J. Am. Chem. Soc. 1987, 109, 417-423

Pentadienyl–Metal–Phosphine Chemistry. 10.[1] Comparison of the Reactions of (η^5-Pentadienyl)Mn[($Me_2PCH_2)_3CMe$] and (η^5-2,4-Dimethylpentadienyl)Re($PMe_2Ph)_3$ with H^+. Isolation of a Protonated Manganese Complex Containing an Agostic C–H–M Interaction

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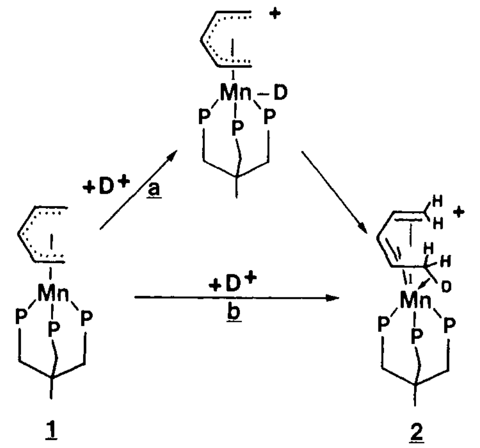
Abstract: (η^5-Pentadienyl)Mn[($Me_2PCH_2)_3CMe$] (**1**) and (η^5-2,4-dimethylpentadienyl)Re($PMe_2Ph)_3$ (**4**) react with acids to generate protonated complexes. In the cationic manganese product, **2**, the added hydrogen resides in an agostic (semibridging) position between the metal center and C1 of the pentadienyl ligand, while the protonated rhenium complex, **5**, contains a normal (terminal) metal hydride. The crystal structure of (η^5-2,4-dimethylpentadienyl)Re(H)($PMe_2Ph)_3{}^+BF_4{}^-\cdot OC_4H_8$ (**5a**) has been determined by X-ray diffraction. The complex crystallizes in the monoclinic space group $P2_1/n$ with a = 10.267 (2) Å, b = 18.487 (5) Å, c = 19.843 (4) Å, β = 98.83 (2)°, V = 3721 (2) Å^3, and Z = 4. The hydride ligand resides beneath the "backbone" of the dimethylpentadienyl ligand between phosphorus atoms P1 and P2. Experiments involving D^+ have probed the mechanisms of the protonation reactions. In the manganese system, reaction with D^+ at −130 °C leads to deuterium incorporation exclusively in the semibridging position, indicating initial endo attack either at the metal center or directly at the semibridging site. In the rhenium system, initial D^+ attack appears to occur at the metal center from the open ("mouth") side of the 2,4-dimethylpentadienyl ligand. This mouth deuteride then rapidly exchanges with the hydrogens on pentadienyl carbons C1 and C5 before moving to its thermodynamic position under the pentadienyl backbone. The cationic manganese complex, (C_5H_7-μ-H)Mn[($Me_2PCH_2)_3CMe]^+$ (**2**), undergoes three fluxional processes in solution, as evidenced by variable-temperature NMR spectroscopy. The first process, which involves the intermediacy of a 16e$^-$ η^4-pentadiene–metal complex, exchanges the three hydrogens in the agostic methyl group (C1). The second process involves a η^5-pentadienyl-metal-hydride intermediate and exchanges the agostic methyl group hydrogens with the hydrogens bonded to C5. The third fluxional process exchanges the three phosphorus atoms in the phosphine ligand via pentadienyl ligand rotation. Line shape simulations of the variable-temperature NMR spectra yield free energies of activation ($\Delta G^\ddagger$'s) of 9.5 ± 0.4, 16.5 ± 0.4, and 11.4 ± 0.5 kcal, respectively, for these processes. **2** reacts with additional ($Me_2PCH_2)_3CMe$ to release *cis*-1,3-pentadiene and produce Mn[($Me_2PCH_2)_3CMe]_2{}^+$ (**3**). Cation **5** also undergoes dynamic processes in solution. The hydride ligand can migrate to either end of the 2,4-dimethylpentadienyl ligand, causing exchange of the hydride with the four hydrogens on C1 and C5 of the pentadienyl chain ($\Delta G^\ddagger$ = 17.3 ± 0.2 kcal). The 2,4-dimethylpentadienyl ligand can also rotate with respect to the MP_3 fragment, resulting in exchange of the three phosphorus atoms ($\Delta G^\ddagger$ = 16.9 ± 0.3 kcal).

During the past several years there has been a surge of interest in the synthesis, structure, and spectroscopy of metal complexes containing the acyclic pentadienyl ligand (pd).[2] However, the *reactions* of these species, particularly those reactions which involve the pd ligand as a participant, remain largely unexplored.[3]

In order to elucidate the chemistry of metal-bound pentadienyl groups, we have begun a systematic investigation of a new class of highly reactive pd–M complexes, the pentadienyl–metal–phosphine complexes.[1] The incorporation of phosphine ligands into these molecules increases electron density at the metal center and promotes electrophilic and oxidative addition reactions, enabling us to study the interactions of ligands such as hydrides, alkyls, and acyls with the pd group.

We now report the contrasting reactions of two electron-rich pentadienyl–metal–phosphine complexes with H^+. (η^5-Pentadienyl)Mn[($Me_2PCH_2)_3CMe$][1f] reacts with acids to produce a cationic complex in which the added hydrogen is in an agostic (semibridging) position between the metal center and C1 of the pd ligand.[4] In contrast, the protonation of (η^5-2,4-dimethylpentadienyl)Re($PMe_2Ph)_3$[1g] produces a cationic complex containing a normal (terminal) metal hydride. However, each of these protonated complexes undergoes fluxional processes involving migration of the hydrogen ligand between the metal center and the termini of the pentadienyl ligand.

Scheme I



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[1] The previous papers in this series are as follows: (a) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1983**, *2*, 1263. (b) Bleeke, J. R.; Hays, M. K. *Ibid.* **1984**, *3*, 506. (c) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1984**, *3*, 1422. (d) Bleeke, J. R.; Kotyk, J. J. *Ibid.* **1985**, *4*, 194. (e) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1986**, *5*, 635. (f) Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Ibid.* **1986**, *5*, 1642. (g) Bleeke, J. R.; Moore, D. A. *Inorg. Chem.* **1986**, *25*, 3522. (h) Bleeke, J. R.; Donaldson, A. J. *Organometallics*, in press. (i) Bleeke, J. R.; Hays, M. K. *Ibid.*, in press.

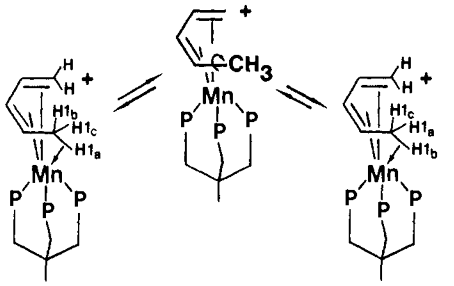
[2] See, for example: (a) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56 and references cited therein. (b) Seyferth, D.; Goldman, E. W.; Pornet, J. *J. Organomet. Chem.* **1981**, *208*, 189. (c) Lehmkuhl, H.; Naydowski, C. *Ibid.* **1982**, *240*, C30. (d) Hegedus, L. S.; Varaprath, S. *Organometallics* **1982**, *1*, 259. (e) Leyendecker, M.; Kreiter, C. G. *J. Organomet. Chem.* **1983**, *249*, C31. (f) Paz-Sandoval, M. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026. (g) Lush, S.-F.; Liu, R.-S. *Ibid.* **1986**, *5*, 1909.

[3] One such reaction has recently been reported by Ernst et al.: Kralik, M. S.; Hutchinson, J. P.; Ernst, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 8296.

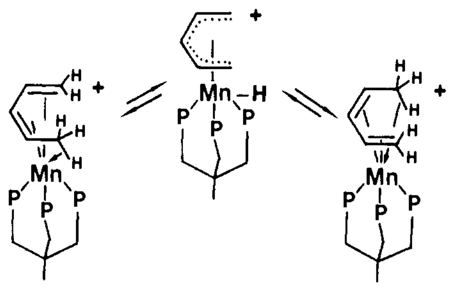
[4] See the following review article on agostic C–H–M interactions: Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

0002-7863/87/1509-0417$01.50/0

Scheme II



Scheme III

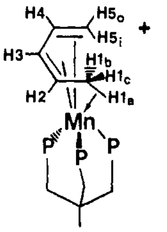


Results and Discussion

A. Synthesis of $(C_5H_7\text{-}\mu\text{-H})Mn[(Me_2PCH_2)_3CMe]^+PF_6^-$ (2a). Mechanism of Attack. The reaction of yellow (η^5-pentadienyl)-$Mn[(Me_2PCH_2)_3CMe]$ (1)[1f] with $NH_4^+PF_6^-$ in tetrahydrofuran leads to the rapid precipitation of the purple protonated complex $(C_5H_7\text{-}\mu\text{-H})Mn[(Me_2PCH_2)_3CMe]^+PF_6^-$ (**2a**). This complex is stable in the solid state but decomposes slowly at room temperature in polar noncoordinating solvents such as methylene chloride and chloroform to yield *cis*-1,3-pentadiene and $Mn[(Me_2PCH_2)_3CMe]_2^+PF_6^-$ (**3a**). Decomposition to **3a** occurs much more rapidly in the presence of coordinating solvents and additional $(Me_2PCH_2)_3CMe$, as described in section D below.

When **1** is reacted with D^+ at −130 °C, the deuterium appears exclusively in the semibridging position of the product, **2** (vide infra). This result clearly indicates endo attack either at the metal center, followed by rapid migration to the semibridging position (Scheme I, a), or directly at the semibridging site (Scheme I, b). External (exo) D^+ attack at the *pentadienyl* ligand would result in deuterium incorporation into the nonbridging sites of the agostic methyl group.

B. Variable-Temperature NMR Spectra of 2. The agostic ground state of the protonated cation, **2** (see below), is clearly indicated by its NMR spectra. Also evident from the variable-temperature spectra are three dynamic processes which occur in solution. These dynamic processes closely parallel those observed by Kreiter[5] for the isoelectronic agostic 2,4-dimethylpentadiene–chromium complex, $(\eta^4\text{-}C_7H_{11}\text{-}\mu\text{-H})Cr(CO)_2[P(OMe)_3]$, and are similar to processes described by Brookhart,[6] Ittel,[7] Moore,[8] and Green[9] for a variety of (η^3-butenyl-μ-H)-metal complexes.



2

1. ^{1}H NMR Spectra. At −130 °C, in a mixture of CD_2Cl_2 and CF_2Cl_2 (Freon-12), all exchange processes are stopped, and the eight protons on the C_5H_8 ligand give rise to eight separate signals in the ^{1}H NMR spectrum. The agostic hydrogen, $H1_a$, resonates at δ −15.31, while $H1_b$ and $H1_c$ appear at δ −3.05 and −0.33, respectively. The protons on C5, $H5_i$ and $H5_o$, give rise to signals at δ 0.20 and 2.95, respectively.[10]

As the temperature is raised to −30 °C in CD_2Cl_2, the signals due to $H1_a$, $H1_b$, and $H1_c$ broaden and then coalesce into a new averaged signal at δ −6.23. The dynamic process responsible for this exchange involves the intermediacy of a η^4-pentadiene complex in which there is free rotation about single bond C1–C2 (see Scheme II). Line shape simulations of the variable-temperature (−70 to −30 °C) ^{1}H NMR spectra have yielded a $\Delta G^\ddagger$ of 9.5 ± 0.4 kcal for this exchange process.

As the temperature of **2** is raised above −30 °C, a second dynamic process is observed by ^{1}H NMR spectroscopy. The signals at δ −6.23 (the fluxional agostic methyl group), 0.20 ($H5_i$), and 2.95 ($H5_o$) begin to broaden and sink into the base line. However, they do not fully coalesce before the sample decomposes by loss of *cis*-1,3-pentadiene at 40 °C. The dynamic process which gives rise to this exchange involves the intermediacy of a metal hydride, as depicted in Scheme III. The hydride ligand in the intermediate can migrate with equal facility to either end of the pd ligand. Again, line shape simulations of the variable-temperature (−30 to 35 °C) ^{1}H NMR spectra yield a $\Delta G^\ddagger$ for this process of 16.5 ± 0.4 kcal.

2. ^{13}C NMR Spectra. Because of solubility problems, we have been unable to obtain the $^{13}C\{^1H\}$ NMR spectrum of **2** at −130 °C in CD_2Cl_2/CF_2Cl_2. However, at −30 °C in CD_2Cl_2, **2** exhibits five distinct ^{13}C NMR signals for the five carbons in the C_5H_8 ligand: C2 at δ 97.1, C4 at 95.2, C3 at 78.5, C5 at 42.4, and C1 at 35.9. The agostic carbon atom, C1, is shifted substantially upfield from its position of δ 45.0 in **1**. The C–H coupling constant for C1, determined from a $^{13}C–^1H$ *J*-resolved 2D NMR experiment (HET 2DJ), is 118.2 Hz at −30 °C. At this temperature, the first fluxional process (Scheme II) is occurring rapidly, and the measured J_{C-H} is the average of J_{C-H1_a}, J_{C-H1_b}, and J_{C-H1_c}. This coupling constant is fully consistent with a fluxional agostic methyl group.[4]

3. ^{31}P NMR Spectra. The ^{31}P NMR spectra of **2** are also temperature dependent. Below −70 °C, the $^{31}P\{^1H\}$ spectrum exhibits two signals, a pseudotriplet of intensity 1 at δ 56.8 ($J_{P-P} = 69$ Hz) due to the phosphorus nucleus under the mouth of the C_5H_8 ligand and a pseudodoublet of intensity 2 at δ 32.6 ($J_{P-P} = 69$ Hz) due to the two backbone phosphorus nuclei. As the temperature is raised to 20 °C, these signals broaden and coalesce to a single peak at δ 40.7.[11] The fluxional process which exchanges the three phosphorus atoms must involve a rotation of the C_5H_8 ligand with respect to the MP_3 fragment, but we do not know whether the agostic C–H–M interaction remains intact during the rotation. The free energy of activation for this process is 11.4 ± 0.5 kcal.[12]

C. Reaction of (η^5-Pentadienyl)$Mn[(Me_2PCH_2)_3CMe]$ with D^+. The reaction of (η^5-pentadienyl)$Mn[(Me_2PCH_2)_3CMe]$ (**1**) with DO_3SCF_3 produces the monodeuteriated complex $(C_5H_7D)Mn$-

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(5) Günther, M.; Kaub, J.; Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 502.

(6) (a) Brookhart, M.; Whitesides, T. H.; Crockett, J. M. *Inorg. Chem.* **1976**, *15*, 1550. (b) Brookhart, M.; Lamanna, W.; Humphrey, J. *J. Am. Chem. Soc.* **1982**, *104*, 2117.

(7) Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem.Soc.* **1979**, *101*, 6905.

(8) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1981**, 506.

(9) Brookhart, M.; Cox, K.; Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Hare, P. M.; Bashkin, J.; Derome, A. E.; Grebenik, P. D. *J. Chem. Soc., Dalton Trans.* **1985**, 423.

(10) This stopped-exchange ^{1}H NMR spectrum is consistent only with the agostic structure. If the ground state were a η^5-pentadienyl–metal–hydride structure (and mirror-plane symmetry were retained, as in the Re system described herein), $H1_i$ would be equivalent to $H5_i$ and $H1_o$ would be equivalent to $H5_o$. Furthermore, none of these protons would resonate as far upfield as the observed peak at δ −3.05.

(11) The ^{1}H and ^{13}C NMR signals due to the phosphine methyl and methylene groups also coalesce as the temperature is raised to 20 °C.

(12) The barrier to pentadienyl ligand rotation in neutral **1** is also 11.4 kcal (ref 1f).

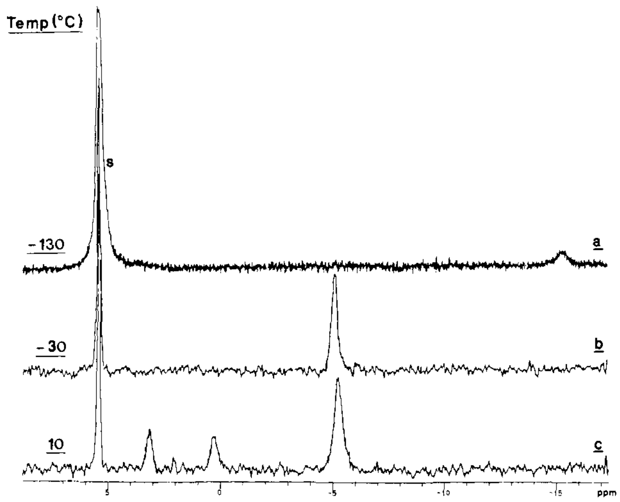
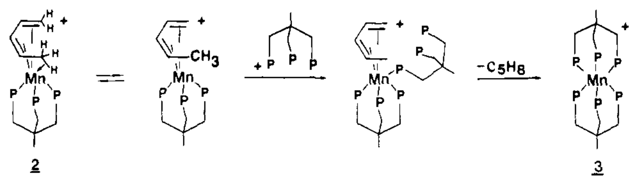


Figure 1. (a) ^2H NMR spectrum of $(C_5H_7\text{-}\mu\text{-}D)Mn[(Me_2PCH_2)_3CMe]^+$ (**2**) produced in the reaction of $(\eta^5\text{-pentadienyl})Mn[(Me_2PCH_2)_3CMe]$ (**1**) with D^+ in CH_2Cl_2/CF_2Cl_2 at -130 °C. Deuterium is found exclusively in the semibridging position (δ -15.3). The large peak labeled "s" at δ 5.3 is due to deuterium in the methylene chloride solvent. (b) ^2H NMR spectrum of **2**, produced in the reaction of **1** with D^+ in CH_2Cl_2 at -80 °C, followed by warming to -30 °C. The peak at δ -5.2 is the averaged signal for deuterium in the three sites of the fluxional agostic methyl group. (c) ^2H NMR spectrum of **2**, produced in the reaction of **1** with D^+ in CH_2Cl_2 at -80 °C, followed by warming to 10 °C. The peaks at δ 2.95 and 0.2 are due to deuterium in the outer and inner sites on C5, while the peak at δ -5.3 is due to deuterium in the fluxional agostic methyl group.

Scheme IV

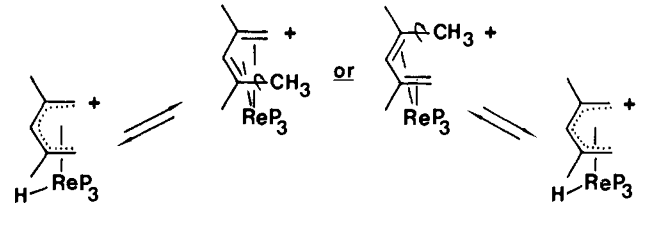


$[(Me_2PCH_2)_3CMe]^+O_3SCF_3^-$ (**2b**). When the reaction is carried out at -130 °C in CH_2Cl_2/CF_2Cl_2, the deuterium atom ends up exclusively in the semibridging site, as evidenced by the ^2H NMR spectrum, which consists of just one peak at δ -15.3 (see spectrum a, Figure 1). As the sample is warmed to -30 °C in CH_2Cl_2, the deuterium atom scrambles among the three positions on the agostic methyl group via the dynamic process outlined in Scheme II. Since there is a thermodynamic preference for hydrogen rather than deuterium to occupy the bridging position,[4,13] the hydrogens in the fluxional agostic CH_2D group are shifted upfield from their normal position of δ -6.23, while the deuterium atom is shifted downfield from δ -6.23 (see spectrum b, Figure 1). Furthermore, the chemical shifts of the hydrogens and the deuterium in the CH_2D group are temperature dependent. For example, at -70 °C the position of the deuterium signal in the ^2H NMR spectrum is δ -5.0. As the temperature is raised to -30 °C, the chemical shift of its signal gradually moves upfield to δ -5.2. Concomitantly, the hydrogen signal in the ^1H NMR spectrum moves downfield from δ -6.8 at -70 °C to δ -6.7 at -30 °C. Similar isotopic perturbation effects were first observed by Shapley[13] and have since been widely used to identify agostic C-H-M systems.[4]

When **2b** is heated above -30 °C, the second fluxional process (Scheme III) begins to occur, and deuterium is incorporated into the two sites on C5, as evidenced by ^2H NMR (see spectrum c, Figure 1).

D. Reaction of 2 with $(Me_2PCH_2)_3CMe$. $(C_5H_7\text{-}\mu\text{-}H)Mn[(Me_2PCH_2)_3CMe]^+$ (**2**) reacts rapidly with $(Me_2PCH_2)_3CMe$ in polar solvents such as tetrahydrofuran to release *cis*-1,3-pentadiene[14] and produce $Mn[(Me_2PCH_2)_3CMe]_2^+$ (**3**) in high yield.

Scheme V



We favor the mechanism shown in Scheme IV, which invokes $16e^-$ $(\eta^4\text{-pentadiene})Mn[(Me_2PCH_2)_3CMe]^+$ as the key intermediate.[15]

The manganese cation, $Mn[(Me_2PCH_2)_3CMe]_2^+$ (**3**), has D_{3d} point group symmetry and gives rise to very simple, characteristic ^1H, ^{13}C, and ^{31}P NMR spectra. The ^1H NMR spectrum consists of just three singlets (phosphine methyl H's, methylene H's, capping methyl H's), while the $^{13}C\{^1H\}$ NMR spectrum has four signals (phosphine methyl C's, methylene C's, bridgehead C's, capping methyl C's). The $^{31}P\{^1H\}$ NMR spectrum of the cation consists of six approximately equal intensity lines which arise from coupling of the equivalent ^{31}P nuclei with the manganese quadrupole ($I = {}^5/_2$ for ^{55}Mn). The coupling constant, $J_{Mn\text{-}P}$, is 177.5 Hz.[16,17]

Cation **2** reacts with a variety of other coordinating molecules, L, including $P(OMe)_3$ and NH_3, to produce $[(Me_2PCH_2)_3CMe]MnL_3^+$ complexes. Details of this work will be reported in a future communication.

E. Synthesis of $(\eta^5$-2,4-Dimethylpentadienyl)Re(H)$(PMe_2Ph)_3^+BF_4^-$ (5a). $(\eta^5$-2,4-Dimethylpentadienyl)Re$(PMe_2Ph)_3$ (**4**)[1g] reacts rapidly with $HBF_4\cdot OEt_2$ in tetrahydrofuran to produce the metal hydride complex $(\eta^5$-2,4-dimethylpentadienyl)Re(H)$(PMe_2Ph)_3^+BF_4^-$ (**5a**). Possible mechanisms for this protonation reaction are discussed in section H.

F. Variable-Temperature NMR Spectra of 5. The NMR spectra of **5** clearly indicate that its ground-state structure is a normal (terminal) metal hydride. Unlike those of **2**, the NMR spectra of **5** are not temperature dependent between -100 and 20 °C.

1. ^1H NMR Spectra. The hydride signal appears at δ -10.90 in the ^1H NMR spectrum of **5** and is split into a triplet by the two equivalent backbone phosphines ($J_{H\text{-}P}$ = 51.5 Hz) and a doublet by the mouth phosphine ($J_{H\text{-}P}$ = 12.1 Hz). Since **5** retains mirror-plane symmetry, the inner hydrogens on C1 and C5, $H1_i$ and $H5_i$, are equivalent (δ 0.06), and the outer hydrogens, $H1_o$ and $H5_o$, are equivalent (δ 2.56). As the temperature is raised to 80 °C in $C_2D_4Cl_2$, the signals due to the hydride, $H1_i/H5_i$, and $H1_o/H5_o$ broaden and disappear into the base line but do not coalesce into a single peak before the sample decomposes. The process which gives rise to this dynamic NMR behavior is shown in Scheme V. The hydride can migrate to either side of the pentadienyl ligand with equal facility, generating $(\eta^4$-2,4-dimethylpentadiene)Re$(PMe_2Ph)_3^+$ intermediates in which there is essentially free rotation of the terminal methyl group.[18] Simulations of the variable-temperature (20–70 °C) ^1H NMR spectra yield a $\Delta G^{\ddagger}$ for this process of 17.3 ± 0.3 kcal.

2. ^{13}C NMR Spectra. The mirror-plane symmetry of **5** is also manifested in its $^{13}C\{^1H\}$ NMR spectra. C1 and C5 are equivalent

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(13) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(14) In contrast, the reaction of $(\eta^3$-pentadienyl)Mn$[Me_2PCH_2CH_2PMe_2]_2$ with NH_4^+ yields a mixture of *cis*- and *trans*-1,3-pentadiene. However, in solution $(\eta^3$-pd)Mn$[Me_2PCH_2CH_2PMe_2]_2$ exists as an equilibrium mixture of *syn*- and *anti*-η^3-pd isomers (ref 1d).

(15) When the reaction is carried out in a coordinating solvent, the solvent molecules may aid in the displacement of the 1,3-pentadiene.

(16) The $^{31}P\{^1H\}$ NMR spectrum of **3** is very similar to that of Mn$(Me_2PCH_2CH_2PMe_2)_3^+$, which we reported earlier (ref 1d).

(17) The sharpness of this ^{31}P NMR signal can be attributed to the symmetrical distribution of electron density around the Mn center. This high-symmetry environment results in a small electric field gradient at the Mn nucleus and slow quadrupolar relaxation. See: Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders: Philadelphia, 1977; pp 225–226.

(18) Reversible hydride migrations to *diene* ligands have been observed in η^4-diene–Re(H)$_3$(PPh$_3$)$_2$ complexes. (a) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *J. Organomet. Chem.* **1984**, *272*, 391. (b) Jones, W. D.; Maguire, J. A. *Organometallics* **1985**, *4*, 951.

Table I. Positional Parameters with Estimated Standard Deviations for Non-Hydrogen Atoms in (η^5-2,4-Dimethylpentadienyl)Re(H)($PMe_2Ph)_3{}^+BF_4{}^-\cdot OC_4H_8$ (**5a**)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Re	0.07038 (4)	0.19979 (2)	0.20133 (2)	C5P2	0.462 (1)	0.3102 (7)	0.0910 (6)
P1	0.2044 (3)	0.0950 (2)	0.2394 (1)	C6P2	0.464 (1)	0.3302 (8)	0.0269 (6)
P2	0.1099 (3)	0.1991 (2)	0.0844 (1)	C7P2	0.359 (1)	0.3145 (7)	−0.0211 (6)
P3	−0.1284 (3)	0.1214 (2)	0.1703 (1)	C8P2	0.250 (1)	0.2752 (7)	−0.0034 (6)
C1	−0.075 (1)	0.2905 (5)	0.1784 (6)	C1P3	−0.136 (1)	0.0569 (7)	0.0990 (6)
C2	0.049 (1)	0.3228 (5)	0.1955 (5)	C2P3	−0.284 (1)	0.1712 (6)	0.1446 (6)
C3	0.133 (1)	0.3054 (6)	0.2578 (5)	C3P3	−0.182 (1)	0.0621 (6)	0.2364 (6)
C4	0.109 (1)	0.2527 (5)	0.3068 (5)	C4P3	−0.243 (1)	0.0944 (7)	0.2878 (5)
C5	−0.009 (1)	0.2108 (6)	0.3007 (5)	C5P3	−0.283 (1)	0.0515 (8)	0.3374 (6)
C6	0.102 (1)	0.3776 (6)	0.1493 (6)	C6P3	−0.272 (1)	−0.0235 (7)	0.3344 (7)
C7	0.218 (1)	0.2412 (6)	0.3671 (5)	C7P3	−0.217 (1)	−0.0536 (7)	0.2839 (7)
C1P1	0.374 (1)	0.1049 (7)	0.2233 (6)	C8P3	−0.172 (1)	−0.0119 (6)	0.2354 (6)
C2P1	0.167 (1)	0.0048 (6)	0.2017 (6)	B	0.569 (1)	0.2940 (8)	0.3155 (6)
C3P1	0.226 (1)	0.0685 (6)	0.3299 (5)	F1	0.5462 (8)	0.2276 (4)	0.3447 (4)
C4P1	0.124 (1)	0.0383 (6)	0.3557 (5)	F2	0.6823 (8)	0.2898 (5)	0.2889 (5)
C5P1	0.140 (2)	0.0152 (8)	0.4241 (7)	F3	0.470 (1)	0.3115 (7)	0.2685 (5)
C6P1	0.258 (2)	0.0249 (8)	0.4644 (7)	F4	0.579 (1)	0.3450 (5)	0.3655 (4)
C7P1	0.360 (2)	0.0565 (7)	0.4402 (7)	O1	0.618 (1)	0.1104 (9)	−1.0249 (7)
C8P1	0.349 (1)	0.0782 (6)	0.3718 (6)	C1S	0.490 (2)	0.1330 (9)	−1.0212 (8)
C1P2	−0.028 (1)	0.2289 (8)	0.0210 (5)	C2S	0.418 (2)	0.108 (1)	−1.0895 (8)
C2P2	0.156 (1)	0.1135 (6)	0.0455 (5)	C3S	0.499 (2)	0.054 (1)	−1.1247 (8)
C3P2	0.250 (1)	0.2550 (6)	0.0629 (5)	C4S	0.632 (2)	0.058 (1)	−1.079 (1)
C4P2	0.359 (1)	0.2719 (6)	0.1117 (6)	H1M	0.23 (1)	0.213 (6)	0.195 (6)

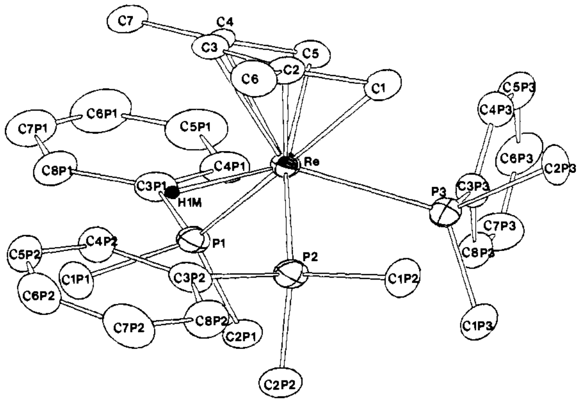


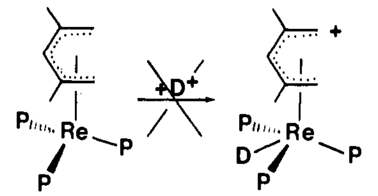
Figure 2. ORTEP drawing of (η^5-2,4-dimethylpentadienyl)Re(H)($PMe_2Ph)_3{}^+BF_4{}^-\cdot OC_4H_8$ (**5a**). Non-hydrogen atoms are represented by thermal ellipsoids drawn to encompass 25% of the electron density. The metal-bound hydrogen atom is drawn with an arbitrary thermal parameter and is darkened for clarity.

and appear at δ 51.3, while equivalent C2 and C4 appear at δ 98.2 and C3 appears at δ 87.5.

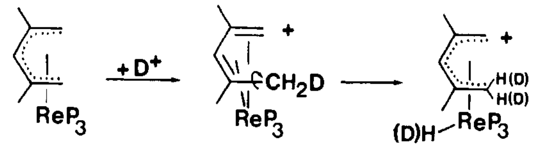
3. ^{31}P NMR Spectra. At 20 °C, the $^{31}P\{^1H\}$ NMR spectrum of **5** consists of two signals, a doublet of intensity 2 at δ −36.6 (J_{P-P} = 41.8 Hz) due to the phosphorus nuclei under the backbone of the dimethylpentadienyl ligand and a triplet of intensity 1 at δ −44.8 (J_{P-P} = 41.8 Hz) due to the mouth phosphorus nucleus. As the temperature is raised to 80 °C, these signals broaden and coalesce into a single peak at δ −39.3.[19] The $\Delta G^{\ddagger}$ for this process, which involves rotation of the dimethylpentadienyl ligand with respect to the phosphine ligands, is 16.9 ± 0.3 kcal, as calculated from lineshape analysis of the variable-temperature (20–70 °C) ^{31}P NMR spectra.[20]

The activation energies for hydride migration [17.3 ± 0.3 kcal] and dimethylpentadienyl ligand rotation [16.9 ± 0.3 kcal] are very similar, suggesting that either (a) the hydride migration is contingent on a rotation of the 2,4-Me_2pd ligand (i.e., the 2,4-Me_2pd ligand must rotate to attain the right orientation for hydride migration) or (b) the dimethylpentadienyl rotation is contingent on hydride migration (i.e., rotation occurs in an η^4-2,4-dimethylpentadiene–$ReP_3{}^+$ intermediate).

Scheme VI



Scheme VII



G. Structure of (η^5-2,4-Dimethylpentadienyl)Re(H)($PMe_2Ph)_3{}^+BF_4{}^-\cdot OC_4H_8$ (5a). An ORTEP drawing of cation **5**, derived from a single-crystal X-ray diffraction study, is presented in Figure 2. Atomic coordinates for the non-hydrogen atoms and the metal-bound hydrogen atom are listed in Table I, while significant bond distances and angles are reported in Table II. The metal-bound hydrogen atom was located on difference Fourier maps, and its position was successfully refined (vida infra). It lies between P1 and P2, 1.7 (1) Å from the rhenium atom.[21] The H–Re–P1, H–Re–P2, and H–Re–P3 angles are 68 (5)°, 68 (5)°, and 147 (4)°, respectively.

Although the gross structural features of **5** are similar to those of the starting complex, **4**, which we reported earlier,[1g] a close comparison of the structures reveals several perturbations caused by the presence of the hydride ligand. First, angle P1–Re–P2 is expanded to 97.1 (1)° in **5** from its value of 90.6 (2)° in **4**.[22] Second, the phenyl ring on P2 in **5** is rotated so that the dihedral angle it makes with P1's phenyl ring is reduced to 9.05° from 39.1° in **4**. Both of these changes in atom positions create room for the hydride ligand between P1 and P2. Third, the Re–P3 bond distance in **5** is increased to 2.502 (3) Å from its value of 2.343 (5) Å in **4**.[23] This is the expected effect of a *trans*-hydride ligand.[24]

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[19] The ^{1}H and ^{13}C NMR signals due to the phosphine methyl and phenyl groups also coalesce as the temperature is raised to 80 °C.

[20] The barrier for rotation of the 2,4-Me_2pd ligand in the starting material, **4**, is 13.7 kcal (ref 1g).

[21] It resides on the C3–Re–P3 plane and 2.4 Å below the pentadienyl plane.

[22] Angles P1–Re–P3 and P2–Re–P3 are contracted to 91.0 (1)° and 90.7 (1)° in **5** from their values of 98.2 (2)° and 94.9 (2)° in **4**.

[23] The Re–P1 and Re–P2 distances in **5** are only slightly longer than those in **4**. In **5**, Re–P1 = 2.428 (3) and Re–P2 = 2.417 (3) Å, while in **4**, Re–P1 = 2.364 (4) and Re–P2 = 2.350 (5) Å.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for $(\eta^5\text{-2,4-Dimethylpentadienyl})\text{Re(H)(PMe}_2\text{Ph)}_3{}^+\text{BF}_4{}^-\cdot\text{OC}_4\text{H}_8$ (**5a**)

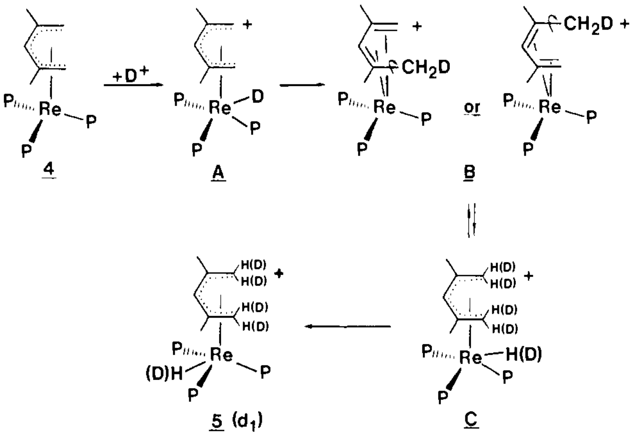
Bond Distances			
Re–P1	2.428 (3)	Re–H1M	1.7 (1)
Re–P2	2.417 (3)	C1–C2	1.40 (2)
Re–P3	2.502 (3)	C2–C3	1.43 (2)
Re–C1	2.25 (1)	C3–C4	1.43 (2)
Re–C2	2.29 (1)	C4–C5	1.43 (2)
Re–C3	2.29 (1)	C2–C6	1.52 (2)
Re–C4	2.29 (1)	C4–C7	1.52 (1)
Re–C5	2.26 (1)		
Bond Angles			
P1–Re–P2	97.1 (1)	C1–Re–C3	65.9 (4)
P1–Re–P3	91.0 (1)	C1–Re–C5	77.9 (4)
P2–Re–P3	90.7 (1)	C3–Re–C5	67.0 (4)
P1–Re–C1	170.5 (3)	P1–Re–H1M	68 (5)
P1–Re–C3	115.1 (3)	P2–Re–H1M	68 (5)
P1–Re–C5	93.7 (3)	P3–Re–H1M	147 (4)
P2–Re–C1	90.8 (3)	C3–Re–H1M	73 (4)
P2–Re–C3	113.4 (3)	C1–C2–C3	121 (1)
P2–Re–C5	167.5 (3)	C2–C3–C4	127 (1)
P3–Re–C1	83.7 (3)	C3–C4–C5	123 (1)
P3–Re–C3	140.4 (3)	C1–C2–C6	122 (1)
P3–Re–C5	82.9 (3)	C5–C4–C7	120 (1)

H. Reaction of (η^5-2,4-Dimethylpentadienyl)Re(PMe$_2$Ph)$_3$ (4) with D$^+$. Mechanism of the Initial Attack. When (η^5-2,4-Me$_2$pd)Re(PMe$_2$Ph)$_3$ (**4**) is reacted with DO$_3$SCF$_3$ at -90 °C in CH$_2$Cl$_2$/CF$_2$Cl$_2$, the added deuterium atom scrambles between the four sites on the terminal carbon atoms of the 2,4-Me$_2$pd ligand and the site on the metal center. Hence the ^{2}H NMR spectrum of this cation at -90 °C consists of peaks at δ -10.9 (Re–D), 0.06 (D1$_i$/D5$_i$), and 2.56 (D1$_o$/D5$_o$).

Clearly, this observation rules out a direct D$^+$ attack at rhenium from the closed (backbone) side of the 2,4-Me$_2$pd ligand (Scheme VI). Such an attack would result in deuterium incorporation *only* at the metal-bound site, since at this temperature deuteride migration from the backbone metal-bound site to the 2,4-Me$_2$pd ligand is stopped (section F.1). External (exo) attack of D$^+$ at C1 of the 2,4-Me$_2$pd ligand (followed by rapid migration of a hydrogen atom from C1 to Re), as shown in Scheme VII, cannot be excluded, but it seems unlikely, given that attack in our Mn system (section A) and most other electron-rich polyenyl–metal systems occurs in an endo fashion.[25]

An alternative mechanism, which we currently favor, involves the sequence of steps shown in Scheme VIII: (a) initial kinetic attack of D$^+$ at the rhenium center from the open (mouth) side of the 2,4-Me$_2$pd ligand (**4** → A, Scheme VIII); (b) rapid exchange of the resulting mouth deuterium atom with hydrogens on C1 and C5 of the 2,4-Me$_2$pd ligand (A → B → C, Scheme VIII); and (c) rapid conversion of the kinetic product to the thermodynamic product, in which the metal-bound hydrogen resides under the backbone (C3) of the 2,4-Me$_2$pd group (C → **5**, Scheme VIII). This proposed mechanism is consistent with all of our current data[26] and with our expectation that the electrophilic attack should occur in an endo fashion[25] from the more open side of the molecule. Intermediates A, B, and C are not directly observed by NMR, but this is not unexpected, since the concentrations of these species are probably very low at any given time.

Scheme VIII



Experimental Section

A. General Comments. All manipulations were carried out under inert atmosphere, using either drybox or Schlenk techniques. Tetrahydrofuran was dried over sodium/benzophenone and distilled before use. Pentane was dried over calcium hydride and distilled. Methylene chloride and acetonitrile were refluxed over P$_2$O$_5$ and distilled. Dichlorodifluoromethane (Matheson), ammonium hexafluorophosphate (Alfa), and tetrafluoroboric acid–diethyl ether (Alfa) were used without further purification. Trifluoromethanesulfonic acid-d_1 was prepared from the reaction of trifluoromethanesulfonic anhydride with D$_2$O. (Me$_2$PCH$_2$)$_3$CMe was synthesized by the procedure of Whitesides,[27] except for the following modification, which was suggested by K. Caulton and R. Geerts (Indiana University): Me$_2$PPMe$_2$, an intermediate in the synthesis, was produced by heating a mixture of Me$_2$P(S)P(S)Me$_2$ and iron metal with a natural gas–oxygen torch.

All NMR experiments were performed on a Varian XL-300 NMR spectrometer. ^{1}H (300 MHz), ^{2}H (46 MHz), and ^{13}C (75 MHz) NMR spectra are referenced to tetramethylsilane. ^{31}P NMR spectra (121 MHz) are referenced to external H$_3$PO$_4$. In general, ^{13}C NMR peak assignments were made from gated decoupled spectra. ^{1}H NMR peak assignments were then obtained from ^{13}C–^{1}H shift-correlated (HETCOR) 2D spectra. In some cases, connectivities were ascertained from ^{1}H–^{1}H shift-correlated (COSY) 2D spectra and C–H coupling constants were obtained from ^{13}C–^{1}H *J*-resolved (HET 2DJ) spectra. Infrared spectra were recorded on a Perkin-Elmer 283B Spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

B. Synthesis of (C$_5$H$_7$-μ-H)Mn[(Me$_2$PCH$_2$)$_3$CMe]$^+$PF$_6^-$ (2a). At -30 °C, 0.13 g (8.0 × 10^{-4} mol) of NH$_4$$^+PF_6$$^-$ was added to 0.30 g (8.0 × 10^{-4} mol) of (η^5-pentadienyl)Mn[(Me$_2$PCH$_2$)$_3$CMe] (**1**)[1f] in 30 mL of tetrahydrofuran. As the solution was stirred for 15 min, a pale-purple solid, **2a**, precipitated out. This material was collected by filtration and washed with two 10-mL portions of tetrahydrofuran and two 10-mL portions of methylene chloride: yield 0.29 g (70%). Anal. Calcd for C$_{16}$H$_{35}$MnP$_4$F$_6$: C, 36.93; H, 6.79. Found: C, 36.19; H, 7.15.

See the drawing in section B of the Results and Discussion for the labeling scheme of cation **2**: ^{1}H NMR (stopped exchange, -130 °C, CD$_2$Cl$_2$/CF$_2$Cl$_2$) δ -15.31 (H1$_a$, 1, br s), -3.05 (H1$_b$, 1, br s), -0.33 (H1$_c$, 1, br s), 0.20 (H5$_i$, 1, br s), 0.70, 0.74, 1.10, 1.21, 1.32, 1.68, 1.86 (phosphine H's, 27, complex series of peaks), 2.95 (H5$_0$, 1, br s), 4.91 (H4, 1, br s), 5.09 (H2, 1, br s), 5.83 (H3, 1, br s). As the temperature was raised to -30 °C in CD$_2$Cl$_2$, the signals due to H1$_a$, H1$_b$, and H1$_c$ broadened and then coalesced into a single sharp peak at δ -6.23. A further increase in temperature (to 20 °C) caused the peak at δ -6.23 and the peaks at δ 0.20 (H5$_i$) and 2.95 (H5$_o$) to broaden. In addition, the phosphine region of the spectrum was considerably simplified at 20 °C, consisting of just three signals: ^{1}H NMR (20 °C, CD$_2$Cl$_2$) δ -6.23 (agostic Me group, 3, v br s), 0.20 (H5$_i$, 1, v br s), 0.80 (phosphine capping Me, 3, m), 1.00–1.11 (phosphine methylene H's, 6, m), 1.28–1.35 (phosphine methyl H's, 18, m), 2.95 (H5$_o$, 1, v br s), 5.01 (H2/H4, 2, br s), 5.82 (H3, 1, s). ^{13}C{^{1}H} NMR (-30 °C, CD$_2$Cl$_2$) δ 97.1 (C2), 95.2 (C4), 78.5 (C3), 42.4 (C5), 36–38 (CH$_2$'s), 35.9 (C1),

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(24) Frenz, B. A.; Ibers, J. A. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 41–44.

(25) See, for example: (a) Byrne, J. W.; Blaser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871. (b) Nixon, J. F.; Wilkins, B. *J. Organomet. Chem.* **1974**, *80*, 129. (c) Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 6905.

(26) We have demonstrated by mass spectrometry and ^{13}C{^{1}H} NMR spectroscopy that only *one* deuterium is incorporated into each molecule of **5**; i.e., multiple exchanges between the 2,4-Me$_2$pd ligand and the D$^+$ reagent do not occur. In this experiment, **4** was reacted with D$^+$ as described in section F of the Experimental Section. Acetonitrile was then added to the solution, causing displacement of 2,4-dimethylpentadiene. This 2,4-dimethylpentadiene was shown by GC/MS (Finnigan 3200, 70 eV, 6-ft × $^1/_4$-in. 5% SE-30 column, 35 °C) to possess a molecular ion of mass 97 (C$_7$H$_{11}$D). Furthermore, the ^{13}C{^{1}H} NMR spectrum of the 2,4-dimethylpentadiene exhibited overlapping singlets and 1:1:1 triplets (C–D coupling) for the terminal methylene and methyl carbons, again indicating a maximum of monodeuteriation at each of these positions.

(27) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379.

34.0 (bridgehead C), 31.8 (capping Me), 24–36 (phosphine Me's, v br). The phosphine methyl groups were in intermediate exchange at −30 °C and hence gave rise to a very broad signal. The J_{C-H} coupling constants for the pentadienyl carbon atoms were 118.2 (C1), 141.4 (C2), 134.2 (C3), 143.4 (C4), and 138.9 Hz (C5). $^{31}P\{^1H\}$ NMR (stopped exchange, −70 °C, CD_2Cl_2) δ 56.8 (mouth P, 1) 32.6 (backbone P's, 2), −144.0 (PF_6^-, 1, binomial heptet, J_{P-F} = 706 Hz). At 20 °C, the two signals have coalesced into a single peak at δ 40.7. IR (Nujol mull, selected peaks) 2360–2300 (w, br, agostic C–H), 1300, 1286 (s, C–H bends), 935 (s, P–C stretch), 830 cm^{-1} (s, P–F stretch).

C. Reaction of (η^5-Pentadienyl)Mn[($Me_2PCH_2)_3$CMe] (1) with DO_3SCF_3. (C_5H_7-μ-D)Mn[($Me_2PCH_2)_3CMe]^+O_3SCF_3^-$ (**2b**) was produced in situ by reacting 1.0 × 10^{-2} g (2.7 × 10^{-5} mol) of (η^5-pentadienyl)Mn[($Me_2PCH_2)_3$CMe] (**1**) in 0.8 mL of CH_2Cl_2/CF_2Cl_2 with 4.0 μL (2.7 × 10^{-5} mol) of DO_3SCF_3 at −130 °C. The deuterium atom was incorporated exclusively into the semibridging position: ^2H NMR (−130 °C, CD_2Cl_2/CF_2Cl_2) δ −15.3. A second sample of **2b** was prepared in 0.8 mL of CH_2Cl_2 by reacting 4.9 × 10^{-2} g (1.3 × 10^{-4} mol) of **1** with 20.0 μL (1.3 × 10^{-4} mol) of DO_3SCF_3. As this sample was warmed to −30 °C, the deuterium scrambled among the three sites in the agostic methyl group. The chemical shift of the ^2H NMR signal for this fluxional group was temperature dependent: ^2H NMR (CD_2Cl_2) δ −5.0 (−70 °C), −5.1 (−50 °C), −5.2 (−30 °C). As the temperature was raised above −30 °C, deuterium was incorporated into the sites on C5, and signals appeared at δ 0.20 ($D5_i$) and 2.95 ($D5_o$) in the ^2H NMR spectrum.

D. Synthesis of Mn[($Me_2PCH_2)_3CMe]_2^+PF_6^-$ (3a). ($Me_2PCH_2)_3$CMe (0.10 g; 4.0 × 10^{-4} mol) was added to a suspension of 0.21 g (4.0 × 10^{-4} mol) of (C_5H_7-μ-H)Mn[($Me_2PCH_2)_3CMe]^+PF_6^-$ (**2a**) in 25 mL of tetrahydrofuran. Upon stirring for several hours, the solution turned yellow. The volatiles (tetrahydrofuran and *cis*-1,3-pentadiene[28]) were then removed under vacuum, and the remaining yellow product was washed with two 10-mL portions of pentane and recrystallized from acetonitrile at −30 °C: yield 0.25 g (89%); ^1H NMR (20 °C, CD_3CN) δ 1.48 (methylene H's, 12, s), 1.39 (phosphine methyl H's, 36, s), 1.08 (capping methyl H's, 3, s); $^{13}C\{^1H\}$ NMR (20 °C, CD_3CN) δ 43.55 (methylene C's), 37.22 (capping methyl C), 34.93 (bridgehead C), 27.88 (phosphine methyl C's); $^{31}P\{^1H\}$ NMR (20 °C, CD_3CN) δ 26.6 (cation P's, 6, six lines of approximately equal intensity, J_{P-Mn} = 178 Hz), −144.0 (PF_6^-, 1, binomial heptet, J_{P-F} = 706 Hz). Anal. Calcd for $C_{22}H_{54}P_7MnF_6$: C, 37.51; H, 7.74. Found: C, 37.57; H, 8.01.

E. Synthesis of (η^5-2,4-Dimethylpentadienyl)Re(H)($PMe_2Ph)_3^+BF_4^-$ (5a). To a cold (−30 °C) solution of 0.30 g (4.3 × 10^{-4} mol) of (η^5-2,4-Me_2pd)Re($PMe_2Ph)_3$ in 25 mL of tetrahydrofuran was added via syringe 100 μL (5.0 × 10^{-4} mol) of $HBF_4\cdot OEt_2$. The pale-yellow precipitate of **5a**, which formed within 10 min of mixing, was filtered, washed with pentane, and recrystallized at −30 °C from a saturated tetrahydrofuran solution. The yield was 0.31 g (90.6%) of pale-lavender crystals containing one molecule of tetrahydrofuran per molecule of **5a**. The tetrahydrofuran molecule of crystallization was removed by prolonged evacuation. Anal. Calcd for $C_{31}H_{45}ReP_3BF_4$: C, 47.51; H, 5.80. Found: C, 46.93; H, 6.12.

See Figure 2 for the labeling scheme: ^1H NMR (stopped exchange, 20 °C, CD_2Cl_2) δ −10.90 (metal hydride, 1, t of d, J_{H-P_3} = 12.1, $J_{H-P1,2}$ = 51.5 Hz), 0.06 ($H1_i/H5_i$, 2, s), 1.70 (phosphine Me's, 6, d, J_{H-P} = 14.7 Hz), 1.78 (2,4-Me_2pd Me's, 6, s), 1.84 (phosphine Me's, 6, d, J_{H-P} = 14.6 Hz), 2.27 (phosphine Me's, 6, d, J_{H-P} = 14.7 Hz), 2.56 ($H1_o/H5_o$, 2, s), 5.28 (H3, 1, s), 7.29–7.60 (phenyl H's, 15, complex m). As the temperature of a sample in $C_2D_4Cl_2$ was raised to 80 °C, the signals at δ −10.9 (Re–H), 0.06 ($H1_i/H5_i$), and 2.56 ($H1_o/H5_o$) broadened and disappeared into the base line but did not reemerge as a coalesced peak before the sample decomposed. The three peaks due to the phosphine methyl groups coalesced to a single peak at δ 1.94. $^{13}C\{^1H\}$ NMR (stopped exchange, 20 °C, CD_2Cl_2) δ 18.4 (phosphine Me's, d, J_{C-P} = 37 Hz), 21.3 (phosphine Me's, d, J_{C-P} = 36 Hz), 26.2 (2,4-Me_2pd Me's, s), 26.9 (phosphine Me's, d, J_{C-P} = 35.5 Hz), 51.3 (C1/C5, s), 87.5 (C3, s), 98.2 (C2/C4, s), 127–132 (phenyl C's, complex m), 140.9 (ipso C's of P1/P2 phenyls, d, J_{C-P} = 70 Hz) (ipso C of P3 phenyl was unresolved); $^{31}P\{^1H\}$ NMR (stopped exchange, 20 °C, CD_2Cl_2) δ −44.8 (P3, t, J_{P-P} = 41.8 Hz), −36.6 (P1/P2, d, J_{P-P} = 41.8 Hz). As the temperature of a sample in $C_2D_4Cl_2$ was raised to 80 °C, these two peaks coalesced into a single peak at δ −40.7. IR (CH_2Cl_2, selected peaks) 3060–2920 (s, C–H stretches), 1430, 1255 (s, C–H bends), 1055 (vs, B–F stretch), 940, 895 cm^{-1} (s, P–C stretches).

F. Reaction of (η^5-2,4-Dimethylpentadienyl)Re($PMe_2Ph)_3$ (4) with D^+. At −90 °C, 2.0 × 10^{-2} g (2.8 × 10^{-5} mol) of (η^5-2,4-Me_2pd)Re($PMe_2Ph)_3$ in 0.6 mL of CH_2Cl_2/CF_2Cl_2 was reacted with 4.2 μL (2.8 × 10^{-5} mol) of DO_3SCF_3 to produce in situ the monodeuteriated analogue of cation **5**. ^2H NMR showed that the added deuterium atom was scrambled between the metal-bound site and the four sites on C1 and C5 of the 2,4-Me_2pd ligand: ^2H NMR (−90 °C, CH_2Cl_2/CF_2Cl_2) δ −10.9 (M–D), 0.06 ($D1_i/D5_i$), 2.56 ($D1_o/D5_o$). The spectrum did not change significantly when the sample was warmed to room temperature.

Table III. Crystal and Diffraction Data for Compound **5a**

formula	$C_{35}H_{53}BF_4OP_3Re$
molecular weight	855.74
space group	$P2_1/n$
a, Å	10.267 (2)
b, Å	18.487 (5)
c, Å	19.843 (4)
β, deg	98.83 (2)
V, Å^3	3721 (2)
Z	4
crystal color	pale lavender
crystal dimens, mm	0.2 × 0.2 × 0.4
d_{calcd}, g/cm^3	1.527
radiation, Å	Mo Kα, λ = 0.71069
scan type	ω
scan rate, deg/min	variable, 6–29
scan width, deg	0.6
2θ min, deg	3.0
2θ max, deg	45.0
octants collected	$h,k,\pm l$
no. of unique reflcts measd	4412
no. of reflcts with $I > 3\sigma(I)$	3155
decay of standards, %	5.1
max, min, avg decay corr. applied for f_{obsd}	1.1575, 0.9899, 1.0583
no. of parameters varied	384
data/parameter ratio	8.22
μ_{calcd}, cm^{-1}	34.800
abs corr.	DIFABS[a]
transmission factors; max, min, avg	1.038, 0.945, 0.981
extinction corr.	none
final R_F[b]	0.036
final R_{wF}[c]	0.048

[a] See: Walker, N.; Stuart, D. *Acta Crystallogr., Sect A: Found. Crystallogr.* **1983**, *A39*, 158. [b] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

G. X-ray Diffraction Study of (η^5-2,4-Dimethylpentadienyl)Re(H)($PMe_2Ph)_3^+BF_4^-\cdot OC_4H_8$ (5a). Single crystals suitable for X-ray diffraction study were grown from a saturated tetrahydrofuran solution and sealed in glass capillaries under an inert atmosphere. Data were collected at room temperature on a Nicolet P3 diffractometer using graphite monochromated Mo Kα radiation. A minimum ω scan rate of 6°/min was employed, since preliminary work indicated a decay problem. All data reduction and refinement were done by using the Enraf-Nonius structure-determination package SDP/VAX (modified by B. A. Frenz and Assoc., Inc., College Station, TX). Crystal data and details of data collection and structural analysis are summarized in Table III.

The data were corrected for anisotropic decay, and equivalent reflections were averaged. The non-hydrogen atom structure was developed and refined isotropically by standard Fourier techniques, following the location of the rhenium atom from a Patterson map. An empirical absorption correction (using the unaveraged data set) was then performed using the program DIFABS.[29] With the corrected, averaged data, all non-hydrogen atoms in the cation and anion were refined anisotropically, while the non-hydrogen atoms in the tetrahydrofuran molecule of crystallization were refined with isotropic thermal parameters. Hydrogen atoms on the cation, except the hydride, were added at idealized positions, riding upon their respective carbon atoms with C–H = 0.95 Å, and were included in the structure factor calculations. Hydrogen atoms on methyl carbons were assigned fixed isotropic thermal parameters of 9.00, while the phenyl and remainder of the pentadienyl hydrogen atoms were assigned fixed isotropic thermal parameters of 7.00. A consistent large peak (0.74 e Å^{-3})[30] due to the metal-bound hydrogen atom was located on the difference Fourier maps at 1.87 Å from the Re center. The positional parameters of this atom, H1M, were refined with the use of a maximum sin θ/λ cutoff value of 0.35, while all other atomic positions

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(28) This *cis*-1,3-pentadiene product was identified by ^1H and ^{13}C NMR spectroscopy. The absence of *trans*-1,3-pentadiene was confirmed by gas chromatography using a 12-ft × $^1/_8$-in. column containing OV-1 on Chrom-W-HP at 30 °C.

(29) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

(30) This was the largest peak in the vicinity of the Re atom. Only one larger peak (0.77 e Å^{-3}) appeared on the difference Fourier maps, and it was located near the tetrahydrofuran molecule of crystallization.

and thermal parameters were kept constant. The esd's for H1M were obtained from the last refinement cycle in which the $\sin\theta/\lambda$ cutoff was used. Finally, the refinement was completed by carrying out one last least-squares cycle on the non-hydrogen atoms without using the $\sin\theta/\lambda$ cutoff.

H. **Solution Dynamics.** Samples were dissolved in CD_2Cl_2/CF_2Cl_2, CD_2Cl_2, or $C_2D_4Cl_2$, and NMR spectra were recorded over the temperature range -130 to 80 °C. Probe temperatures were calibrated by using the temperature dependence of the difference in chemical shift between the ^1H resonances of the methyl and hydroxyl groups of methanol below ambient temperatures and between the ^1H resonances of the methylene and hydroxyl groups of ethylene glycol above ambient temperatures.[31] Theoretical line shapes were calculated for a series of rates by using the method of C. S. Johnson.[32,33] Exchange rate constants for each temperature were determined by matching the theoretical spectra to experimental spectra (measured at various temperatures). These exchange rate constants, k, were then used to calculate the free energy of activation, ΔG^*, at each temperature, T, by using the Eyring equation: $k = (k'/h)Te^{-\Delta G^*/RT}$.[34]

Conclusions

(η^5-Pentadienyl)Mn[$(Me_2PCH_2)_3CMe$] (**1**) and (η^5-2,4-dimethylpentadienyl)Re$(PMe_2Ph)_3$ (**4**) react readily with acids. In the manganese system, H^+ attack occurs in an endo fashion, either at the metal center, followed by rapid migration to a semibridging position between the Mn center and C1 of the pd ligand, or directly at the semibridging site. In the rhenium system, we propose that the kinetic H^+ attack occurs at the metal center from the open mouth side of the 2,4-Me_2pd ligand. This metal-bound mouth hydrogen then rapidly exchanges with the hydrogens on C1 and C5 of the 2,4-Me_2pd ligand before moving to its thermodynamic metal-bound position under C3 of the 2,4-Me_2pd ligand.

Several factors may contribute to the observed shift from a ground-state agostic structure in the manganese system to a ground-state η^5-pentadienyl-metal-hydride structure in the rhenium system. First, the strength of metal-hydrogen bonds increases down a triad, and this stabilizes the η^5-pentadienyl-rhenium-hydride structure with respect to its agostic isomer.[35] Second, the larger radial expansion of rhenium's orbitals allows it to interact more strongly with the large, planar η^5-pentadienyl ligand,[36] again favoring the η^5-pentadienyl-rhenium-hydride structure over the agostic isomer. Third, rhenium can more easily accommodate the formally seven-coordinate geometry of a η^5-pentadienyl-Re(H)P_3^+ complex.

Although their ground states differ, both protonated complexes undergo fluxional processes in solution involving migration of the hydrogen ligand between the metal center and the termini of the pentadienyl ligand. This propensity of the pd ligand to participate in intramolecular migration reactions differs from the behavior exhibited by cyclopentadienyl, whose aromaticity makes it much less susceptible to attack. We hope to utilize the pd ligand's susceptibility to attack in a variety of stoichiometric and catalytic applications.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. Additional support was provided by Monsanto Co. and by BRSG S07 RR07054-20 awarded by the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health. NMR spectra were obtained with the expert assistance of Dr. Andre d'Avignon, director of the Washington University High Resolution NMR Service Facility. This facility was funded in part by NIH Biomedical Research Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co. We also thank Professor G. G. Stanley (Washington University) for assistance with the single-crystal X-ray diffraction study of **5a**.

Supplementary Material Available: Listing of final atomic coordinates, thermal parameters, bond lengths, bond angles, and significant least-squares planes including subtended dihedral angles for **5a** (10 pages); tables of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

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(36) The central angle of the pd ligand (angle C2-C3-C4) typically expands to about 127°, which increases the distance between terminal carbon atoms C1 and C5 to about 2.8 Å.