that produces synthetically interesting, highly functionalized organic heterocycles.

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Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters of the hydrogen atoms, anisotropic thermal parameters, and complete bond distances and angles of both the hydrogen and non-hydrogen atoms of complexes **9b** and **10** (12 pages). Ordering information is given on any current masthead page.

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Open and Half-Open Manganocene Chemistry: More Associated Salts

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The reaction of $MnCl_2$ with 1 equiv each of NaC_5H_5 and $K(2,4\text{-}C_7H_{11})$ (C_7H_{11} = dimethylpentadienyl) leads to $Mn_2(C_5H_5)_2(2,4\text{-}C_7H_{11})$. This species may be considered to be an associated salt of high-spin $Mn(C_5H_5)^+$ and the 18-electron $Mn(C_5H_5)(2,4\text{-}C_7H_{11})^-$. In accord with this, magnetic susceptibility measurements demonstrate the presence of five unpaired electrons. A single-crystal X-ray diffraction study has been undertaken. The space group is $P2_1/m$ with $a = 7.495$ (2), $b = 12.500$ (7), $c = 8.678$ (3) Å, $\beta = 106.88$ (2)°, and $V = 778.0$ Å^3, for $Z = 2$. The structure has been refined to discrepancy indexes of $R = 0.075$ and $R_w = 0.078$. The reaction of $MnCl_2$ with 2 equiv of $K[3\text{-}CH_3\text{-}1,5\text{-}(Me_3Si)_2C_5H_4]$ also leads to an associated salt, $K\{Mn[3\text{-}CH_3\text{-}1,5\text{-}(Me_3Si)_2C_5H_4]_3\}$, again with high-spin Mn^{2+} (five unpaired electrons). An X-ray diffraction study revealed that the Mn^{2+} center experiences trigonal planar coordination with the three η^1-bound dienyl ligands, while K^+ is encapsulated within the three dienyl chains. The space group at −140° is *Pcab* (No. 61), with $a = 19.180$ (4), $b = 26.895$ (4), $c = 18.843$ (5) Å, and $V = 9720.1$ Å^3 for $Z = 8$. The structure has been refined to discrepancy indexes of $R = 0.068$ and $R_w = 0.068$.

While bis(cyclopentadienyl)metal complexes, the metallocenes, have been known for some time, it has only been fairly recently that a series of "open metallocenes", or bis(pentadienyl)metal complexes, has been reported.[2] Such complexes are now known for titanium, zirconium, vanadium, chromium, iron, ruthenium, and osmium and have provided for some interesting structural and reactivity comparisons between the two series. It is important to note that the behavior of manganese in each series is quite anomalous. For example, manganocene's chemical behavior is generally regarded as highly ionic, and a polymeric structure has been determined in the solid state, although the high-spin monomeric species is present in the gas phase. Conversion to a low-spin form may be brought about by the introduction of methyl groups onto the rings.[3] In contrast, attempts to prepare a bis(3-methylpentadienyl)manganese complex, $Mn(3\text{-}C_6H_9)_2$, led instead to an unusual $Mn_3(3\text{-}C_6H_9)_4$ species, which was initially formulated as an associated salt of high-spin Mn^{2+} and two diamagnetic $Mn(3\text{-}C_6H_9)_2^-$ units.[4] It was believed that the reaction did indeed first lead to an "open manganocene" but that some of these species underwent an intramolecular coupling reaction, leading to a methylpentadienyl dimer which was subsequently replaced from the manganese atom by two $Mn(3\text{-}C_6H_9)_2$ units, forming the observed trimetallic product. Since this unexpected reaction prevented study of a true "open manganocene", alternative approaches must be considered. For example, a half-open manganocene such as $Mn(C_5H_5)(2,4\text{-}C_7H_{11})$ (C_7H_{11} = dimethylpentadienyl) might be more feasible. In such a complex, a coupling reaction between pentadienyl ligands should be less favorable and would have to take place intermolecularly. Alternatively, preparation of an open manganocene might be possible if the sites most prone to undergoing coupling reactions were sterically blocked by appropriate substituents. In the hope of obtaining some information about the open and half-open manganocenes, we have attempted the preparations of $Mn(C_5H_5)(2,4\text{-}C_7H_{11})$ and $Mn[3\text{-}CH_3\text{-}1,5\text{-}(Me_3Si)_2C_5H_4]_2$. In fact, once again more complex associated salt species have been isolated. Herein we describe the nature of the complex products, $Mn_2(C_5H_5)_2(2,4\text{-}C_7H_{11})$ and $KMn[3\text{-}CH_3\text{-}1,5\text{-}(Me_3Si)_2C_5H_4]_3$.

Experimental Section

All procedures were carried out under a nitrogen atmosphere, and all solvents were dried by treatment with Na/K and benzophenone and distilled under a nitrogen atmosphere. Elemental analyses were carried out by Analytische Laboratorien (Gummersbach) and Beller Mikroanalytisches Laboratorium (Göttingen).

(2,4-Dimethylpentadienyl)bis(cyclopentadienyl)dimanganese, $Mn_2(C_5H_5)_2(2,4\text{-}C_7H_{11})$. A stirred suspension of 1.00 g (8.0 mmol) of manganous chloride in 50 mL of THF was cooled to −78 °C. To this slurry was added dropwise a mixture of 1.07 g (8.0 mmol) of potassium 2,4-dimethylpentadienide and 0.70 g (8.0 mmol) of sodium cyclopentadienide dissolved in 50 mL of THF. The resulting solution was allowed to warm slowly to room temperature, after which stirring was continued for another 4 h. At this time, the solvent was removed in vacuo, and the product was extracted with three 20-mL portions of hexane and filtered

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through a coarse frit with Celite. The microcrystalline product was isolated by slowly cooling these concentrated hexane solutions. The product was obtained in yields of up to 70% (0.97 g). The complex may also be isolated by the reaction of 1 equiv of the 2,4-dimethylpentadienyl anion with 1 equiv of $[Mn(C_5H_5)Cl(L)]_2$ (L = THF, PEt_3) in THF at −78 °C, utilizing a similar extractive procedure.

Complete infrared data (Nujol mull): 3071 mw, 1105 mw, 1125 m, 999 ms, 970 mw, 934 w, 926 w, 912 w, 891 w, 871 ms, 813 ms, 766 s cm^{-1}. Anal. Calcd for $C_{17}H_{21}Mn_2$: C, 60.91; H, 6.31. Found: C, 60.68; H, 6.21. Magnetic susceptibility: μ_B (Evans method, THF solvent) = 5.84 μ_B.

Potassium Tris(3-methyl-1,5-bis(trimethylsilyl)pentadienyl)manganate(II), $K[Mn(3-CH_3-1,5-(Me_3Si)_2C_5H_4)_3]$. $K[3-CH_3-1,5-(Me_3Si)_2C_5H_4]$ was prepared from $K(3-CH_3C_5H_6)$ by the procedure used to prepare $K[1,5-(Me_3Si)_2C_5H_5]_2$ from KC_5H_7.[5] A solution of 0.51 g (2.0 mmol) of $K[3-CH_3-1,5-(Me_3Si)_2C_5H_4]$ in 30 mL of THF was added slowly to a slurry of 0.13 g (1.0 mmol) of $MnCl_2$ in 30 mL of THF under nitrogen. After the addition was complete, the mixture was allowed to warm slowly to room temperature, during which time it assumed a reddish to reddish-brown color. After being stirred overnight, the solution was pumped to dryness, and the product extracted with hexane. These extracts were filtered through a coarse frit, concentrated in vacuo, and cooled to −90 °C. Well formed, blood-red crystals, extremely soluble in hydrocarbon solvents, formed and could be collected after careful draining of the supernatant. The yield seems primarily limited by the high solubility of the product in hexanes, and the collection of several crops of crystals by continued concentration of the supernatant is generally required for a good yield.

^1H NMR (for $1-Me_3Si-3-CH_3-C_5H_6$) δ 6.42 (dd, 1 H, J = 10, 17 Hz), 5.52 (t, 1 H, J = 9 Hz), 5.02 (d, 1 H, J = 17 Hz), 4.88 (d, 1 H, J = 10 Hz), 1.65 (s, 3 H), 1.47 (d, 2 H, J = 9 Hz), −0.06 (s, 9 H); (for $1,5-(Me_3Si)_2-3-CH_3-C_5H_5$) δ 6.76 (d, 1 H, J = 19 Hz), 5.74 (d, 1 H, J = 19 Hz), 5.65 (t, 1 H, J = 9 Hz), 1.70 (s, 3 H), 1.51 (d, 2 H, J = 9 Hz), 0.15 (s, 9 H), −0.07 (s, 9 H); (for $K[3-CH_3-1,5-(Me_3Si)_2C_5H_4]$) δ 6.35 (d, 2 H, J = 17 Hz), 3.11 (d, 2 H, J = 17 Hz), 1.47 (s, 3 H), −0.10 (s, 18 H). Anal. Calcd for $C_{36}H_{75}MnSi_6K$: C, 56.12; H, 9.81. Found: C, 55.60; H, 9.73. Magnetic susceptibility: μ_B (Evans method, THF solvent) = 5.91 μ_B.

X-ray Diffraction Studies. Well-formed single crystals of $Mn_2(C_5H_5)_2(2,4-C_7H_{11})$ could be obtained by slowly cooling hot saturated solutions of the compound in hexane. These were then sealed in glass capillaries under nitrogen and mounted on a standard goniometer head. Single crystals could also be grown by slowly cooling saturated solutions from room temperature to −20 °C, but these were of poorer quality. However, identical cell constants were determined, indicating that the heating process did not result in transformation of the compound. Unit cell data were obtained from a combination of oscillation photographs and Nicolet P$\bar{1}$ software programs and confirmed by cell reduction. Accurate cell constants were subsequently determined from a least-squares refinement of 15 centered reflections using the Mo Kα peak, and backgrounds were estimated from the program CARESS.[6] Additional data collection parameters are given in Table I.

Systematic absences suggested the presence of a 2_1 screw axis, indicating either space group $P2_1$ or $P2_1/m$, the latter of which subsequently was determined to be correct. For Z = 2 dimetallic units in space group $P2_1/m$, the molecule had to reside on either a mirror plane or a center of inversion; the former proved to be correct. The positions of the metal atoms were determined from a Patterson map, and the remaining non-hydrogen atoms were located on subsequent difference Fourier maps. Following subsequent refinement of the non-hydrogen atom positional and anisotropic thermal parameters, most of the hydrogen atoms for the independent 2,4-dimethylpentadienyl ligand could be located; these and those for the cyclopentadienyl ligands were than placed in idealized or calculated positions, with C–H bond distances fixed at 0.95 Å. Final refinement of all data led to agreement indexes of R = 0.075 and R_w = 0.078. A final difference Fourier map revealed no peaks greater than 0.59 e/Å^3. It should be noted that large degrees of disorder and/or thermal libration of the C_5H_5 ligands were present. Several attempts to model this were made, but no significant differences in metal–carbon bond distances for the various models were observed; hence, the simplest possibility was chosen for each, in which the major orientation seems to involve the cyclopentadienyl ligands being bisected by the imposed mirror plane of symmetry.

Table I. X-ray Data Collection Parameters for $Mn_2(C_5H_5)_2(2,4-C_7H_{11})$ (A) and $K\{Mn[3-CH_3-1,5-(Me_3Si)_2C_5H_4]_3\}$ (B)

	A	B
formula	$C_{17}H_{21}Mn_2$	$C_{36}H_{75}MnSi_6K$
mol wt	345.94	770.54
space group	$P2_1/m$	*Pcab*
a, Å	7.495 (2)	19.180 (4)
b, Å	12.500 (7)	26.895 (4)
c, Å	8.678 (3)	18.843 (5)
β, deg.	106.88 (2)	90
V, Å^3	778.0	9720.1
Z	2	8
d_{calc}, g/cm^3	1.43	1.32
λ	0.71073	0.71073
temp, °C	20	−140
scan type	θ–2θ	θ–2θ
scan speed, deg/min	1.5	2.0
μ, cm^{-1}	15.44	5.12
2θ limits, deg	3–50	3–45
min *hkl*	0,0,-10	0,0,0
max *hkl*	8,14,10	18,25,20
unique, obsd data	792	1821
variables	94	321
R(*F*)	0.075	0.068
$R_w(F)$	0.078	0.068

Table II. Positional Parameters for the Non-Hydrogen Atoms of $Mn_2(C_5H_5)_2(2,4-C_7H_{11})$

atom	*x*	*y*	*z*
Mn1	0.14858 (24)	0.25	−0.22938 (22)
Mn2	0.37820 (27)	0.25	0.03869 (24)
C1	0.1126 (12)	0.1356 (10)	−0.0560 (10)
C2	−0.0524 (13)	0.1494 (10)	−0.1937 (11)
C3	−0.1291 (16)	0.25	−0.2388 (13)
C4	−0.1328 (17)	0.0513 (12)	−0.2902 (13)
C5	0.1298 (24)	0.25	−0.4740 (17)
C6	0.2349 (25)	0.1610 (16)	−0.3919 (20)
C7	0.3889 (16)	0.1977 (14)	−0.2902 (14)
C8	0.5362 (29)	0.25	0.3187 (21)
C9	0.5936 (29)	0.1638 (19)	0.2498 (23)
C10	0.6920 (17)	0.2002 (17)	0.1610 (17)

The final positional parameters for the non-hydrogen atoms obtained from the last cycle of least-squares refinement are presented in Table II, along with their estimated standard deviations, while pertinent bonding parameters are given in Table III. The remaining atomic parameters and the structure factor tables are available as supplementary material (see paragraph at end of table). No unusual intermolecular contacts were observed.

For $K\{Mn[3-CH_3-1,5-(Me_3Si)_2C_5H_4]_3\}$ single crystals were grown by slowly cooling concentrated solutions in hexane. Systematic absences were consistent with space group *Pcab*. Diffraction intensities at room temperature were quite poor, so data were collected at −140 °C. Even at this temperature, however, much of the data was still weak. Relevant data collection parameters are provided in Table I. The positions of the metal and silicon atoms were determined readily by direct methods, after which the remaining non-hydrogen atoms could be located from a difference Fourier map. Whenever possible, these atoms were treated anisotropically; however, as an apparent result of the low temperature of data collection, some of these required isotropic treatment. Hydrogen atoms were placed in calculated positions but not refined. Final refinement led to agreement indexes of R = 0.068 and R_w = 0.068. A final difference Fourier map revealed no peaks greater than 0.50 e/Å^3. No unusual intermolecular

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Table III. Pertinent Bonding Parameters for $Mn_2(C_5H_5)_2(2,4\text{-}C_7H_{11})$

Bond Distances (Å)									
Mn1–C1	2.149 (10)	Mn2–C1	2.394 (10)	Mn1–Mn2	2.459 (3)	C6–C7	1.315 (19)		
Mn1–C2	2.054 (10)	Mn2–C7	2.952 (12)	C1–C2	1.459 (12)	C7–C7′	1.307 (36)		
Mn1–C3	2.059 (12)	Mn2–C8	2.374 (18)	C2–C3	1.391 (12)	C8–C9	1.362 (29)		
Mn1–C5	2.086 (14)	Mn2–C9	2.326 (16)	C2–C4	1.508 (18)	C9–C10	1.294 (24)		
Mn1–C6	2.043 (13)	Mn2–C10	2.365 (12)	C5–C6	1.428 (21)	C10–C10′	1.246 (42)		
Mn1–C7	2.122 (11)								

Bond Angles (deg)					
C1–C2–C3	121.3 (11)	C5–C6–C7	108.2 (16)	C8–C9–C10	106.9 (21)
C2–C3–C2′	129.5 (12)	C6–C5–C6′	102.3 (16)	C9–C8–C9′	104.7 (23)
C1–C2–C4	117.8 (11)	C6–C7–C7′	110.4 (12)	C9–C10–C10′	110.6 (16)
C3–C2–C4	120.9 (9)				

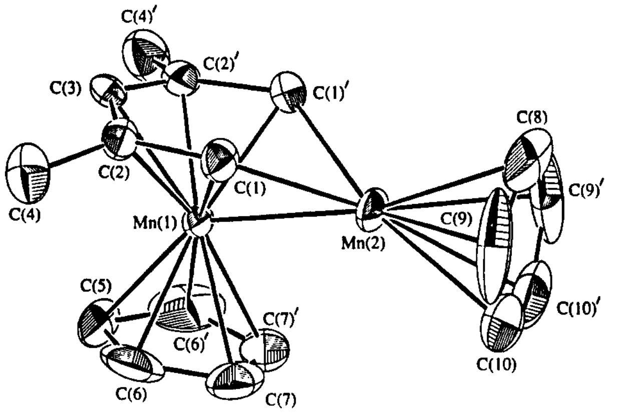


Figure 1. Perspective view and numbering scheme for $Mn_2(C_5H_5)_2(2,4\text{-}C_7H_{11})$.

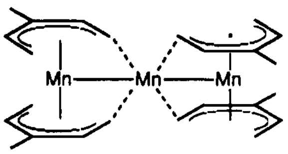
contacts were observed. Final bonding parameters for the nonhydrogen atoms are contained in Tables IV and V, while additional data are available as supplementary material.

Results and Discussion

The reaction of $MnCl_2$ with a mixture of the cyclopentadienyl and 2,4-dimethylpentadienyl anions in a 1:1:1 ratio in THF led to a product of very similar general appearance and properties as found for $Mn_3(3\text{-}C_6H_9)_4$. The same product also resulted from the reaction of $[Mn(C_5H_5)Cl(L)]_2$ (L = THF, PEt_3)[7] with 2 equiv of $K(2,4\text{-}C_7H_{11})$. Analytical data, however, were not consistent with the formulation $Mn(C_5H_5)(2,4\text{-}C_7H_{11})$ but did agree with the formula $Mn_2(C_5H_5)_2(C_7H_{11})$. A magnetic moment of 5.84 μ_B was observed, close to the value of 5.92 μ_B expected for five unpaired electrons.

To establish the nature of the product, resort was necessarily made to X-ray diffraction. The structural result may be seen in Figure 1, along with the numbering scheme. Positional parameters for the non-hydrogen atoms are listed in Table II, while pertinent bond distances and angles are contained in Table III.

As can be seen in Figure 1, the molecule has crystallographically imposed mirror-plane symmetry. One portion of the molecule does indeed seem to contain a "half-open manganocene" unit, which is capped by a $Mn(C_5H_5)$ unit. This situation is reminiscent of the $Mn_3(3\text{-}C_6H_9)_4$ complex which, while not being the "open manganocene" complex initially desired, still contained two "open manganocene" units bound by an additional, central manganese atom (I).



I

Interestingly, both species may be formulated in a similar fashion. Thus, while $Mn_3(3\text{-}C_6H_9)_4$ could be formulated as the associated salt $Mn^{2+}[Mn(3\text{-}C_6H_9)_2^-]_2$, containing a high-spin Mn(II) ion and two 18-electron open-manganocene anions (cf. $[Mn(C_5Me_5)_2^-]$[3]), $Mn_2(C_5H_5)_2(2,4\text{-}C_7H_{11})$ may similarly be formulated as a salt of $Mn(C_5H_5)^+$ (high-spin Mn(II)) and the 18-electron half-open manganocene counterion. Apparently in these nonligated complexes manganese exhibits a propensity toward forming such saltlike products. As previously speculated, it is quite possible that a wide variety of such species can be prepared from various organometallic anions and Mn(II).[4]

The bonding distances in the complex are in reasonable accord with the saltlike formulation. For the $Mn(C_5$-

Table IV. Positional Parameters for the Non-Hydrogen Atoms of $KMn[1,5\text{-}(Me_3Si)_2\text{-}3\text{-}CH_3C_5H_4]_3$

atom	x	y	z
K	0.1839 (3)	0.2550 (2)	0.1808 (2)
Mn	0.2050 (2)	0.0986 (1)	0.1576 (2)
Si1	0.3741 (3)	0.0619 (2)	0.1613 (3)
Si2	0.3438 (3)	0.3522 (2)	0.1945 (3)
Si3	0.1353 (3)	0.0473 (2)	0.0113 (3)
Si4	0.1187 (3)	0.3412 (2)	−0.0004 (3)
Si5	0.1252 (3)	0.0418 (2)	0.2938 (3)
Si6	0.0549 (3)	0.3218 (2)	0.3643 (3)
C1	0.3142 (10)	0.1083 (7)	0.1277 (9)
C2	0.3256 (9)	0.1594 (6)	0.1527 (9)
C3	0.3261 (10)	0.2052 (7)	0.1182 (10)
C4	0.3381 (9)	0.2495 (7)	0.1588 (9)
C5	0.3336 (10)	0.2968 (8)	0.1345 (10)
C6	0.3193 (11)	0.2064 (7)	0.0385 (9)
C7	0.3506 (12)	−0.0023 (9)	0.1270 (12)
C8	0.4651 (13)	0.0766 (9)	0.1311 (13)
C9	0.3730 (11)	0.0599 (8)	0.2599 (11)
C10	0.3659 (11)	0.4082 (8)	0.1401 (11)
C11	0.2595 (11)	0.3630 (8)	0.2444 (12)
C12	0.4126 (11)	0.3395 (8)	0.2615 (11)
C1′	0.1228 (10)	0.0966 (7)	0.0765 (9)
C2′	0.1334 (10)	0.1485 (7)	0.0513 (10)
C3′	0.0991 (9)	0.1925 (7)	0.0727 (9)
C4′	0.1190 (10)	0.2386 (9)	0.0389 (10)
C5′	0.0914 (11)	0.2827 (8)	0.0497 (11)
C6′	0.0386 (10)	0.1935 (7)	0.1231 (10)
C7′	0.1452 (11)	−0.0131 (8)	0.0583 (11)
C8′	0.2150 (11)	0.0576 (8)	−0.0427 (11)
C9′	0.0596 (11)	0.0427 (7)	−0.0521 (10)
C10′	0.1511 (11)	0.3900 (7)	0.0616 (10)
C11′	0.0394 (11)	0.3640 (8)	−0.0492 (11)
C12′	0.1900 (11)	0.3230 (8)	−0.0642 (11)
C1″	0.1784 (10)	0.0967 (7)	0.2696 (9)
C2″	0.1397 (9)	0.1431 (7)	0.2810 (9)
C3″	0.1620 (9)	0.1876 (7)	0.3097 (9)
C4″	0.1121 (10)	0.2272 (7)	0.3182 (10)
C5″	0.1236 (9)	0.2726 (6)	0.3440 (9)
C6″	0.2373 (10)	0.1968 (7)	0.3349 (10)
C7″	0.0426 (11)	0.0373 (8)	0.2417 (11)
C8″	0.1787 (10)	−0.0156 (7)	0.2772 (10)
C9″	0.1007 (11)	0.0424 (8)	0.3909 (11)
C10″	0.0701 (12)	0.3783 (8)	0.3080 (12)
C11″	0.0630 (11)	0.3388 (8)	0.4589 (11)
C12″	−0.0334 (12)	0.2959 (9)	0.3445 (13)

Table V. Pertinent Bonding Parameters for $KMn[1,5\text{-}(Me_3Si)_2\text{-}3\text{-}CH_3C_5H_4]_3$

Bond Distances (Å)

Mn–C1	2.186 (18)	C1–C2	1.468 (24)	C1′–C2′	1.489 (26)	C1″–C2″	1.469 (25)
Mn–C1′	2.196 (18)	C2–C3	1.394 (23)	C2′–C3′	1.412 (26)	C2″–C3″	1.379 (24)
Mn–C1″	2.172 (18)	C3–C4	1.434 (24)	C3′–C4′	1.446 (27)	C3″–C4″	1.439 (25)
K–C3	3.259 (20)	C3–C6	1.506 (24)	C3′–C6′	1.500 (26)	C3″–C6″	1.542 (24)
K–C4	2.990 (18)	C4–C5	1.355 (26)	C4′–C5′	1.314 (28)	C4″–C5″	1.335 (22)
K–C5	3.204 (20)	Si1–C1	1.810 (19)	Si3–C1′	1.823 (18)	Si5–C1″	1.850 (20)
K–C3′	3.103 (18)	Si1–C7	1.898 (24)	Si3–C7′	1.860 (22)	Si5–C7″	1.868 (21)
K–C4′	2.983 (19)	Si1–C8	1.878 (25)	Si3–C8′	1.857 (22)	Si5–C8″	1.880 (20)
K–C5′	3.132 (21)	Si1–C9	1.860 (21)	Si3–C9′	1.885 (21)	Si5–C9″	1.889 (21)
K–C3″	3.059 (18)	Si2–C5	1.881 (22)	Si4–C5′	1.908 (22)	Si6–C5″	1.906 (17)
K–C4″	3.026 (19)	Si2–C10	1.869 (21)	Si4–C10′	1.865 (20)	Si6–C10″	1.876 (22)
K–C5″	3.319 (17)	Si2–C11	1.893 (22)	Si4–C11′	1.881 (21)	Si6–C11″	1.846 (21)
		Si2–C12	1.858 (22)	Si4–C12′	1.886 (22)	Si6–C12″	1.868 (23)

Bond Angles (deg)

C1–Mn–C1′	120.8 (7)	C1–Mn–C1″	118.6 (7)	C1′–Mn–C1″	120.5 (7)
Mn–C1–Si1	115.9 (9)	Mn–C1′–Si3	113.1 (9)	Mn–C1″–Si5	112.8 (9)
Mn–C1–C2	99.8 (12)	Mn–C1′–C2′	95.8 (11)	Mn–C1″–C2″	103.9 (12)
Si1–C1–C2	116.1 (13)	Si3–C1′–C2′	116.7 (13)	Si5–C1″–C2″	111.3 (13)
C1–C2–C3	132.7 (17)	C1′–C2′–C3′	129.1 (17)	C1″–C2″–C3″	129.6 (17)
C2–C3–C4	119.1 (16)	C2′–C3′–C4′	118.0 (16)	C2″–C3″–C4″	118.6 (17)
C2–C3–C6	118.9 (17)	C2′–C3′–C6′	123.9 (17)	C2″–C3″–C6″	123.4 (17)
C4–C3–C6	121.9 (17)	C4′–C3′–C6′	117.8 (17)	C4″–C3″–C6″	118.0 (16)
C3–C4–C5	126.1 (17)	C3′–C4′–C5′	126.8 (19)	C3″–C4″–C5″	127.5 (18)
C4–C5–Si2	122.3 (15)	C4′–C5′–Si4	123.8 (17)	C4″–C5″–Si6	126.5 (14)
C1–Si1–C7	111.0 (9)	C1′–Si3–C7′	109.1 (9)	C1″–Si5–C7″	113.0 (9)
C1–Si1–C8	109.8 (10)	C1′–Si3–C8′	111.7 (10)	C1″–Si5–C8″	108.3 (9)
C1–Si1–C9	111.2 (9)	C1′–Si3–C9′	112.0 (9)	C1″–Si5–C9″	111.7 (9)
C7–Si1–C8	108.0 (11)	C7′–Si3–C8′	107.9 (10)	C7″–Si5–C8″	108.8 (9)
C7–Si1–C9	108.1 (10)	C7′–Si3–C9′	108.8 (9)	C7″–Si5–C9″	107.3 (9)
C8–Si1–C9	108.6 (10)	C8′–Si3–C9′	107.2 (9)	C8″–Si5–C9″	107.6 (9)
C5–Si2–C10	109.4 (9)	C5′–Si4–C10′	111.3 (9)	C5″–Si6–C10″	109.9 (9)
C5–Si2–C11	109.3 (9)	C5′–Si4–C11′	106.9 (10)	C5″–Si6–C11″	107.9 (9)
C5–Si2–C12	109.7 (9)	C5′–Si4–C12′	107.5 (10)	C5″–Si6–C12″	109.1 (9)
C10–Si2–C11	110.1 (9)	C10′–Si4–C11′	110.2 (9)	C10″–Si6–C11″	109.4 (10)
C10–Si2–C12	111.1 (10)	C10′–Si4–C12′	109.9 (9)	C10″–Si6–C12″	109.2 (10)
C11–Si2–C12	107.3 (10)	C11′–Si4–C12′	111.1 (9)	C11″–Si6–C12″	111.2 (10)

$H_5)(2,4\text{-}C_7H_{11})^-$ portion, the average Mn(1)–C (pentadienyl) and Mn(1)–C (cyclopentadienyl) bond distances of 2.093 (7) and 2.083 (6) Å, respectively, are reasonably similar to the values observed for the isoelectronic $Fe(C_5H_5)(2,4\text{-}C_7H_{11})$ (2.062 (4) and 2.053 (5) Å, respectively).[8] Interestingly, however, the individual average values for the 1 (and 5), 2 (and 4), and 3 positions do show significant differences. For the iron compound, the respective values of 2.080 (6), 2.048 (5), and 2.052 (6) Å were observed, while for the present case the numbers are 2.149 (10), 2.054 (10), and 2.059 (12) Å. The lengthening of the Mn(1)–C(1,5) distances is clearly notable and can be ascribed to the additional interactions of C(1) with Mn(2).[9] A similar effect was observed for the analogous bridging carbon atoms in $Mn_3(3\text{-}C_6H_9)_4$. Both the iron and the manganese "half-open" complexes seem to exist in the "eclipsed" conformation, although the large thermal parameters for the cyclopentadienyl carbon atoms do not preclude the presence of slightly staggered conformations.

In contrast to most metal–pentadienyl compounds,[10] the "internal" C–C bonds of the pentadienyl ligand appear to be shorter than the "external" ones, 1.391 (12) vs 1.459 (12) Å, possibly as a result of the extra Mn(2)–C(1) interactions. Normally the "external" bonds appear to be slightly shorter, due to the contribution of the resonance hybrid having negative charge localized at the central pentadienyl carbon atom, although this was also not the case for the $Mn_3(3\text{-}C_6H_9)_4$. One could in this case propose the intervention of a trianionic form of the dienyl ligand, as in II.

II

This would entail a Mn(III) formulation for Mn1 but would not change its electron count. A similar hybrid has also been invoked in a Ru(II) complex containing the $2,4\text{-}(CF_3)_2C_5H_5$ ligand.[11] As is generally observed, backbone C–C–C angles in the pentadienyl ligand contract when methyl substituents are present, cf., ∠C(1)–C(2)–C(3) = 121.3 (11)°, while ∠C(2)–C(3)–C(2′) = 129.5 (12)°. The 2,4-dimethylpentadienyl ligand is reasonably planar, the main distortion involving a bend of the methyl substituent down toward the Mn(1) atom.

The remaining $M(C_5H_5)$ unit also possesses bonding parameters consistent with the ionic formulation, i.e., $Mn(C_5H_5)^+$. The average Mn(2)–C (Cp) bond distance of 2.351 (9) Å is considerably longer than those of "covalent" first-row metallocenes (V, Cr, Fe, Co, Ni, and low-spin $Mn(C_5Me_5)_2$,[3] 2.112 (3) Å).[12] The average Mn(2)–C distance, however, is also shorter than that in high-spin manganocene, 2.38 Å.[12] However, the rather low extent of coordination for Mn(2) on the opposite side of its C_5H_5 ligand would be expected to lead to enhanced $Mn(2)–C_5H_5$ bonding relative to manganocene. Hence, it appears that the $Mn(2)–C_5H_5$ bonding is reasonably comparable with the bonding in manganocene. The overall coordination geometry about Mn(2) might be best considered as a

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[8] Ernst, R. D.; Kralik, M. S.; Arif, A. M. Unpublished results.

[9] An additional result of the location of Mn(2) near the terminal pentadienyl CH_2 groups seems to be that the endo hydrogens are bent even more than usual away from Mn(1). However, the hydrogen atom positions are not that well-determined, and hence there is significant uncertainty in this observation.

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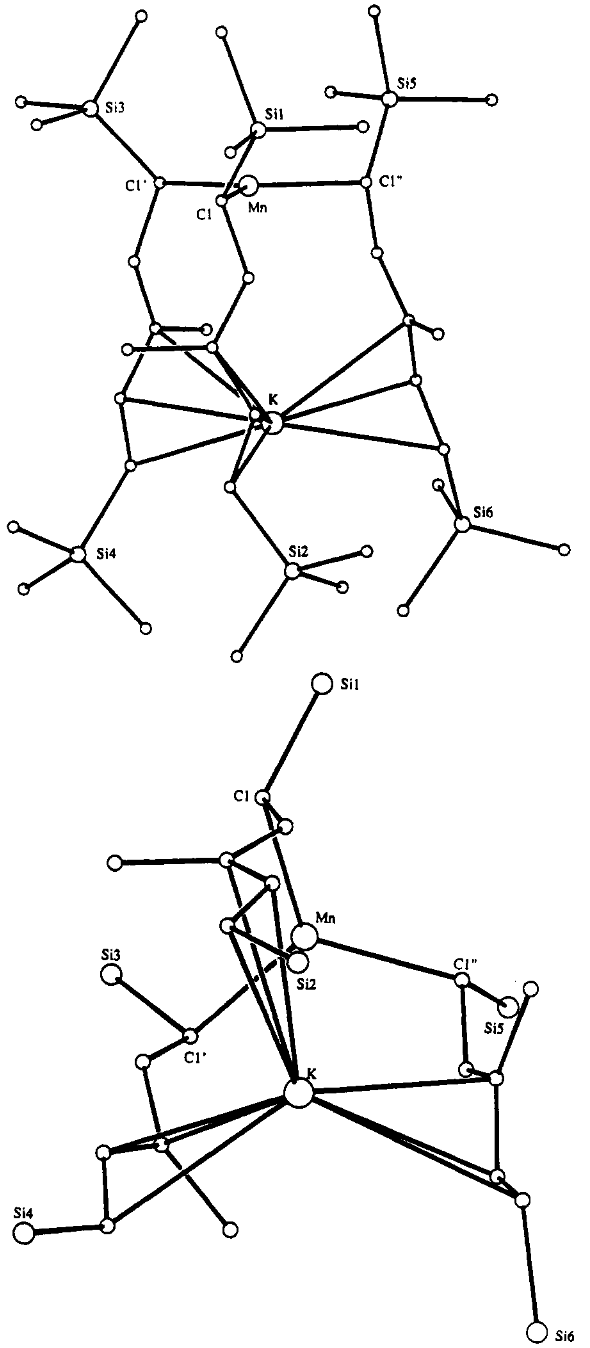
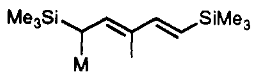


Figure 2. Perspective views and partial numbering scheme for $K\{Mn[3\text{-}CH_3\text{-}1,5\text{-}(Me_3Si)_2C_5H_4]_3\}$. For each dienyl ligand the numbering continues down the chain from C(1)–C(5). The methyl groups on the silicon atoms have been omitted for clarity from the lower view.

"piano-stool", such as in $Mn(C_5H_5)(CO)_3$. The Mn(2)–C(1) distance is 2.394 (10) Å, which can be compared to the related average value of 2.331 (4) Å in $Mn_3(3\text{-}C_6H_9)_4$. The Mn(1)–Mn(2) bond distance of 2.459 (3) Å is somewhat shorter than the value of 2.516 (1) Å for those in $Mn_3(3\text{-}C_6H_9)_4$. There may be weak interactions present between the Mn(2) and C(7) atoms (2.952 (12) Å).

The structure of $K\{Mn[3\text{-}CH_3\text{-}1,5\text{-}(Me_3Si)_2C_5H_4]_3\}$ is illustrated in Figure 2, while bonding parameters are given in Table V. The Mn^{2+} ion can be seen to have quite regular trigonal planar coordination, with an average Mn–C bond length of 2.185 (10) Å, and an average C–Mn–C bond angle of 120°. Such low coordination numbers are uncommon but have been observed in other crowded Mn^{2+} complexes.[13] For comparison, the Mn–C distances in $Mn(mesityl)_3^-$ average 2.141 (3) Å,[14] while some MnR_4^{2-} species[15] have Mn–C distances ranging from 2.22 (1) to 2.28 (1) Å. As a result of the η^1 coordination mode, an alternation in C–C bond lengths along the dienyl chain would be expected (see III), and appears to be observed, with the respective average C(1)–C(2), C(2)–C(3), C(3)–C(4), and C(4)–C(5) bond lengths being 1.475 (15), 1.395 (14), 1.440 (15), and 1.335 (15) Å.



III

The coordination of the potassium ion is indeed curious. The potassium ion is encapsulated within the three dienyl chains, interacting primarily with the C(3), C(4), and C(5) atoms. The interactions with the C(4) atoms are shortest, ranging from 2.983 (19) to 3.026 (19) Å, while the interactions with the C(3 and 5) atoms appear longer, ranging from 3.059 (18) to 3.319 (17) Å. Although one would expect most of the dienyl negative charge to be present at the C(1) positions, which interact with Mn^{2+}, it is possible that some charge still resides in the C(3) and C(5) positions, leading to some degree of K^+- -allyl$^-$ interaction. Interestingly, the K- -C distances appear reasonably consistent with the K–N and K–O bond lengths in crown ether and cryptate complexes,[16] given the larger size of carbon relative to these heteroatoms. One could consider the possibility that neutral poly(olefin) cages might in some cases be capable of selective binding to other main group metal ions.

Once again, manganese(II) has demonstrated a tendency to form associated salt complexes incorporating a high-spin Mn(II) ion. It still seems possible, however, that the proper choice of conditions or open dienyl ligand might allow for the isolation of a true open or half-open manganocene. In fact, the reaction of MnI_2 with $K[3\text{-}CH_3\text{-}1,5\text{-}(Me_3Si)_2C_5H_4]$ has led to a seemingly different product, not soluble in hexane but soluble in ether.[17] Possibly this could possess the desired stoichiometry, yet still be an associated salt, $Mn^{2+}\{Mn[3\text{-}CH_3\text{-}1,5\text{-}(Me_3Si)_2C_5H_4]_3^-\}_2$.

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Registry No. $Mn_2(C_5H_5)_2(2,4\text{-}C_7H_{11})$, 143745-06-6; $MnCl_2$, 7773-01-5; $K(2,4\text{-}C_7H_{11})$, 74205-98-4; $Na(C_5H_5)$, 4984-82-1; $[Mn(C_5H_5)Cl(THF)]_2$, 143745-05-5; $[Mn(C_5H_5)Cl(PEt_3)]_2$, 143733-82-8; $K[Mn(3\text{-}CH_3\text{-}1,5\text{-}(Me_3Si)_2C_5H_4)]_3$, 143733-83-9; $K[(3\text{-}CH_3\text{-}1,5\text{-}(Me_3Si)_2C_5H_4)]_3$, 143733-81-7.

Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, and positional parameters (4 pages). Ordering information is given on any current masthead page.

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