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Pentadienyl–Metal–Phosphine Chemistry. 6.[1] Syntheses, Structures, and Solution Dynamics of (η^5-Pentadienyl)[tris(phosphine)]manganese Complexes

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Reaction of $MnBr_2$ with potassium pentadienide–tetrahydrofuran and the electron-rich chelating tris(phosphine) ligands $(Me_2PCH_2)_3CMe$ or $(Et_2PCH_2CH_2)_2PPh$ produces (η^5-pentadienyl)Mn[$(Me_2PCH_2)_3CMe$] (1) or (η^5-pentadienyl)Mn[$(Et_2PCH_2CH_2)_2PPh$] (2) in high yield. Substitution of potassium 2,4-dimethylpentadienide–tetrahydrofuran for potassium pentadienide–tetrahydrofuran in the above reaction system leads to the syntheses of the 2,4-dimethylpentadienyl analogues of 1 and 2, namely, (η^5-2,4-dimethylpentadienyl)Mn[$(Me_2PCH_2)_3CMe$] (3) and (η^5-2,4-dimethylpentadienyl)Mn[$(Et_2PCH_2CH_2)_2PPh$] (4). Single-crystal X-ray diffraction studies of 2 and 3 have been carried out. 2 crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 16.69 (1) Å, b = 17.06 (1) Å, c = 8.513 (3) Å, V = 2423 (4) Å^3, and Z = 4. 3 also crystallizes in space group $P2_12_12_1$ with a = 14.788 (3) Å, b = 9.709 (3) Å, c = 14.761 (4) Å, V = 2119 (2) Å^3, and Z = 4. Both complexes assume approximate octahedral geometries with C1, C3, and C5 of the pentadienyl ligands and the three phosphorus atoms of the tris(phosphine) ligands occupying the six coordination sites. In 2, the chelating tris(phosphine) ligand is oriented unsymmetrically with one of the terminal phosphine groups situated beneath the open mouth of the pentadienyl ligand and the other terminal phosphine group under an edge of the pentadienyl ligand. This unsymmetrical orientation of the tris(phosphine) ligand also manifests itself in the room-temperature NMR spectra of 2. However, as the temperature is raised, the rate of rotation of the pentadienyl group with respect to the MnP_3 fragment increases, exchanging the ends of the tris(phosphine) ligand and the ends of the pentadienyl ligand. Line-shape simulations of the variable-temperature ^{31}P NMR spectra have enabled us to calculate rotational barriers ($\Delta G^{\ddagger}$'s) of 18.3 ± 0.5 kcal/mol for 2 and 17.3 ± 0.2 kcal/mol for 4. For compounds 1 and 3, rotation is rapid at room temperature but can be slowed by cooling the solutions. Again, line-shape simulations of the variable-temperature ^{31}P NMR spectra have yielded rotational barriers ($\Delta G^{\ddagger}$'s) of 11.4 ± 0.6 kcal/mol and 10.9 ± 0.2 kcal/mol for 1 and 3, respectively.

Introduction

During the past several years, there has been increasing interest in the syntheses, structures, and physical properties of metal complexes containing the acyclic pentadienyl ligand (pd).[2] We are particularly intrigued by the possibility that facile interconversions between pd bonding modes (η^5, η^3, and η^1) might give rise to novel stoichiometric or catalytic chemistry. We have, therefore, focussed our efforts in this area on the synthesis and reaction chemistry of electron-rich pd–M–phosphine complexes,[1] a class of compounds in which $\eta^5 \rightarrow \eta^3$ and $\eta^3 \rightarrow \eta^1$ pd ligand rearrangements are promoted.[3]

The pentadienyl–manganese–phosphine system has proven to be a particularly interesting one because the course of the synthetic reaction changes dramatically upon varying the chelating ability of the phosphine reagent. We have already reported that use of the monodentate phosphine PMe_3 in this reaction system leads to the synthesis of the novel paramagnetic complex (η^8-decatetraene)Mn(PMe_3), in which the decatetraene ligand is derived from coupling of two pd ligands.[1a] However, when the chelating bis(phosphine) $Me_2PCH_2CH_2PMe_2$ (dmpe) is employed, the η^3-pd complex (η^3-pd)Mn(dmpe)$_2$ is generated as the exclusive product.[1d] We now report that use of the electron-rich chelating tris(phosphine) ligands $(Me_2PCH_2)_3CMe$ and $(Et_2PCH_2CH_2)_2PPh$ leads to the high yield syntheses of η^5-pd complexes (η^5-pd)Mn[$(Me_2PCH_2)_3CMe$] (1) and (η^5-pd)Mn[$(Et_2PCH_2CH_2)_2PPh$] (2). These reaction pathways are summarized in Figure 1.

Results and Discussion

A. Syntheses. Complexes 1 and 2 and their 2,4-dimethylpentadienyl analogues (η^5-2,4-Me_2pd)Mn[$(Me_2PCH_2)_3CMe$] (3) and (η^5-2,4-Me_2pd)Mn[$(Et_2PCH_2CH_2)_2PPh$] (4) are produced by reacting $MnBr_2$ with 1 equiv of chelating tris(phosphine) and 2 equiv of potassium pentadienide–tetrahydrofuran (or potassium 2,4-dimethylpentadienide–tetrahydrofuran).[4] In these reactions, pentadienide functions as both the alkylating agent and the reducing agent.[5] The capping tris(phosphine) ligand $(Me_2PCH_2)_3CMe$ is prepared by using a slightly modified version of the procedure published by Whitesides,[6] while $(Et_2PCH_2CH_2)_2PPh$ is synthesized in high yield via the radical-catalyzed addition of 2 equiv of diethylvinylphosphine to phenylphosphine (PH_2Ph), following the general approach of Meek.[7]

(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.

(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.

(3) The coordinatively unsaturated intermediates which result from pd ligand rearrangements are stabilized by the electron-donating phosphine ligands.

(4) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036.

(5) We have observed similar behavior in the cobalt system (see ref 1c).

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

(7) See, for example: DuBois, D. L.; Myers, W. H.; Meek, D. W. *J. Chem. Soc., Dalton Trans.* **1975**, 1011.

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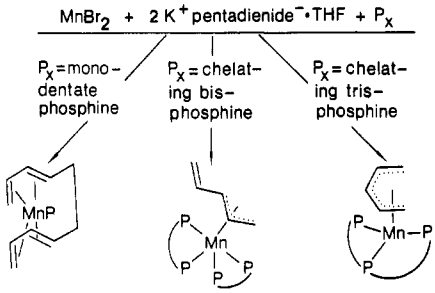

Figure 1. Reaction manifolds for the $MnBr_2$/potassium pentadienide/phosphine system. The course of the reaction depends on the chelating ability of the phosphine ligand.

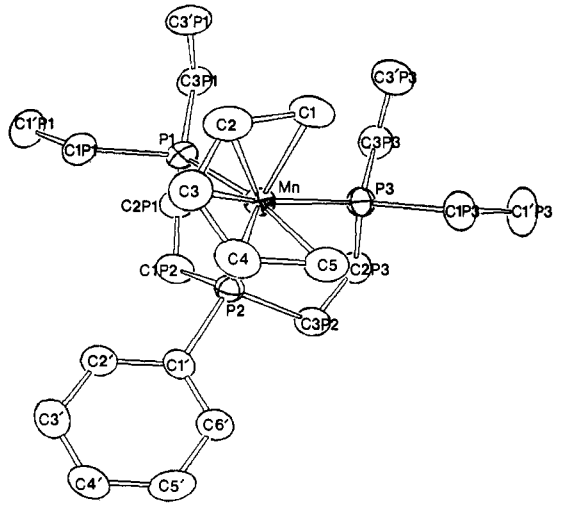

Figure 2. ORTEP drawing of (η^5-pentadienyl)Mn[$(Et_2PCH_2CH_2)_2PPh$] (**2**). Heavy atoms are represented by thermal ellipsoids drawn to encompass 20% of the electron density.

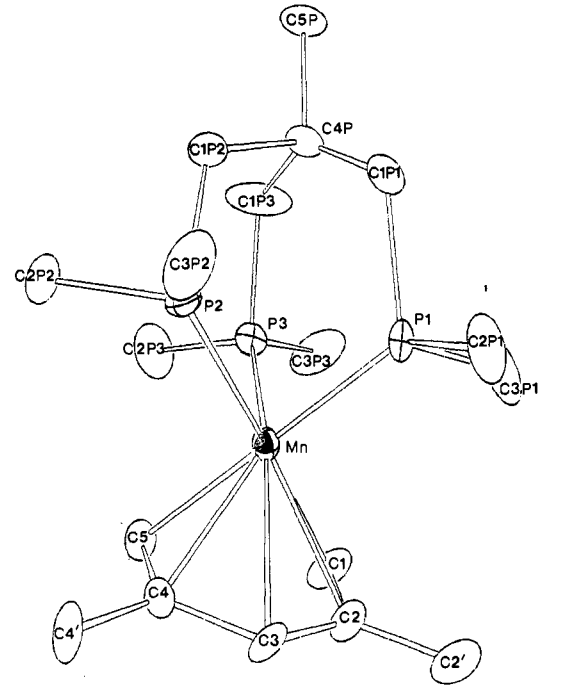

Figure 3. ORTEP drawing of (η^5-2,4-dimethylpentadienyl)Mn[$(Me_2PCH_2)_3CMe$] (**3**). Heavy atoms are represented by thermal ellipsoids drawn to encompass 25% of the electron density.

Use of the commercially available phenylated chelating tris(phosphines) $(Ph_2PCH_2)_3CMe$ and $(Ph_2PCH_2CH_2)_2PPh$ leads to the production of (η^5-pentadienyl)[tris(phosphine)]manganese complexes in low yields as indicated by the NMR spectra. However, we have been unable to separate the manganese complexes from the free tris(phosphine) ligands.

Table I. Positional Parameters with Estimated Standard Deviations for Non-Hydrogen Atoms in (η^5-Pentadienyl)Mn[$(Et_2PCH_2CH_2)_2PPh$] (2)

atom	x	y	z
Mn	0.07076 (5)	0.22017 (5)	0.0875 (1)
P1	−0.00628 (9)	0.2763 (1)	0.2695 (2)
P2	0.13415 (9)	0.33294 (8)	0.0959 (2)
P3	0.16824 (9)	0.17833 (9)	0.2428 (2)
C1	0.0250 (4)	0.1004 (4)	0.0752 (9)
C2	−0.0277 (4)	0.1547 (4)	0.0106 (8)
C3	−0.0103 (4)	0.2109 (4)	−0.1064 (8)
C4	0.0684 (4)	0.2262 (4)	−0.1604 (7)
C5	0.1369 (4)	0.1821 (4)	−0.1194 (8)
C1P1	−0.0948 (4)	0.3282 (4)	0.1881 (9)
C2P1	0.0483 (4)	0.3569 (4)	0.3703 (8)
C3P1	−0.0509 (4)	0.2296 (4)	0.4454 (8)
C1P2	0.0981 (4)	0.4013 (4)	0.2520 (9)
C3P2	0.2404 (4)	0.3171 (4)	0.1495 (9)
C1P3	0.2327 (4)	0.0986 (4)	0.1686 (9)
C2P3	0.2414 (4)	0.2575 (4)	0.283 (1)
C3P3	0.1519 (4)	0.1460 (4)	0.4488 (8)
C1'P1	−0.1463 (4)	0.3771 (5)	0.294 (1)
C3'P1	−0.1126 (4)	0.1675 (4)	0.413 (1)
C1'P3	0.3003 (5)	0.0689 (5)	0.269 (1)
C3'P3	0.1013 (5)	0.0736 (5)	0.469 (1)
C1'	0.1428 (3)	0.3989 (3)	−0.0753 (8)
C2'	0.0759 (4)	0.4390 (4)	−0.1231 (9)
C3'	0.0756 (4)	0.4837 (4)	−0.261 (1)
C4'	0.1420 (4)	0.4904 (4)	−0.3468 (9)
C5'	0.2090 (4)	0.4520 (5)	−0.302 (1)
C6'	0.2095 (4)	0.4060 (4)	−0.1669 (9)

Table II. Positional Parameters with Estimated Standard Deviations for Non-Hydrogen Atoms in (η^5-2,4-Dimethylpentadienyl)Mn[$(Me_2PCH_2)_3CMe$] (3)

atom	x	y	z
Mn	0.2497 (2)	0.21493 (6)	0.23495 (4)
P1	0.3514 (1)	0.3350 (2)	0.1581 (1)
P2	0.1470 (1)	0.3337 (2)	0.1583 (1)
P3	0.2503 (5)	0.0614 (1)	0.12548 (8)
C1	0.3450 (4)	0.0814 (8)	0.3090 (5)
C2	0.3365 (5)	0.2162 (7)	0.3541 (4)
C3	0.2548 (9)	0.2664 (5)	0.3771 (3)
C4	0.1654 (4)	0.2085 (7)	0.3538 (4)
C5	0.1537 (4)	0.0889 (6)	0.3069 (4)
C2'	0.4219 (7)	0.2877 (9)	0.3759 (5)
C4'	0.0868 (4)	0.3018 (8)	0.3856 (5)
C1P1	0.3220 (5)	0.3760 (8)	0.0361 (5)
C2P1	0.3810 (6)	0.5120 (9)	0.1889 (6)
C3P1	0.4693 (6)	0.288 (1)	0.1564 (8)
C1P2	0.1569 (5)	0.3223 (8)	0.0339 (4)
C2P2	0.0268 (5)	0.2726 (8)	0.1499 (5)
C3P2	0.1309 (5)	0.5216 (8)	0.1744 (6)
C1P3	0.237 (1)	0.1264 (6)	0.0104 (4)
C2P3	0.1603 (8)	−0.0792 (8)	0.1261 (7)
C3P3	0.3461 (8)	−0.0450 (9)	0.1057 (6)
C4P	0.2567 (7)	0.2847 (5)	−0.0046 (3)
C5P	0.244 (1)	0.3064 (6)	−0.1084 (3)

B. Structural Studies. Single-crystal X-ray diffraction studies of **2** and **3** have been carried out. ORTEP drawings of the molecular structures are shown in Figures 2 and 3. Atomic coordinates for the non-hydrogen atoms are listed in Tables I and II, while selected bond distances and angles are given in Tables III and IV. Both complexes assume approximate octahedral geometries with C1, C3, and C5 of the pd ligands and P1, P2, and P3 of the tris(phosphine) ligands occupying the six coordination sites.

In **2**, the chelating tris(phosphine) ligand is oriented with one of the terminal phosphine groups situated beneath the open mouth of the pd ligand. This, in turn, places the central phosphine group under one edge of the pd ligand and the other terminal phosphine group under the other

Table III. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (η^5-Pentadienyl)Mn[($Et_2PCH_2CH_2)_2PPh$] (2)

		Bond Distances			
Mn-P1	2.229 (2)	Mn-C2	2.092 (6)	C1-C2	1.392 (10)
Mn-P2	2.197 (2)	Mn-C3	2.140 (7)	C2-C3	1.412 (10)
Mn-P3	2.214 (2)	Mn-C4	2.113 (7)	C3-C4	1.416 (10)
Mn-C1	2.184 (7)	Mn-C5	2.178 (7)	C4-C5	1.413 (10)
		Bond Angles			
P1-Mn-P2	83.06 (7)	P2-Mn-C1	171.6 (2)	C1-Mn-C3	70.9 (3)
P1-Mn-P3	98.45 (8)	P2-Mn-C3	113.2 (2)	C1-Mn-C5	81.9 (3)
P2-Mn-P3	84.79 (7)	P2-Mn-C5	92.5 (2)	C3-Mn-C5	71.0 (3)
P1-Mn-C1	103.5 (2)	P3-Mn-C1	89.1 (2)	C1-C2-C3	126.9 (7)
P1-Mn-C3	101.7 (2)	P3-Mn-C3	154.3 (2)	C2-C3-C4	123.0 (7)
P1-Mn-C5	169.3 (2)	P3-Mn-C5	90.8 (2)	C3-C4-C5	124.9 (7)

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (η^5-2,4-Dimethylpentadienyl)Mn[($Me_2PCH_2)_3CMe$] (3)

		Bond Distances			
Mn-P1	2.216 (4)	Mn-C3	2.158 (5)	C3-C4	1.48 (2)
Mn-P2	2.216 (4)	Mn-C4	2.15 (1)	C4-C5	1.36 (2)
Mn-P3	2.198 (1)	Mn-C5	2.15 (1)	C2-C2′	1.48 (2)
Mn-C1	2.21 (1)	C1-C2	1.47 (2)	C4-C4′	1.55 (3)
Mn-C2	2.18 (1)	C2-C3	1.35 (2)		
		Bond Angles			
P1-Mn-P2	85.98 (4)	P2-Mn-C1	175.3 (4)	C1-Mn-C3	68.4 (5)
P1-Mn-P3	88.7 (2)	P2-Mn-C3	113.5 (4)	C1-Mn-C5	80.9 (2)
P2-Mn-P3	88.9 (2)	P2-Mn-C5	95.5 (4)	C3-Mn-C5	71.0 (6)
P1-Mn-C1	97.4 (4)	P3-Mn-C1	87.9 (4)	C1-C2-C3	121 (1)
P1-Mn-C3	110.6 (4)	P3-Mn-C3	150.6 (2)	C2-C3-C4	127.4 (6)
P1-Mn-C5	177.1 (3)	P3-Mn-C5	88.9 (4)	C3-C4-C5	124 (1)

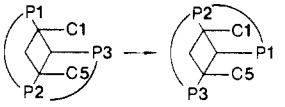

Figure 4. Rotation of the pentadienyl ligand with respect to the MnP_3 fragment in **2**. This process exchanges the ends of the tris(phosphine) ligand as well as the ends of the pentadienyl ligand.

pd edge. Hence, the molecule possesses C_1 symmetry. The phenyl ring on the central phosphine group is oriented such that the dihedral angle between its plane and the pd plane is minimized (dihedral angle = 15.9 (7)°). This orientation minimizes steric contacts between the hydrogen atom on pd carbon atom C4 and the ortho hydrogens on the phenyl ring.

In the structures of both **2** and **3** phosphorus atom P3 is bent up into the mouth of the pd ligand, i.e., P3 resides closer than P1 or P2 to the pd plane. In **2**, P3 is 2.327 (2) Å from the pd plane, compared to 3.069 (2) and 3.013 (2) Å for P1 and P2, respectively. Similarly in **3**, P3 is 2.224 (2) Å from the pd plane, while P1 and P2 are 3.128 (2) Å and 3.088 (2) Å away, respectively.

C. Dynamic NMR Studies. The room-temperature NMR spectra of **2** and **4** reflect the unsymmetrical orientation of the tris(phosphine) ligand observed in the solid-state structure of **2**; the two ends of the chelating tris(phosphine) ligand are inequivalent and the two ends of the pd or 2,4-Me_2pd ligand are inequivalent. These inequivalencies give rise to ^{31}P NMR spectra which exhibit a very characteristic pattern of three equal-intensity singlets, ^{13}C NMR spectra which show five peaks for the manganese-bound pd carbons, and ^1H NMR spectra which exhibit distinct signals for pd protons $H1_{syn}$, $H5_{syn}$, $H1_{anti}$, and $H5_{anti}$.

However, as the temperature is raised, the rate of rotation of the pd or 2,4-Me_2pd group with respect to the MnP_3 fragment increases (see Figure 4). This process, in turn, exchanges the ends of the tris(phosphine) ligand as well as the ends of the pd or 2,4-Me_2pd ligand. The ^{31}P NMR signals due to the terminal phosphorus nuclei begin to broaden and coalesce (see Figure 5). Similar coalescences of the signals due to C1/C5, C2/C4, $H1_{anti}/H5_{anti}$, and $H1_{syn}/H5_{syn}$ are observed by ^{13}C and ^1H NMR. NMR line-shape simulations of the variable-temperature ^{31}P NMR spectra (see Figure 5) have enabled us to calculate a $\Delta G^{\ddagger}$ of 18.3 ± 0.5 kcal/mol for the pd ligand rotation in **2** and a $\Delta G^{\ddagger}$ of 17.3 ± 0.2 kcal/mol for the 2,4-Me_2pd

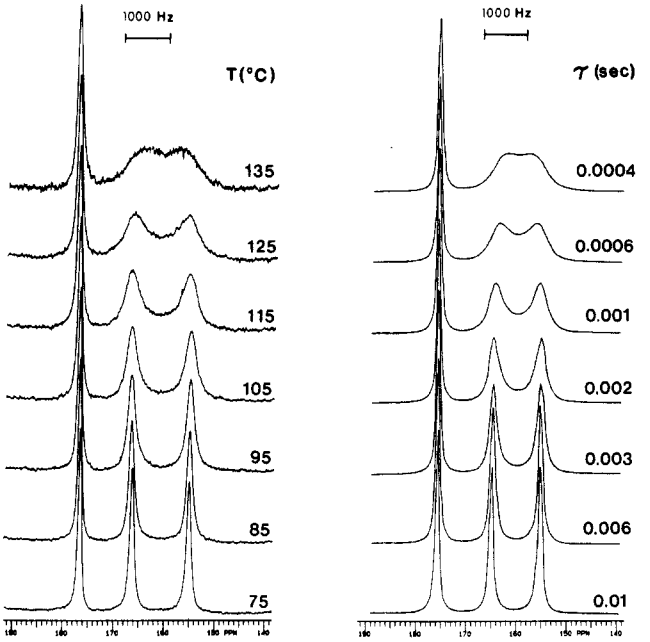

Figure 5. Left: variable-temperature $^{31}P\{^1H\}$ NMR spectra of (η^5-2,4-dimethylpentadienyl)Mn[($Et_2PCH_2CH_2)_2PPh$] (**4**). The signals due to the terminal phosphorus nuclei, P1 and P3, broaden and coalesce as the temperature is raised, while the signal due to P2 remains essentially unchanged. Right: calculated ^{31}P NMR line shapes with preexchange lifetimes τ (in s) between successive pentadienyl ligand rotations. (Note that k, the exchange rate constant, is equal to $1/\tau$.)

ligand rotation in 4. The $\Delta G^{\ddagger}$ values do not have a significant temperature dependence, indicating that the $\Delta S^{\ddagger}$ values for the fluxional process are small. This is consistent with an intramolecular ligand rotational process.

Compounds 1 and 3 are fluxional at room temperature. Rotation of the pd or 2,4-Me_2pd ligand with respect to the chelating tris(phosphine) ligand is rapid, giving rise to a single ^{31}P NMR signal and single signals for the phosphine methyl groups in the ^{13}C and ^{1}H NMR spectra. As the samples are cooled, however, rotation is slowed and the NMR signals begin to broaden and split. The ^{31}P signals split into two peaks with a 1:2 intensity ratio, while the ^{13}C and ^{1}H signals due to phosphine methyl groups split into three peaks with equal intensities.[8] Stopped-exchange ^{31}P spectra are obtained at −70 °C for 1 and 3. Again, NMR line-shape simulations of the variable-temperature ^{31}P spectra have enabled us to calculate rotational barriers ($\Delta G^{\ddagger}$'s) of 11.4 ± 0.6 kcal/mol for 1 and 10.9 ± 0.2 kcal/mol for 3.[9]

D. Mechanism of Pentadienyl Ligand Rotation. Two plausible mechanisms for the pentadienyl ligand rotation in compounds 1–4 can be envisaged. The first is a simple rotation of the ligand in the η^5-bonding mode. The second mechanism involves three steps: (a) an initial $\eta^5 \rightarrow \eta^3$ pd ligand rearrangement, (b) rotation of the η^3-bound ligand, and (c) rearrangement back to the η^5 mode. Both steps a and b in mechanism II are expected to have substantial free energies of activation, $\Delta G^{\ddagger}_a$ and $\Delta G^{\ddagger}_b$, which would contribute to the overall free energy of activation for the process, $\Delta G^{\ddagger}_{total}$. Although mechanism I cannot be ruled out at this time, mechanism II nicely accounts for our experimental observation that $\Delta G^{\ddagger}_{total}$ *decreases* as the electron-donating ability of the ligands *increases*, because $\Delta G^{\ddagger}_a$, the barrier to $\eta^5 \rightarrow \eta^3$ pd ligand isomerization (and a contributor to $\Delta G^{\ddagger}_{total}$ in mechanism II), would be lower in more electron-rich systems.[10]

Experimental Section

A. General Comments. All manipulations were carried out under inert atmosphere, using either drybox or Schlenk techniques. Tetrahydrofuran was dried with sodium/benzophenone and distilled before use. Pentane and cyclohexane were dried over calcium hydride and distilled. 1,1,1-Tris(chloromethyl)ethane and tetramethylbiphosphine disulfide [for the synthesis of $(Me_2PCH_2)_3CMe$)] were purchased from Organometallics and Pressure Chemical Co., respectively. Diethylchlorophosphine and phenylphosphine [for the synthesis of $(Et_2PCH_2CH_2)_2PPh$] were obtained from Strem Chemical Co. 1,1,1-Tris((diphenylphosphino)methyl)ethane (TRIPOD) and bis((2-diphenylphosphino)ethyl)phenylphosphine (TRIPHOS) were obtained from Strem. Anhydrous manganese bromide was purchased from Thiokol, Alfa Products. Pentadiene and 2,4-dimethylpentadiene were obtained from Wiley Organics. All reagents were used without further purification.

NMR experiments were performed on a Varian XL-300 NMR spectrometer.[11] ^{1}H (300 MHz) and ^{13}C (75 MHz) spectra were referenced to tetramethylsilane. ^{31}P spectra (121 MHz) were referenced to free PMe_3. 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. Some connectivities were ascertained from ^{1}H–^{1}H shift-correlated (COSY) 2D spectra. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

B. Synthesis of $(Me_2PCH_2)_3CMe$. $(Me_2PCH_2)_3CMe$ was synthesized via the procedure of Whitesides[6] except for the following modification, which was suggested by K. Caulton and R. Geerts (Indiana University): Me_2PPMe_2, an intermediate in the synthesis, was produced by heating a mixture of $Me_2P(S)P(S)Me_2$ and iron metal with a natural gas–oxygen torch.

C. Synthesis of $(Et_2PCH_2CH_2)_2PPh$. $(Et_2PCH_2CH_2)_2PPh$ was prepared by using the general approach developed by Meek, radical-catalyzed P–H addition to vinylic C–C double bonds.[7] Diethylvinylphosphine (5.86 g, 5.0×10^{-2} mol), phenylphosphine (2.75 g, 2.5×10^{-2} mol), and azobis(isobutyronitrile) (AIBN, 0.20 g, 1.2×10^{-3} mol) were diluted with 50 mL of cyclohexane and refluxed for 24 h. The resulting pale yellow solution was filtered and passed through a 2-in. column of neutral alumina. Following removal of the cyclohexane solvent, the tris(phosphine product) (a colorless oil) was distilled under reduced pressure; yield of $(Et_2PCH_2CH_2)_2PPh$, 7.3 g (85%). ^{1}H NMR (20 °C, benzene-d_6): δ 7.53–7.12 (phenyl H's, 5, complex m's), 1.85–1.77 (bridge methylene H's, 4, m), 1.55–1.30 (bridge methylene H's, 4, m), 1.24–1.08 (terminal methylene H's, 8, m), 0.98–0.84 (methyl H's, 12, m). $^{13}C\{^{1}H\}$ NMR (20 °C, benzene-d_6): δ 139.5–139.3 (phenyl ipso C), 133.07–132.81 (phenyl o-C's), 129.12–128.66 (phenyl m-C's and p-C), 24.72–24.33 (bridge methylene C's), 22.65–22.40 (bridge methylene C's), 19.17–18.91 (terminal methylene C's), 9.87–9.59 (methyl C's). $^{31}P\{^{1}H\}$ NMR (40.25 MHz, 20 °C, benzene-d_6, referenced to PMe_3): δ 44.32, 43.88, 43.73, 43.29, 42.08, 42.01, 41.52, 41.40. This is a second-order AB_2 spectrum with δ_A 43.73, δ_B 41.80, and J_{AB} = 25.89 Hz.

D. Synthesis of (η^5-Pentadienyl)Mn[$(Me_2PCH_2)_3CMe$] (1). Under nitrogen, 0.93 g (4.32×10^{-3} mol) of $MnBr_2$ was refluxed in 250 mL of tetrahydrofuran for 0.5 h. The resulting pale yellow solution was cooled to −78 °C, and 0.88 g (3.47×10^{-3} mol) of $(Me_2PCH_2)_3CMe$ was added. While the solution was maintained at −78 °C, 1.33 g (7.46×10^{-3} mol) of $K^+C_5H_7^-$·THF was added dropwise, producing a bright red solution. The solution was allowed to warm to room temperature, stirred for an additional 5 h, filtered, and evaporated to dryness. The yellow product was extracted with pentane and crystallized from pentane at −30 °C; yield of crystalline 1, 0.91 g (70%, based on the limiting phosphine reagent). MS (electron impact, solid probe, 70 eV): M^+ at 374, $(M - pd + H)^+$ at 308. Anal. Calcd for $C_{16}H_{34}MnP_3$: C, 51.33; H, 9.17. Found: C, 50.93; H, 9.17. ^{1}H NMR (20 °C/fast exchange, benzene-d_6): δ 4.86 (H3, 1, br s), 4.28 (H2/H4, 2, br s), 1.70 ($H1_{syn}/H5_{syn}$, 2, br s), 1.12 (phosphine methyl H's, 18, br s), 0.85 (phosphine methylene H's, 6, s), 0.74 (capping methyl H's, 3, s), −0.57 ($H1_{anti}/H5_{anti}$, 2, br s). $^{13}C\{^{1}H\}$ NMR (20 °C/fast exchange, benzene-d_6): 91.8 (C2, C4), 84.7 (C3), 45.0 (C1, C5), 41.4 (phosphine methylene C's), 37.6 (capping methyl C), 36.5 (quaternary C), 23.7 (phosphine methyl C's). $^{31}P\{^{1}H\}$ NMR (20 °C/fast exchange, benzene-d_6, referenced to PMe_3): δ 123.0. $^{31}P\{^{1}H\}$ NMR (−70 °C/stopped exchange, toluene-d_8, referenced to PMe_3): δ 127.0 (P3), 121.0 (P1, P2). IR (benzene): 3000–2860 cm^{-1} (s, C–H stretch), 1426, 1418, 1286, 1272, 1210, 1086, 1052, 915 cm^{-1} (s, C–H bends, P–C stretches).

E. Synthesis of (η^5-2,4-Dimethylpentadienyl)Mn[$(Me_2PCH_2)_3CMe$] (3). A procedure identical with that described in section D was followed except that $K^+C_5H_7^-$·THF (1.33 g) was replaced with $K^+C_7H_{11}^-$·THF (1.54 g); yield of crystalline 3, 0.90 g (65%, based on limiting phosphine reagent). Anal. Calcd for $C_{18}H_{38}MnP_3$: C, 53.72; H, 9.54. Found: C, 52.17; H, 9.55. ^{1}H NMR (20 °C/fast exchange, benzene-d_6): δ 4.82 (H3, 1, s), 2.18 (pd methyl H's, 6, s), 1.46 ($H1_{syn}/H5_{syn}$, 2, s), 1.17 (phosphine methyl H's, 18, s), 0.95 (phosphine methylene H's, 6, s), 0.79 (capping methyl H's, 3, s), −0.57 ($H1_{anti}/H5_{anti}$, 2, s). $^{13}C\{^{1}H\}$ NMR (20 °C/fast exchange, benzene-d_6): δ 100.71 (C2/C4), 84.75 (C3), 47.16 (C1/C5), 43.41 (phosphine methylene C's), 37.75 (capping methyl C), 35.60 (quaternary C), 28.86 (pd methyl C's), 25.64 (phosphine methyl C's). $^{31}P\{^{1}H\}$ NMR (20 °C/fast exchange, benzene-d_6, referenced to PMe_3): δ 118.1. $^{31}P\{^{1}H\}$ NMR (−70

(8) Note that the two methyl groups on each edge phosphorus atom (P1 and P2) are diastereotopic.

(9) Exchange of the mouth phosphorus nucleus with an edge phosphorus nucleus can occur by either a 120° clockwise rotation or an equivalent 120° counterclockwise rotation. Hence, the total rate of exchange, k_{total}, is equal to the sum of the rates of exchange due to clockwise and counterclockwise rotation ($k_{total} = 2k_{clockwise} = 2k_{counterclockwise}$). $\Delta G^{\ddagger}$'s are calculated by using $k_{clockwise}$ or $k_{counterclockwise}$.

(10) In more electron-rich systems, the 16e (η^3-pd)MnP_3 intermediates are more effectively stabilized. For a more detailed discussion of these rotation mechanisms, see: Bleeke, J. R.; Moore, D. A., submitted for publication in *Inorg. Chem.*

(11) One experiment—the ^{31}P NMR study of $(Et_2PCH_2CH_2)_2PPh$—was performed on a JEOL FX-100 spectrometer at 40.25 MHz.

°C/stopped exchange, toluene-d_8, referenced to PMe_3): δ 127.9 (P3), 113.2 (P1, P2). IR (benzene): 2960–2895 cm^{-1} (s, C–H stretches), 1470, 1426, 1286, 1260, 1089, 1030, 912 cm^{-1} (C–H bends, P–C stretches).

F. Synthesis of (η^5-Pentadienyl)Mn[($Et_2PCH_2CH_2)_2PPh$] (2). Under nitrogen, 0.93 g (4.32×10^{-3} mol) of $MnBr_2$ was refluxed in 250 mL of tetrahydrofuran for 0.5 h. The resulting pale yellow solution was cooled to −78 °C, and 1.19 g (3.47×10^{-3} mol) of $(Et_2PCH_2CH_2)_2PPh$ was added. While the solution was maintained at −78 °C, 1.33 g (7.46×10^{-3} mol) of $K^+C_5H_7^-$·THF was added dropwise, producing a bright red solution. The solution was allowed to warm to room temperature, stirred for an additional 2 h, filtered, and evaporated to dryness. The maroon product was extracted with pentane and crystallized from pentane at −30 °C; yield of crystalline **2**, 1.21 g (75%, based on limiting phosphine reagent). Anal. Calcd for $C_{23}H_{40}MnP_3$: C, 59.47; H, 8.70. Found: C, 59.29; H, 8.34. The two ends of the pd ligand were distinguished by doing NOE difference NMR spectroscopy: irradiation of the ^1H NMR signal due to H4 affected the intensities of the phenyl ^1H NMR signals, indicating that the central (phenylated) phosphine group resides beneath C4, while irradiation of the H2 signal had no such effect. ^1H NMR (25 °C/stopped exchange, benzene-d_6): δ 7.25–7.05 (phenyl H's, 5, complex m), 5.00 (H3, 1, br s), 4.63 (H4, 1, br s), 3.43 (H2, 1, br s), 2.59 ($H5_{syn}$, 1, br s), 2.20–0.70 (phosphine methylene and methyl H's, 27, complex m's), 1.54 ($H1_{syn}$, 1, partially obscured), 0.09 (phosphine methylene H, 1, q), −0.85 ($H5_{anti}$, 1, br s), −1.92 ($H1_{anti}$, 1, br s). $^{13}C\{^1H\}$ NMR (25 °C/stopped exchange, benzene-d_6): δ 142.18 (phenyl ipso C, d, J_{C-P} = 16 Hz), 130.04–127.90 (phenyl o-, m-, p-C's), 92.57 (C4), 85.30 (C2), 85.11 (C3), 44.66 (C5, d, J_{C-P} = 15.1 Hz), 40.57 (C1, d, J_{C-P} = 12.6 Hz), 29.98–23.26 (phosphine methylene C's, complex m's), 9.14–8.70 (phosphine methyl C's). $^{31}P\{^1H\}$ NMR (25 °C/stopped exchange, benzene-d_6, referenced to PMe_3): δ 192.30 (P2), 169.67 (P1 or P3), 155.00 (P1 or P3). IR (benzene): 2950–2870 cm^{-1} (s, C–H stretches), 1455, 1433, 1023, 804 cm^{-1} (s, C–H bends, P–C stretches).

G. Synthesis of (η^5-2,4-Dimethylpentadienyl)Mn[($Et_2PCH_2CH_2)_2PPh$] (4). A procedure identical with that described in section F was followed except that $K^+C_5H_7^-$·THF (1.33 g) was replaced with $K^+C_7H_{11}^-$·THF (1.54 g); yield of crystalline **4**, 1.25 g (73%, based on limiting phosphine reagent). Anal. Calcd for $C_{25}H_{44}MnP_3$: C, 60.96; H, 9.02. Found: C, 59.89; H, 8.69. ^1H NMR (25 °C/stopped exchange, benzene-d_6): δ 7.35–6.95 (phenyl H's, 5, m), 5.0 (H3, 1, s), 2.25 (pd methyl H's, 3, s), 2.08 (pd methyl H's, 3, s), 2.20–0.85 (phosphine methylene and methyl H's, 27, complex m's), 1.00 ($H5_{syn}$, 1, partially obscured), 0.70 (phosphine methylene H, 1, m), 0.13 ($H1_{syn}$, 1, m), −0.90 ($H5_{anti}$, 1, br s), −1.88 ($H1_{anti}$, 1, br s). $^{13}C\{^1H\}$ NMR (25 °C/stopped exchange, benzene-d_6): δ 142.98 (phenyl ipso C, d, J_{C-P} = 13.1 Hz), 129.55–125.95 (phenyl o-, m-, p-C's), 95.63 (C4), 94.51 (C2), 86.40 (C3), 41.70 (C5, d, J_{C-P} = 30 Hz), 40.50 (C1, d, J_{C-P} = 20.8 Hz), 31.00–20.00 (pd methyl C's and phosphine methylene C's, complex m's), 9.64–7.60 (phosphine methyl C's). $^{31}P\{^1H\}$ NMR (25 °C/stopped exchange, benzene-d_6, referenced to PMe_3): δ 176.68 (P2), 165.74 (P1 or P3), 155.93 (P1 or P3). IR (benzene): 2972–2880 cm^{-1} (s, C–H stretches), 1455, 1432, 1021, 809 cm^{-1} (s, C–H bends, P–C stretches).

H. X-ray Diffraction Studies of 2 and 3. Single crystals suitable for X-ray diffraction were grown from a saturated pentane solution. Data were collected at room temperature on a Nicolet P3 diffractometer, using graphite-monochromated Mo Kα radiation. All data reduction and structure refinement were done using the Enraf-Nonius structure determination package (on a VAX 11/780 computer modified by B.A. Frenz and Assoc., Inc., College Station, TX). Crystal data and details of data collection and structure analysis are summarized in Table V.

In each case, the structure was solved by standard Fourier techniques, following the location of the manganese atom from a Patterson map. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealized positions and included in the structure factor calculations.

I. Dynamic NMR Studies. Samples were dissolved in toluene-d_8 or *o*-xylene-d_{10} and NMR spectra were recorded over the temperature range −70 °C to 135 °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.[12] Theoretical line shapes were calculated for a series of rates by using the method of C.S. Johnson.[13,14] The experimental spectra (measured at various temperatures) were matched against the theoretical spectra, and, in this way, exchange rate constants were determined for each temperature. These exchange rate constants, k, were then used to calculate the free energy of activation, $\Delta G^\ddagger$, at each temperature, T, by using the Eyring equation

$$k = (k'/h)T\, e^{-\Delta G^\ddagger/RT}$$

where k' = Boltzmann's constant, h = Planck's constant, and R = ideal gas constant.[15]

Table V. Crystal and Diffraction Data for (η^5-Pentadienyl)Mn[($Et_2PCH_2CH_2)_2PPh$] (2) and (η^5-2,4-Dimethylpentadienyl)Mn[($Me_2PCH_2)_3CMe$] (3)

	2	3
space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	16.69 (1)	14.788 (3)
b, Å	17.06 (1)	9.709 (3)
c, Å	8.513 (3)	14.761 (4)
V, Å^3	2423 (4)	2119 (2)
Z	4	4
crystal dimens, mm	0.2 × 0.12 × 0.08	0.7 × 0.4 × 0.15
scan type	ω	θ–2θ
scan rate, deg/min	variable (2–29)	variable (2–29)
$2\theta_{min}$, deg	3	3
$2\theta_{max}$, deg	55	50
no. of reflcts measd	4900	2172
no. of reflcts with $I > 3\sigma(I)$	2780	1521
abs coeff μ, cm^{-1}	7.247	8.187
abs correctn	none	none
final R_F[a]	0.046	0.035
final R_{wF}[b]	0.054	0.047

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|)$.

Conclusion

The reactions of $MnBr_2$ with potassium pentadienide (or potassium 2,4-dimethylpentadienide) and electron-rich chelating tris(phosphines) lead to the high-yield syntheses of (η^5-pentadienyl)[tris(phosphine)]manganese complexes. In the solid state, these complexes exhibit the expected octahedral geometry with C1, C3, and C5 of the pentadienyl ligands and the three phosphorus atoms of the tris(phosphine) ligands occupying the six coordination sites. In solution, the molecules are fluxional as a result of relatively low barriers to pd group rotation. The dependence of the rotational barriers on the electron-donating ability of the ligands suggests that the mechanism involves (a) an $\eta^5 \rightarrow \eta^3$ pd ligand isomerization, (b) rotation of the η^3-bound ligand, and (c) reisomerization back to the η^5-bonding mode.

We have begun to study the reaction chemistry of the electron-rich (η^5-pentadienyl)[tris(phosphine)]manganese complexes described herein. We anticipate that the accessibility of unsaturated η^3-pd intermediates, together with the capacity of electron-rich metal centers to activate normally resistant bonds,[16] will give rise to novel reactivity.

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Registry No. 1, 102747-17-1; 2, 102747-18-2; 3, 102747-19-3; 4, 102747-20-6; $(Et_2PCH_2CH_2)_2PPh$, 102747-21-7; $Et_2PCH{=}CH_2$, 13652-21-6; $PhPH_2$, 638-21-1; $MnBr_2$, 13446-03-2; $K^+C_5H_7^-$, 51391-25-4; $K^+C_7H_{11}^-$, 74205-98-4.

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, observed and calculated structure factor amplitudes, and significant least-squares planes including subtended dihedral angles (36 pages). Ordering information is given on any current masthead page.

(16) During the 1970s, Tolman and Ittel[16a,b] demonstrated that electron-rich $HM(Np)(dmpe)_2$ complexes (Np = 2-naphthyl, M = Fe, Ru, Os) react with a variety of bonds that are normally difficult to activate. The features of this compound class which are apparently crucial to its unique reactivity are the ready accessibility of coordinatively unsaturated intermediates $(M(dmpe)_2)$ and high electron density at the metal center. (a) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (b) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *Ibid.* **1979**, *101*, 1742. More recently, Bergman[16c] and Green[16d] have used electron-rich (η^5-cyclopentadienyl)$M(PR_3)_3$ complexes of the manganese group metals to activate C–H bonds in alkanes and C–O bonds in carbon dioxide, respectively. (c) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358. (d) Green, M. L. H.; Joyner, D. S.; Wallis, J.; Bell, J. P. Presented at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985.

([2.2]Paracyclophane)gallium(I) Tetrabromogallate(III): Its Synthesis and Novel Structural Features

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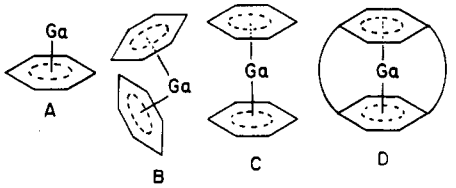
[2.2]Paracyclophane forms 1:1 complexes (1, 2) with Ga_2Cl_4 and Ga_2Br_4, respectively, in benzene at ambient temperature. The products are insoluble in common organic solvents. The crystal and molecular structure determination shows compound 2 to form an intricate highly symmetrical three-dimensional network (orthorhombic, space group *Pnma* with a = 12.836 (4) Å, b = 10.004 (3) Å, c = 14.943 (4) Å, V = 1918.9 Å^3, d_{calcd} = 2.310 g/cm^3 for Z = 4, R_w = 0.038 for 106 refined parameters and 1352 unique reflections with $F_o \geq 4.0\sigma(F_o)$). Each Ga(I) center is complexed by two [2.2]paracyclophane molecules, whose parallel pairs of aromatic rings are tilted relative to each other by 56.7°. The 1:1 stoichiometry implies that each paracyclophane in turn is bonded to two Ga(I) atoms which are situated nearly centrically above each of the arene rings at a distance of 2.72 Å. The polydecker chains of alternating gallium(I) ions and paracyclophane molecules thus formed are cross-linked by tetrahedral $GaBr_4^-$ anions, each of which provides one bromine atom to bridge two Ga(I) centers. Thereby the latter adopt a strongly distorted pseudotetrahedral coordination geometry.

Introduction

Compounds of subvalent gallium, indium, and thallium have recently been found to form a variety of arene complexes in which these elements are η^6-bonded to either one or two aromatic hydrocarbons (A and B).[1-7] In type B,



the two arenes can be equidistant from the metal[3,6,7] or can show significant differences in their metal–ring distances.[2] In all cases investigated to date, the metal is accommodated perpendicular above the ring centers, however, and if two rings are present, their planes form an angle between 37 and 60°.[1] Compounds of unknown structure are formed in arene oxidation using gallium(III).[8] Though theoretical calculations[1] have shown that the bent form B is energetically favored over a situation with parallel arene rings (C), the special geometrical requirements of, e.g., chelating ligands can be expected to make the parallel sandwich structure D for a corresponding complex also feasible.

† X-ray analysis.

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