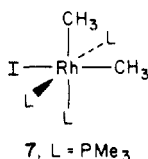


methyl methoxycarbene complex, 4, which then undergoes methyl group migration to form complex 5. Complex 5 decomposes both by reductive elimination to form methyl ethyl ether and a Rh(I) complex<sup>10</sup> and by  $\beta$ -elimination to form methyl vinyl ether and a dihydrido rhodium(III) compound. The dihydrido compound 6 that is detected is actually the tetrakis(trimethylphosphine) complex  $\text{RhH}_2(\text{PMe}_3)_4^+$ ,<sup>11</sup> which means phosphine redistribution reactions complicate the overall reaction kinetics.<sup>12</sup>

Although the proposed intermediate species 4 and 5 of eq 3 have not been observed, supporting evidence for this reaction mechanism comes from studies of related iridium compounds and from the effect of coordinating ligands on the reaction, which must await the full publication for adequate description.<sup>2e</sup> However, reasons for excluding two possible alternative mechanisms are presented briefly below.

One possible alternative to the mechanism of eq 3 is  $\alpha$ -hydrogen migration from the methyl group followed by methoxymethyl group migration to the methylene carbon atom. But, if a methyl group can function as a source of a migrating  $\alpha$ -hydrogen atom, the dimethylrhodium complex 7<sup>13</sup> should evolve ethylene when treated with hal-



ide-abstracting reagents. Complex 7 does react with halide-abstracting reagents, but no ethylene, ethane, or methane is formed and the dimethylrhodium complex can be recovered by adding halide. This implies that methyl groups do not function as  $\alpha$ -hydrogen sources (in this coordination environment), consistent with the earlier suggestion that mononuclear Rh(III) methylene complexes are not readily accessible. The methoxymethyl group may function as an  $\alpha$ -hydrogen source, as the resulting methoxycarbene group is relatively more stable.

A second possible alternate mechanism is the direct reductive elimination of methyl ethyl ether from compound 1, or perhaps from compound 3, with subsequent dehydrogenation of the ethyl group. However, the <sup>13</sup>C<sub>3</sub>-labeled compound 1<sup>5a</sup> undergoes the halide abstraction reaction forming <sup>13</sup>C-labeled methyl vinyl ether,<sup>14</sup> and no unlabeled methyl vinyl ether, even in the presence of 1.5 equiv of unlabeled methyl ethyl ether. Therefore, the methyl vinyl ether cannot result from dehydrogenation

of free methyl ethyl ether. The most plausible mechanism for vinyl ether formation remains the " $\alpha$ -elimination" mechanism summarized in eq 3.

**Acknowledgment.** I was first made aware of  $\alpha$ -hydrogen processes in reactions of alkylmetal compounds<sup>15</sup> and was introduced to synthetic organometallic chemistry in general by Professor Earl Muetterties and his co-workers while at Cornell University. Without his inspiration the present work would not have been attempted.

**Registry No.** 1 (L = PMe<sub>3</sub>), 92670-91-2; 2 (L = PMe<sub>3</sub>), 92670-92-3; 3 (L = PMe<sub>3</sub>), 92670-93-4; 7 (L = PMe<sub>3</sub>), 92670-94-5; Rh(CH<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub>, 92670-95-6; Rh(PMe<sub>3</sub>)<sub>4</sub>Cl, 92670-96-7.

(15) Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* 1978, 100, 6978-6989.

### Synthesis and Crystal Structure of (*syn*- $\eta^3$ -Pentadienyl)Mn[(CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and Its Reactions To Produce Mn[(CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup> and *cis*-Mn[(CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup>

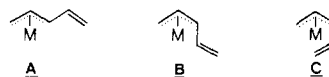
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**Summary:** Reaction of MnBr<sub>2</sub> with 1,2-bis(dimethylphosphino)ethane (dmpe) and potassium pentadienide results in the formation of (*syn*- $\eta^3$ -pentadienyl)Mn(dmpe)<sub>2</sub> (1). A single-crystal X-ray diffraction study of 1 has established that the *syn*- $\eta^3$ -pentadienyl ligand is essentially W-shaped, with carbon atom C5 rotated slightly out of the plane made by C1, C2, C3, and C4. Reaction of 1 with NH<sub>4</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup> produces Mn(dmpe)<sub>3</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup> (2), the first example of a homoleptic manganese-phosphine complex. Treatment of 1 with NH<sub>4</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup> in the presence of trimethyl phosphite produces *cis*-Mn(dmpe)<sub>2</sub>[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup> (3).

In recent years, the acyclic pentadienyl group has begun to be utilized as a ligand in organotransition metal complexes.<sup>1</sup> One of the intriguing features of this ligand is its ability to adopt a variety of bonding modes and geometries. Recent structural reports of pentadienylmetal complexes, for example, have described three different solid-state geometries for  $\eta^3$ -pentadienyl ligands, W-shaped *syn*- $\eta^3$  (A),<sup>1m</sup> sickle-shaped anti- $\eta^3$  (B),<sup>1l</sup> and U-shaped anti- $\eta^3$  (C).<sup>1n</sup> The U-shaped  $\eta^5$ -bonding mode is also



\*Dedicated to the memory of Earl Muetterties—mentor and friend.

(1) Recent reports of pentadienyl transition-metal complexes include the following: (a) Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* 1980, 102, 5928. (b) Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *Ibid.* 1982, 104, 1120. (c) Liu, J.-Z.; Ernst, R. D. *Ibid.* 1982, 104, 3737. (d) Ernst, R. D.; Cymbaluk, T. H. *Organometallics* 1982, 1, 708. (e) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Ibid.* 1983, 2, 1220. (f) Stahl, L.; Ernst, R. D. *Ibid.* 1983, 2, 1229. (g) Ernst, R. D.; Liu, J.-Z.; Wilson, D. R. *J. Organomet. Chem.* 1983, 250, 257. (h) Seyferth, D.; Goldman, E. W.; Pomet, J. *Ibid.* 1981, 208, 189. (i) Paz-Sandoval, M. A.; Powell, P. *Ibid.* 1981, 219, 81. (j) Lehmkuhl, H.; Naydowski, C. *Ibid.* 1982, 240, C30. (k) Paz-Sandoval, M. A.; Powell, P. *Ibid.* 1983, 252, 205. (l) Paz-Sandoval, M. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* 1984, 3, 1026. (m) Bleeke, J. R.; Hays, M. K. *Ibid.* 1984, 3, 506. (n) Bleeke, J. R.; Peng, W.-J. *Ibid.* 1984, 3, 1422.

(9) (a) <sup>1</sup>H NMR of methyl vinyl ether (CD<sub>2</sub>Cl<sub>2</sub>): OCH<sub>3</sub>, 3.55 (s); =CH(OMe), 6.54 (d of d (14.2, 6.9 Hz)); =CH<sub>2</sub>, 4.01 (d of d (6.9, 2.2)), 4.18 (d of d (14.2, 2.2)).<sup>9b</sup> <sup>1</sup>H NMR of methyl ethyl ether (CD<sub>2</sub>Cl<sub>2</sub>): CH<sub>3</sub>CH<sub>2</sub>, 1.18 (t), 3.42 (q (7.1 Hz)); OCH<sub>3</sub>, 3.31 (s). These products are formed simultaneously in a 1:1 ratio ( $\pm 10\%$ ) and together account for at least 85% of reacted compound 3. (b) Herberhold, M.; Wiedersatz, G. O.; Kreiter, C. G. *Z. Naturforsch., B:* 1976, 31B, 35-38.

(10) The Rh(I) product(s) appears to react with CD<sub>2</sub>Cl<sub>2</sub> forming several uncharacterized products. Marder, T. B., personal communication.

(11) Schrock, R. R.; Osborne, J. A. *J. Am. Chem. Soc.* 1971, 93, 2397-2407. The inability of this compound to hydrogenate olefins under mild conditions allows the accumulation of methyl vinyl ether.

(12) Another methyl(methoxymethyl)rhodium compound, believed to be Rh(CH<sub>3</sub>)(CH<sub>2</sub>OCH<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub>(acetonitrile)<sub>2</sub><sup>+</sup>, can be detected during the reaction but is eventually consumed. This compound does not appear to be involved in the formation of the organic products but arises, and disappears, as a result of phosphine redistribution reactions.

(13) <sup>1</sup>H NMR of 7 (CD<sub>2</sub>Cl<sub>2</sub>): Rh-CH<sub>3</sub>, 0.08 (d (8.2 Hz)) of t (6.0) of d (2.4); 0.18 (t (7.7) of d (5.8) of d (2.0)); P(CH<sub>3</sub>)<sub>3</sub>, 1.42 (d (6.2)), 1.48 (t (3.0) of d (1 Hz)).

(14) <sup>13</sup>C NMR of <sup>13</sup>CH<sub>2</sub>=CH(OMe) (CD<sub>2</sub>Cl<sub>2</sub>): 85.3; J(C-H) = 161, 156, 9.5 Hz.<sup>9b</sup> No <sup>12</sup>CH<sub>2</sub>=CH(OMe) can be detected in the <sup>1</sup>H NMR spectrum.

Table I. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (*syn*- $\eta^3$ -Pentadienyl)Mn[(CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (1)

Bond Distances					
Mn-P1	2.26 (2)	C3-C4	1.49 (3)	P2-C1P2	1.84 (2)
Mn-P2	2.231 (4)	C4-C5	1.32 (2)	P2-C2P2	1.92 (2)
Mn-P3	2.207 (5)	P1-C1P1	1.92 (3)	P2-C3P2	1.85 (2)
Mn-P4	2.235 (5)	P1-C2P1	1.88 (3)	P4-C1P4	1.86 (1)
Mn-C1	2.21 (2)	P1-C3P1	1.99 (3)	P4-C2P4	1.91 (2)
Mn-C2	2.10 (2)	P3-C1P3	1.88 (2)	P4-C3P4	1.91 (2)
Mn-C3	2.28 (2)	P3-C2P3	1.89 (2)	C1P2-C1P4	1.56 (2)
C1-C2	1.44 (2)	P3-C3P3	1.87 (2)		
C2-C3	1.37 (2)	C1P1-C1P3	1.47 (3)		
Bond Angles					
P1-Mn-P2	91.5 (4)	P1-Mn-C3	87.6 (7)	C1-Mn-C3	68.1 (7)
P1-Mn-P3	81.3 (5)	P2-Mn-C1	168.8 (5)	C1-Mn-C2	39.0 (6)
P1-Mn-P4	169.3 (3)	P2-Mn-C3	102.1 (5)	C2-Mn-C3	36.0 (6)
P2-Mn-P3	99.3 (2)	P3-Mn-C1	91.4 (5)	C1-C2-C3	127 (2)
P2-Mn-P4	82.0 (2)	P3-Mn-C3	156.1 (5)	C2-C3-C4	122 (2)
P3-Mn-P4	91.4 (2)	P4-Mn-C1	94.6 (5)	C3-C4-C5	129 (2)
P1-Mn-C1	93.4 (6)	P4-Mn-C3	102.0 (5)		

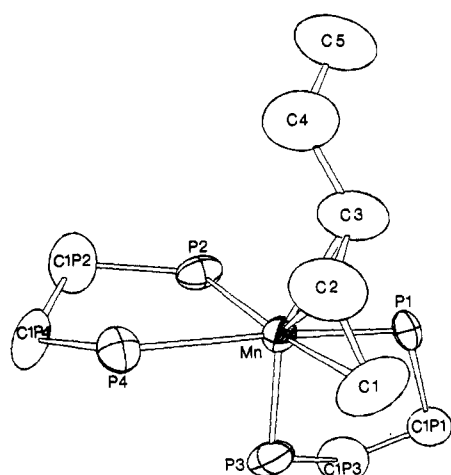


Figure 1. ORTEP drawing for (*syn*- $\eta^3$ -pentadienyl)Mn[(CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 1. Atoms are represented by thermal vibration spheres drawn to encompass 50% of the electron density. Methyl groups on the 1,2-bis(dimethylphosphino)ethane ligands are omitted for clarity.

well-established, with several ( $\eta^5$ -pentadienyl)metal complexes having been structurally characterized.<sup>1a,d,f,n</sup> We now report the synthesis and crystal structure of a pentadienylmanganese complex containing a W-shaped *syn*- $\eta^3$ -pentadienyl ligand, (*syn*- $\eta^3$ -pentadienyl)Mn[(CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (1),<sup>2</sup> and the reaction chemistry of this complex with NH<sub>4</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup>.

Reaction of MnBr<sub>2</sub> with potassium pentadienide-tetrahydrofuran<sup>3</sup> and (CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub> (dmpe) in tetrahydrofuran at -78 °C, followed by warming to room temperature, produced red pentane-soluble 1 in high yield.<sup>4,5</sup> A single-crystal X-ray diffraction study of 1 was

carried out.<sup>6</sup> An ORTEP drawing of the molecular structure is shown in Figure 1, and selected bond distances and angles are given in Table I.<sup>7</sup> The molecular geometry is pseudooctahedral; the six coordination sites around the manganese atom are occupied by the four phosphorus atoms of the dmpe ligands and atoms C1 and C3 of the pentadienyl ligand.<sup>8</sup> Deviations from true octahedral geometry result from the small bite angles of the dmpe ligands (81.3 (5)° and 82.0 (2)°) and the  $\eta^3$ -pentadienyl ligand (68.1 (7)°).

The structure of the pentadienyl ligand in 1 closely resembles that of the pentadienyl ligand in bis(*syn*- $\eta^3$ -pentadienyl)Fe[P(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>.<sup>1m</sup> However, the following fea-

(5) <sup>1</sup>H NMR (22 °C, benzene-*d*<sub>6</sub>, 100 MHz): mixture of *syn* and *anti* isomers,  $\delta$  0.56–1.96 (complex m, 36, allylic H's and dmpe H's), 5.96–6.38 (complex m, 3, vinylic H's). <sup>13</sup>C{<sup>1</sup>H} NMR (22 °C, benzene-*d*<sub>6</sub>, 25.14 MHz): major (*syn*) isomer,  $\delta$  150.18 (C4), 102.82 (C5), 85.28 (C2), 54.02 (C3), 34.43–13.41 (C1 and dmpe C's); minor (*anti*) isomer,  $\delta$  148.88 (C4), 101.31 (C5), 84.73 (C2), 51.90 (C3), 34.43–13.41 (C1 and dmpe C's). The ratio of *syn* to *anti* isomers did not vary over the temperature range of -80 to +80 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (22 °C, benzene-*d*<sub>6</sub>, 40.25 MHz, referenced to P(CH<sub>3</sub>)<sub>3</sub>):  $\delta$  138.75 (br). IR (benzene) 1598 cm<sup>-1</sup> (C=C stretch), 1425, 1290, 1260, 920 cm<sup>-1</sup> (CH bend, PC stretch in dmpe).

(6) The single crystals, which diffracted rather weakly, were monoclinic of space group *P*<sub>2</sub>/*n* (a nonstandard setting of *P*<sub>2</sub><sub>1</sub>/*c*, No. 14) with *a* = 10.606 (4) Å, *b* = 23.31 (1) Å, *c* = 9.019 (2) Å,  $\beta$  = 94.74 (2)°, *V* = 2222.23 Å<sup>3</sup>, and *Z* = 4. X-ray diffraction data were collected at room temperature on a Nicolet P3 diffractometer, using graphite-monochromated Mo K $\alpha$  radiation. A total of 3543 independent reflections with 0° < 2 $\theta$  < 50° were collected by using the  $\theta$ -2 $\theta$  scanning technique and a scan rate of 2°/min. All of the data reduction and structure refinement were done with a modified Enraf-Nonius structure determination package (modified by B.A. Frenz and Assoc., Inc., College Station, TX) on a VAX 11/780 computer. Only the 1065 independent reflections with intensities greater than three times their esd's and with (sin  $\theta$ )/ $\lambda$  values greater than 0.15 ( $\theta$  greater than 6.1°) were used in the least-squares refinements. An absorption correction was not made. The structure was solved by standard Fourier techniques following the location of the manganese atom from a Patterson map. Large thermal parameters for atom P1 and the three carbon atoms bonded to it (C1P1, C2P1, C3P1) indicated a twofold disorder in the positions of the atoms. The two positions of each disordered atom were located from small-grid difference Fourier maps and were refined; carbon atoms C1P1, C1P1', C2P1, C2P1', C3P1, and C3P1' were refined with isotropic thermal parameters, while the phosphorus atoms (P1, P1') were refined anisotropically. The multiplicities of the disordered atoms were not refined but were estimated to be approximately 0.67 and 0.33 in each case, based on electron densities in the difference Fourier maps. All other heavy atoms in the molecule were refined anisotropically. The convergence values of the agreement indices were *R* = 0.0672 and *R*<sub>w</sub> = 0.0827. The final difference Fourier map showed no peaks with electron density greater than 0.57 e/Å<sup>3</sup>.

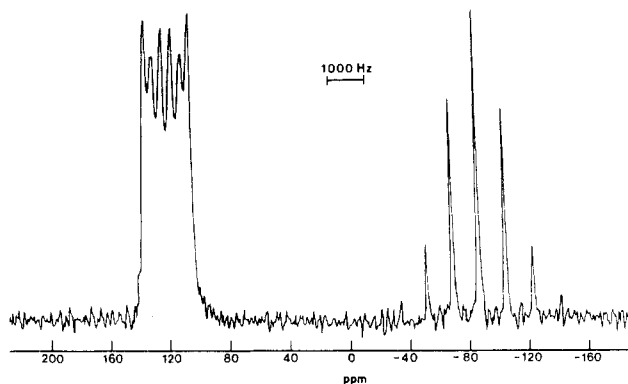
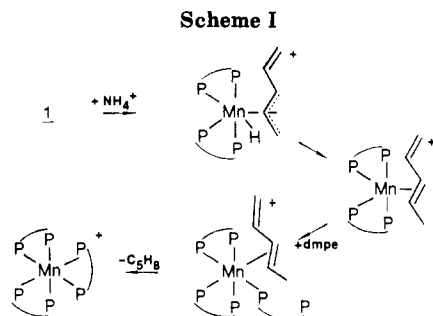
(7) Bond distances and bond angles involving the disordered atoms in the lower multiplicity sites (P1', C1P1', C2P1', and C3P1') are available in supplementary material.

(8) The coordination geometries of allylmetal complexes are, in general, best described by treating the allyl group as a bidentate ligand: Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J., Jr.; Sosinsky, B. A.; Kirner, J. F.; Muettterties, E. L. *J. Am. Chem. Soc.* 1978, 100, 4107.

(2) The simple allyl analogue of 1 ( $\eta^3$ -allyl)Mn[(CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> has not been reported.

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

(4) In a typical reaction, 2.86 g (1.33 × 10<sup>-2</sup> mol) of MnBr<sub>2</sub> was refluxed in 100 mL of tetrahydrofuran for 1 h. The solution was cooled to -78 °C, and 4.00 g (2.66 × 10<sup>-2</sup> mol) of (CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub> was added. While the solution was maintained at -78 °C, 4.74 g (2.66 × 10<sup>-2</sup> mol) of potassium pentadienide-tetrahydrofuran (K<sub>2</sub>C<sub>5</sub>H<sub>7</sub>·C<sub>4</sub>H<sub>8</sub>O) in 50 mL of tetrahydrofuran was added over a period of 45 min, producing a dark reddish brown solution. This solution was then allowed to warm to room temperature, stirred for an additional 2 h, filtered through Celite, and evaporated to dryness. The dark red product was extracted with pentane and crystallized from pentane at -30 °C; yield 3.89 g (69.3%). All manipulations were carried out under N<sub>2</sub>.



**Figure 2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{Mn}[(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]_3^+\text{PF}_6^-$  recorded at 40.25 MHz. The  $^{31}\text{P}$  nuclei of the 1,2-bis(dimethylphosphino)ethane ligands are split into a sextet by the nuclear quadrupole of  $^{55}\text{Mn}$  ( $I = 5/2$ ). The  $^{31}\text{P}$  nucleus of the hexafluorophosphate anion is split into a binomial heptet by the six  $^{19}\text{F}$  nuclei. The chemical shifts are referenced to  $\text{P}(\text{CH}_3)_3$ .

tures are noteworthy:

(a) The vinylic moiety of the pentadienyl ligand points up and away from the rest of the complex. This is a sterically less-hindered orientation than the alternative orientation in which the vinyl group would be directed toward the complex.

(b) The pentadienyl ligand is bonded to the manganese center in an asymmetric fashion, with  $\text{Mn}-\text{C}1 = 2.21$  (2) Å,  $\text{Mn}-\text{C}2 = 2.10$  (2) Å, and  $\text{Mn}-\text{C}3 = 2.28$  (2) Å. This asymmetry is a common structural feature of ( $\eta^3$ -pentadienyl)metal complexes.<sup>11-n</sup>

(c) Carbon atoms C1, C2, C3, and C4 of the pentadienyl ligand are coplanar to within 0.01 Å, while C5 lies out of the plane away from the manganese atom by 0.35 Å. This deviation of C5 from the ligand plane results from a small rotation (22°) about bond C3-C4.<sup>9</sup> However, the planarity of C1, C2, C3, and C4 indicates that a rotation about bond C2-C3 has not occurred. Rotation about bond C2-C3 appears to be a common structural feature among  $\eta^3$ -pentadienyl ligands bound in an anti fashion<sup>11,n</sup> but not among those bound in a syn fashion. This difference probably arises from the fact that rotation about C2-C3 in an *anti*- $\eta^3$ -pentadienyl ligand directs the p orbital on C3 toward the metal atom and pushes the vinyl group away from the metal atom. In contrast, rotation about bond C2-C3 in a *syn*- $\eta^3$ -pentadienyl ligand would direct the p orbital on C3 and push the vinyl group in the same direction (both toward the metal atom or both away from the metal atom).

In solution, (*syn*- $\eta^3$ -pentadienyl) $\text{Mn}(\text{dmpe})_2$  equilibrates with its *anti*- $\eta^3$ -pentadienyl isomer. The two isomers are most clearly seen in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum,<sup>5</sup> where the *syn*- $\eta^3$ -pentadienyl carbon nuclei and the *anti*- $\eta^3$ -pentadienyl carbon nuclei give distinct signals. At equilibrium, the two isomers are present in a ratio of approximately 60:40. The detailed mechanism of the *syn*  $\rightleftharpoons$  *anti* isomerization is not known. However, preliminary spin saturation transfer NMR studies of ( $\eta^3$ -2,4-dimethylpentadienyl) $\text{Co}[\text{P}(\text{CH}_3)_3]_3$  have suggested that isomerization of the 2,4-dimethylpentadienyl ligand in this complex proceeds via a C3-bound ( $\eta^1$ -pentadienyl)metal intermediate.<sup>1n</sup> Spin saturation transfer NMR experiments are underway to probe the mechanism of the pentadienyl ligand isomerization in 1.<sup>10</sup>

Reaction of 1 with  $\text{NH}_4^+\text{PF}_6^-$  in tetrahydrofuran at -78 °C, followed by warming to room temperature, produced

(9) The *syn*- $\eta^3$ -pentadienyl ligand in  $\text{bis}(\text{syn}-\eta^3\text{-pentadienyl})\text{Fe}[\text{P}(\text{CH}_3)_3]_2$  exhibits a similar rotation of 16.7° about bond C3-C4. In this case, C5 lies out of the plane of C1, C2, C3, and C4 by 0.26 Å: see ref 1m.

(10) Yasuda et al. have shown by chemical trapping and  $^1\text{H}$  NMR studies that potassium pentadienide exists almost exclusively as the U-shaped isomer in tetrahydrofuran solution: (a) Yasuda, H.; Yamauchi, M.; Ohnuma, Y.; Nakamura, A. *Bull. Chem. Soc. Jpn.* 1981, 54, 1481. (b) Yasuda, H.; Yamauchi, M.; Nakamura, A. *J. Organomet. Chem.* 1980, 202, C1. This suggests that in our synthesis of 1, the pentadienyl group initially bonds to the manganese center in an anti (U-shaped) geometry and then isomerizes to the observed equilibrium mixture of anti and syn geometries.

$\text{Mn}(\text{dmpe})_3^+\text{PF}_6^-$ , 2, the first example of a homoleptic manganese-phosphine complex.<sup>11,12</sup> We believe that this reaction proceeds by initial protonation at the metal center, followed by hydride migration to the  $\eta^3$ -pentadienyl ligand. The resulting weakly bound  $\eta^2$ -pentadiene ligand is then displaced by dmpe, which is scavenged from another molecule (see Scheme I). The crude yield of 2, 64% based on 1, is close to the theoretical value of 66.7%.<sup>11</sup> This yield can be increased to 85% (based on 1) by addition of excess dmpe to the solution of 1 before protonation.<sup>13</sup> Gas chromatographic studies<sup>14</sup> have established that 1,3-pentadiene is the exclusive organic product of this reaction.<sup>15</sup>

The manganese cation  $\text{Mn}(\text{dmpe})_3^+$  has  $D_3$  point group symmetry. The symmetry operations for this point group partition the methyl carbon atoms of the dmpe ligands into two sets of six interchangeable atoms and also interchange the six methylene carbon atoms. As a result, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2 simply consists of three signals, two in the methyl region and one in the methylene region.<sup>12</sup>

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the cation  $\text{Mn}(\text{dmpe})_3^+$  consists of six lines, which arise from coupling of the  $^{31}\text{P}$  nuclei with the manganese quadrupole ( $I = 5/2$  for  $^{55}\text{Mn}$ )<sup>12</sup> (see Figure 2). The coupling constant  $J_{\text{Mn}-\text{P}}$  is 242 Hz. The sharpness of the  $^{31}\text{P}$  signal for this cation can be attributed to the symmetrical distribution of electron density around the manganese center. This high-symmetry environment results in a small electric field gradient at the

(11) In a typical reaction, 1.20 g ( $7.37 \times 10^{-3}$  mol) of  $\text{NH}_4^+\text{PF}_6^-$  in 50 mL of tetrahydrofuran was added dropwise to 3.11 g ( $7.37 \times 10^{-3}$  mol) of 1 in 100 mL of tetrahydrofuran maintained at -78 °C. The solution was then allowed to warm to room temperature and stirred for 12 h. The resulting yellow precipitate was collected and washed with two 10-mL portions of pentane. The yellow product 2 was extracted with five 20-mL portions of methanol and crystallized from methanol/pentane at -30 °C: yield of crude product, 3.05 g (63.6%, based on reagent 1); yield of crystallized product, 2.21 g (46.1%, based on reagent 1). All manipulations were carried out under  $\text{N}_2$ .

(12)  $^1\text{H}$  NMR (22 °C, methylene- $d_2$  chloride, 100 MHz):  $\delta$  1.40 (br s),  $^{13}\text{C}\{^1\text{H}\}$  NMR (22 °C, methylene- $d_2$  chloride, 25.14 MHz):  $\delta$  23.32 (s, methyl), 24.84 (s, methyl), 33.38 (s, methylene). These signals exhibit some fine structure due to C-P coupling.  $^{31}\text{P}\{^1\text{H}\}$  NMR (22 °C, methylene- $d_2$  chloride, 40.25 MHz, referenced to  $\text{P}(\text{CH}_3)_3$ ):  $\delta$  124.65 (symmetrical pattern of 6 lines with similar intensities,  $J_{\text{P}-\text{Mn}} = 242$  Hz), -81.97 (binomial heptet,  $J_{\text{P}-\text{F}} = 706$  Hz). IR (methylene chloride): 1425, 1305, 930, 885 (CH bend, PC stretch), 850  $\text{cm}^{-1}$  (PF stretch). Anal. Calcd for  $\text{C}_{18}\text{H}_{48}\text{F}_6\text{MnP}_7$ : C, 33.24; H, 7.45. Found: C, 33.33; H, 7.25.

(13) Addition of 2.21 g ( $1.474 \times 10^{-2}$  mol) of dmpe to the reaction solution described in ref 11 leads to a crude yield of 4.06 g of 2 (84.7%, based on 1) and a crystallized yield of 3.58 g (74.7%, based on 1).

(14) Separations were performed on a 12 ft  $\times$  1/8 in. column containing 3% OV-1 on Chrom-W-HP. An oven temperature of 30 °C and a carrier gas flow rate of 19 mL/min were used.

(15) Both *cis*- and *trans*-1,3-pentadiene are observed. 1,4-Pentadiene is not isomerized to 1,3-pentadiene under the reaction conditions.

manganese nucleus and slow quadrupole relaxation.<sup>16</sup>

Protonation of 1 with  $\text{NH}_4^+\text{PF}_6^-$  in the presence of excess trimethyl phosphite leads to the formation of *cis*- $\text{Mn}(\text{dmpe})_2[\text{P}(\text{OCH}_3)_3]_2\text{PF}_6^-$ , 3, in high yield.<sup>17,18</sup> In this reaction, the phosphite molecules fill the coordination sites vacated by pentadiene, and 2 is not produced. The *cis* orientation of the trimethyl phosphite ligands is evident from the  $^{13}\text{C}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra of 3.<sup>18</sup> The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum exhibits a complex series of resonances for the dmpe methyl carbon nuclei, two distinct sets of multiplets for the dmpe methylene carbon nuclei, and a virtual triplet for the trimethyl phosphite carbon nuclei.<sup>19</sup> The  $^1\text{H}$  NMR spectrum consists of a complex series of resonances for the dmpe protons and a sharp doublet for the trimethyl phosphite protons ( $J_{\text{P-H}} = 10$  Hz).<sup>20</sup>

Reactions of 1 with  $\text{NH}_4^+\text{PF}_6^-$  in the presence of other phosphine and phosphite ligands are currently under investigation in our laboratories.

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**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 (12 pages). Ordering information is given on current masthead page.

(16) Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: Philadelphia, 1977; pp 225-226.

(17) In a typical reaction, 0.56 g ( $3.43 \times 10^{-3}$  mols) of  $\text{NH}_4^+\text{PF}_6^-$  in tetrahydrofuran was added dropwise to a solution of 1.45 g ( $3.43 \times 10^{-3}$  mol) of 1 and 4.26 g ( $3.43 \times 10^{-2}$  mol) of  $\text{P}(\text{OCH}_3)_3$  in tetrahydrofuran maintained at  $-78^\circ\text{C}$ . The solution was warmed to room temperature and stirred for 12 h. The product 3 was isolated in the same manner as 2: yield of crude product, 2.32 g (90.4%); yield of crystallized product, 2.16 g (84.2%). All manipulations were carried out under  $\text{N}_2$ .

(18)  $^1\text{H}$  NMR (22  $^\circ\text{C}$ , methylene- $d_2$  chloride, 100 MHz):  $\delta$  1.17-1.50 (complex m, dmpe), 3.64 (d,  $J_{\text{P-H}} = 10$  Hz, phosphite).  $^{13}\text{C}\{^1\text{H}\}$  NMR (22  $^\circ\text{C}$ , acetonitrile- $d_3$ , 25.14 MHz):  $\delta$  21.7-24.0 (complex m, dmpe methyl), 30.1-31.6 (m, dmpe methylene), 33.2-34.1 (m, dmpe methylene), 53.6 (virtual triplet,  $J = 5.7$  Hz, phosphite).  $^{31}\text{P}\{^1\text{H}\}$  NMR (22  $^\circ\text{C}$ , methylene chloride, 40.25 MHz, referenced to  $\text{P}(\text{CH}_3)_3$ ):  $\delta$  118.8, 131.5 (br), -82.96 (heptet,  $J_{\text{P-F}} = 712$  Hz). IR (methylene chloride): 1422, 1268, 938, 898 (CH bend, PC stretch), 1071, 1031 (POC stretch/bend), 848  $\text{cm}^{-1}$  (PF stretch).

(19) (a) The virtual triplet in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum is not inconsistent with a *cis* coordination geometry: see ref 16, p 223, and references cited therein. (b) In *trans*- $\text{Mn}(\text{dmpe})_2[\text{P}(\text{OCH}_3)_3]_2$ , all of the dmpe methyl carbon nuclei would be chemically equivalent, as would all of the dmpe methylene carbon nuclei.

(20) The  $^1\text{H}$  NMR spectrum of *trans*- $\text{Mn}(\text{dmpe})_2[\text{P}(\text{OCH}_3)_3]_2$  would be expected to exhibit a *triplet* for the trimethyl phosphite protons as a result of virtual coupling between the two magnetically inequivalent trimethyl phosphite phosphorus nuclei ( $J_{\text{PP}} \gg J_{\text{PH}}$ ): see ref 16, p 223.

complexes (K-Crown)[CoCp(CO)(CN)] and (PNP)[CoCp(CO)(CN)], whose spectroscopic and chemical properties indicate a high electron density on cobalt. In ligand exchange reactions, the cyanide dissociates exclusively, but slowly. The reactivity of the anion is dominated by its electron-transfer ability and basicity rather than its nucleophilicity.

While many compounds of the type  $\text{CpML}_2$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ) have been characterized from the cobalt triad ( $\text{L} = \text{PR}_3$ ,  $\text{P}(\text{OR})_3$ , CO, CS, NO, CNR, etc.),<sup>1</sup> attempts to isolate complexes in which  $\text{L} = \text{CN}^-$  have to date been unsuccessful.<sup>2,3</sup> Although there could be many reasons for failure in these instances, it is noteworthy that only alcohols were chosen as solvents in these experiments. We assumed that the desired product might be sufficiently basic so as to be incompatible with protic solvents and that an aprotic solvent was therefore indicated.

In a recent paper,<sup>4</sup> we reported the development of low-valent cyanonickelate chemistry using 18-crown-6 as a solubilizing agent in aprotic media. The same strategy enables  $\text{CoCp}(\text{CO})_2$  to react with (K-Crown) $\text{CN}^-$  (or a combination of KCN and crown ether) at room temperature in acetonitrile, affording red-brown needles of the compound (K-Crown)[CoCp(CO)(CN)]<sup>6</sup> (1) which can be isolated in better than 90% yield.

The electron-rich nature of the cobalt center is clearly in evidence from the relatively low-frequency stretches of the cyanide and carbonyl in the infrared (2066 and 1891  $\text{cm}^{-1}$ , respectively) and the moderately upfield position of the Cp resonance in the  $^1\text{H}$  NMR ( $\delta$  4.61). The strongly basic character of 1 is also supported by the observation that in solution it decomposes on contact with silica and that it is instantaneously protonated by trifluoroacetic acid at room temperature to give a brown uncharacterized precipitate and gas evolution. The salt is soluble in acetonitrile and DMF and sparingly soluble in THF and acetone. Compound 1, while thermally stable, is extremely air sensitive in both solution and the solid state. The counterion of the salt can be varied by using other suitably soluble cyanides in the monosubstitution reaction, for example,  $\text{PNP}[\text{CoCp}(\text{CO})(\text{CN})]^-$  (2), which can be prepared in similar yield.

When 1 is refluxed with  $\text{PPh}_3$  in acetonitrile or *n*-butyronitrile, equilibrium is reached after about 2 days. Product composition as established by  $^1\text{H}$  NMR shows that only 4% of the starting material has been converted to  $\text{CoCp}(\text{CO})(\text{PPh}_3)$  (3) and that no CO is lost. If the phosphine complex is employed as the starting material, about 66% of 1 can be isolated following the same set of reaction conditions. The half-life for this exchange at room

<sup>†</sup>Dedicated to the memory of my mentor Professor Earl L. Muetterties, whose enthusiasm for the synthesis and study of novel types of compounds directly inspired our efforts.

(1) See for example: Kemmitt, R. D. W.; Russell, D. R. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982; Vol. 5, pp 145-258. Hughes, R. P. *Ibid.* p 358.

(2) Coffey, C. E. *J. Inorg. Nucl. Chem.* 1963, 25, 179.

(3) Dineen, J. A.; Pauson, P. L. *J. Organomet. Chem.* 1972, 43, 209.

(4) del Rosario, R.; Stuhl, L. S. *J. Am. Chem. Soc.* 1984, 106, 1160.

(5) Crown = 18-crown-6-ether.

(6) 1: mp 197-199  $^\circ\text{C}$  (corrected); IR ( $\text{CH}_3\text{CN}$ ) 2066 ( $\nu_{\text{CN}}$ , s), 1891 ( $\nu_{\text{CO}}$ , s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (90 MHz)  $\delta$  ( $\text{CD}_3\text{CN}$ ) 4.61 (s, Cp), 3.63 (s, crown ether);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{DMF-}d_7$ ,  $-45^\circ\text{C}$ )  $\delta$  70.4 (s, Crown) 81.4 (s, Cp), 145.0 (s, br, CN), 211.5 (s, br, CO). Anal. Calcd for  $\text{C}_{10}\text{H}_{25}\text{NO}_7\text{CoK}$ : C, 47.40; H, 6.07; N, 2.91. Found: C, 47.24; H, 6.18; N, 3.00.

(7) 2: mp 189-190  $^\circ\text{C}$  (corrected). Anal. Calcd for  $\text{C}_{43}\text{H}_{35}\text{N}_2\text{P}_2\text{OCo}$ : C, 72.07; H, 4.92; N, 3.90. Found: C, 71.49; H, 4.98; N, 4.16. The spectroscopic properties of 2 are not significantly different from 1.

## Low-Valent Cyanocobaltate Chemistry. 1. Synthesis, Characterization, and Reactivity of (K-Crown)[CoCp(CO)(CN)]<sup>†</sup>

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**Summary:**  $\text{CoCp}(\text{CO})_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) reacts in aprotic solvents with (K-Crown)CN or (PNP)CN to give the novel