxidation with *sec*-butyl bromide gives rise to a doublet at g = 1.995 (a $\langle ^{31}\mathrm{P}\rangle$ = 21 G). These observations corroborate the proposed initiation of oxidation by atom abstraction and support assignment of the doublet to the expected intermediate, Cp$_2$Zr^{III}X(PPh$_2$Me).[8] Consistent with the proposed mechanism, the intensity of the doublet increases with the proportion of Cp$_2$ZrX$_2$ formed in the reaction: t-BuCl > *sec*-BuCl > n-BuCl. These can be explained according to Scheme I since the free alkyl radicals produced in these reactions compete with organic halide for monophosphine Zr(II). For *tert*-butyl chloride, the rate of radical capture (leading to oxidative addition) is negligible compared with the rate of atom abstraction; consequently, the EPR doublet is very intense. In contrast, the reaction between a primary alkyl radical and Zr(II) (leading to oxidative addition) is fast compared with abstraction; the intensity of the

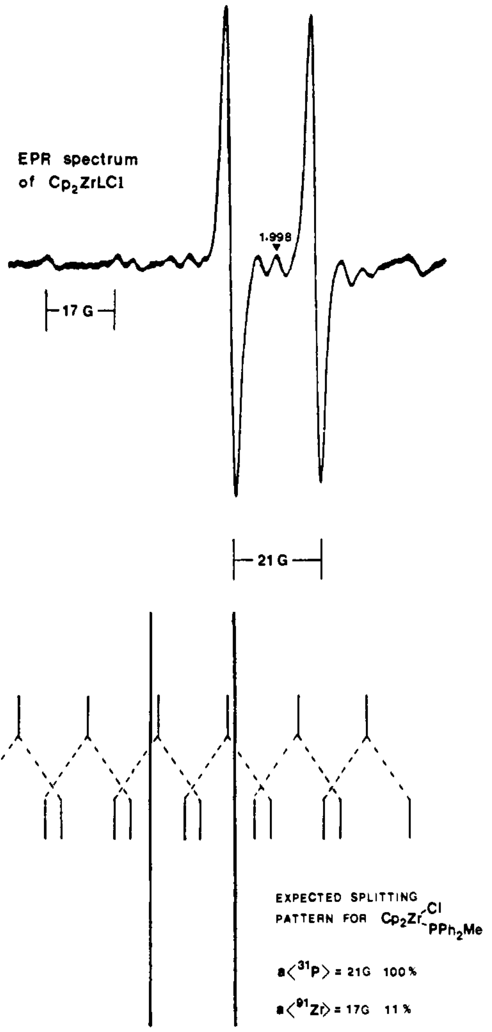


Figure 1.

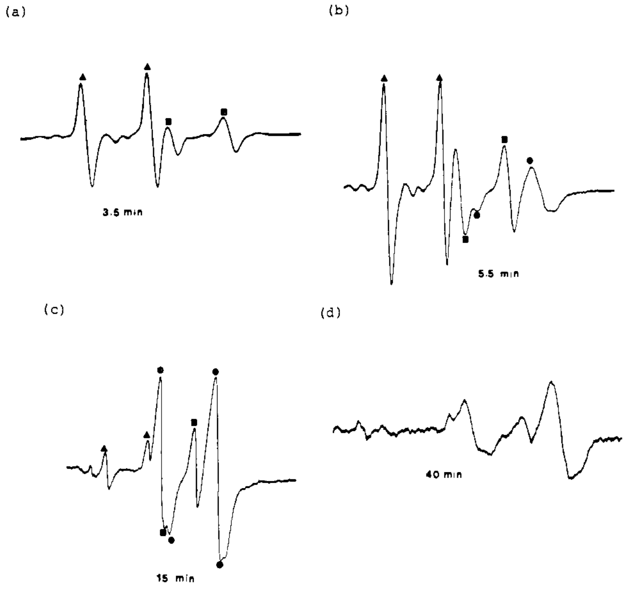


Figure 2. EPR-monitored reaction between Cp$_2$Zr(PPh$_2$Me)$_2$ and n-BuCl: (▲) Cp$_2$ZrCl(PPh$_2$Me); (●) Cp$_2$ZrBu(PPh$_2$Me)$_3$; (■) unassigned.[11] Individual spectra are not to scale.

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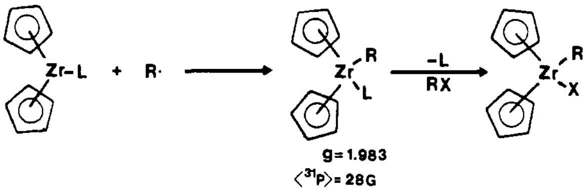
(6) The starting Zr(II) solutions (0.093 M in Zr and 0.21 M in free PPh$_2$Me) were placed in quartz EPR tubes and capped with septa. Alkyl halides (8 equiv) were injected from gastight syringes. Spectral data are reported relative to DPPH = 2.0037. The preparation and chemistry of Cp$_2$ZrL$_2$ has been presented: Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 244. Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.

(7) Connelly, N. G.; Kitchen, M. D. *J. Chem. Soc., Dalton Trans.* **1976**, 2165. Connelly, N. G.; Kitchen, M. D. *Ibid.* **1977**, 931. Hudson, A.; Lappert, M. F.; Nicholson, B. K. *Ibid.* **1977**, 551.

(8) This assignment is substantiated by a recent report of the EPR spectrum of a halozirconium(III) phosphine complex prepared by an independent pathway; the EPR spectrum reported for this species is comparable to the one reported herein: Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251.

doublet is accordingly low.[9] Alkyl radical capture by Zr(II) would give a new paramagnetic species. Consistent with this notion, we find that EPR spectra recorded during the reaction between $Cp_2Zr(PPh_2Me)_2$ and *n*-butyl chloride display a pair of doublets which appear and decay consecutively with different kinetics (see Figure 2).[10] One is the halide-containing intermediate described above; the other ($g = 1.983$) has a hyperfine coupling constant of 28 G, consistent with greater unpaired spin density on phosphorus than is found for the initial doublet assigned to $Cp_2ZrCl(PPh_2Me)$. This behavior is consistent with changing the ligand on zirconium from an electron-withdrawing halide to an electron-donating alkyl group. This second signal is, therefore, attributed to $Cp_2Zr^{III}R(PPh_2Me)$.[11,12]

Monitored by EPR spectroscopy, the oxidation of $Cp_2Zr(PPh_2Me)_2$ by *sec*-butyl halides provides further evidence in support of Scheme I. At 29 °C reaction with *sec*-butyl chloride yields a mixture of Cp_2ZrCl_2 and $Cp_2Zr(Bu)Cl$ (68:32). Accordingly, the "initiation doublet" is observed, and a weak signal is found in the alkylzirconium(III) region. At 6 °C, however, no doublet attributable to the alkylzirconium(III) complex is noted in the reaction between $Cp_2Zr(PPh_2Me)_2$ and *sec*-butyl bromide (which produces Cp_2ZrRX/Cp_2ZrX_2 in the ratio 69:31). These observations are a function of relative rates for the two steps of the propagation sequence [addition step (k_1) vs. abstration step (k_2)] leading to oxidative addition. Fast R· capture (see reaction 2) (1° > 2° > 3°) relative to subsequent abstraction (I > Br > Cl) would result in a buildup of $Cp_2Zr^{III}RL$ and allow its detection by EPR spectroscopy. This situation would be maximized[1] for R = primary alkyl radical and X = Cl; Zr(II) capture of secondary alkyl radicals is slower and subsequent oxidation of Zr(III) to Zr(IV) can become competitive with this capture. The different intensities for the paramagnetic intermediates formed in the reactions of *sec*-butyl bromide and *sec*-butyl chloride with the bis(phosphine)zirconium(II) complex are readily understood: capture rates for each substrate should be the same; however, the subsequent abstraction should occur significantly faster for the bromide than for the chloride.



(2)

Classical product analysis studies originally enabled us to outline a mechanistic scheme to account for observed competitive oxidation of Zr(II) complexes by alkyl halides. Support for this scheme has been accomplished by EPR observation of reaction intermediates as noted herein, a result that demonstrates the utility of this spectroscopic technique for the elucidation of organometallic reaction mechanisms.

Acknowledgment. We acknowledge support for this work provided by the National Science Foundation (Grant CHE-79-00996). We also thank Professor C. Dismukes and D. Abramowicz for helpful comments and discussions.

Registry No. $Cp_2Zr(PPh_2Me)_2$, 71844-71-8; $Cp_2ZrCl(PPh_2Me)$, 80642-23-5; $Cp_2ZrBr(PPh_2Me)$, 80642-24-6; $Cp_2Zr(n\text{-}Bu)(PPh_2Me)$, 80642-25-7; Cp_2ZrCl_2, 1291-32-3; $Cp_2Zr(Bu)Cl$, 71844-78-5; $Cp_2Zr(sec\text{-}Bu)Br$, 80642-26-8; Cp_2ZrBr_2, 1294-67-3; *t*-BuCl, 507-20-0; *sec*-BuCl, 78-86-4; *n*-BuCl, 109-69-3; *sec*-BuBr, 78-76-2.

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(9) These data were collected without use of an external calibration standard; exact quantitative conclusions, therefore, cannot be drawn. The fact that similar relative intensities for the Zr(III) species were observed for a large number of runs, performed at different times under the same conditions, justifies our conclusions qualitatively.

(10) Under these conditions both Cp_2ZrCl_2 and $Cp_2Zr(Cl)(Bu)$ are formed in the ratio 18:72.

(11) A third doublet has been noted ($g = 1.986$, $a\langle ^{31}P\rangle = 18$ G), which forms and decays with a shorter lifetime than Cp_2ZrRL and remains unassigned. The relatively sharp lines for this doublet and the small hyperfine constant suggest that it is not an alkyl-containing metallic species. This last doublet was observed *only* for *n*-BuCl oxidation; it was not detected in reactions involving *tert* or *sec*-butyl chlorides or *sec*-butyl bromide.

(12) Proton hyperfine splitting ($\approx$3 G) is not well resolved in this signal. A similar, low hyperfine splitting by alkyl group protons for an EPR study has been noted for a cyclopentadienyl(alkyl)zirconium species: Lappert, M. F.; Pickett, C. J.; Riley, P. I.; Yarrow, P. I. *J. Chem. Soc., Dalton Trans.* **1981**, 805.

A Silicon-Mediated Homo-Claisen Rearrangement

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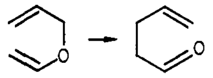
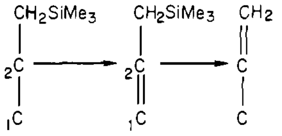
The Claisen rearrangement (reaction 1) is a well-known and exceptionally versatile reaction as evidenced, for example, by the number and frequency of its reviews.[1] The reaction is important in part because its high stereospecificity has found application in the construction of acyclic systems and trisubstituted olefins. The selectivity is a consequence of the highly ordered transition state in the Claisen rearrangement, a feature it has in common with the Diels–Alder reaction. We have now uncovered a variant of the Claisen rearrangement that leads to homologous products[2] and moreover has, we believe, significant and far-reaching consequences.



(1)

Our basic strategy for specific homologation involves silicon chemistry (reaction 2).[3-5] If a reaction can be conceived that



(2)

1 2 3

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