Synthesis, Structure, and Reactivity of β -Diketiminate **Complexes of Manganese(II)**

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Reaction of the β -diketiminate lithium salt LLi(OEt₂) (1) (L = HC(CMeNAr)₂, Ar = 2,6 $iPr_2C_6H_3$) with MnCl₂ in diethyl ether provided the metalate complex LMn(μ -Cl)₂Li(OEt₂)₂ (3) in high yield. The dimeric compound $[LMn(\mu-Cl)]_2$ (4) free of alkaline salt was obtained when the β -diketiminate potassium salt LK (2) was used instead of 1. The substitution reactions of 4 with CpNa, MeLi, and PhLi resulted in the formation of organomanganese complexes LMnCp(THF) (7), $[LMn(\mu-Me)]_2$ (8), and LMnPh (9), respectively. The novel ionic compound $[LMnCl_2][{C(Me)N(iPr)}_2CH]$ (6) was obtained, when the N-heterocyclic carbene $\{C(Me)N(iPr)\}_2C$ was used as a proton acceptor. The first doubly carboxylato-bridged complex with four-coordinate manganese(II), $[LMn(\mu-O_2CMe)]_2$ (5), was synthesized from the reaction of 2 and $Mn(O_2CMe)_2$ in THF. Complexes 3–7 were characterized by single-crystal X-ray structural analysis. The structures show that the β -diketiminate ligand backbone is essentially planar and the metal centers reside in distorted tetrahedral geometry.

Introduction

In the past few years there has been increasing interest in the β -diketiminate ligands, especially those with bulky aryl groups at the nitrogen, which have excellent steric and electronic properties to stabilize unusual complexes.¹ A variety of main group element, transition metal, and lanthanide complexes containing such ligands have been synthesized and characterized, some of which have novel structures and good catalytic activities.¹ For example, the first monomeric Al(I) compound LAl (L = HC(CMeNAr)₂, Ar = $2,6-iPr_2C_6H_3$) as a stable carbene analogue was synthesized in our group.² Very recently, the aluminum dihydroxide with terminal OH groups and the first terminal hydroxide containing alumoxane were also obtained using the same bulky β -diketiminate ligand.³

Manganese complexes are important since they are involved in many natural processes, such as decomposition of peroxide and water oxidation of the photosystem II.⁴ In view of this, it was of interest to assemble manganese complexes and explore their reactivity. Despite the impressive results obtained by using β -diketiminate ligands now known, little work has appeared on manganese β -diketiminate complexes. Chlorides are normally the most common and inexpensive source of manganese(II); however, manganese chlorides containing β -diketiminate ligands remain rare prior to this work. There are only a few reports on wellcharacterized manganese complexes containing β -diketiminate ligands in the literature. Power et al. prepared manganese silylamide LMnN(SiMe₃)₂ using $Mn[N(SiMe_3)_2]_2$, which has a three-coordinate manganese center.⁵ Two homoleptic manganese β -diketiminate complexes were formed when less bulky ligands were employed.^{1,6} Recently we have synthesized some manganese iodides and their derivatives by taking advantage of anhydrous MnI₂ as starting material.⁷ Some interesting results have been obtained; for example, the first complex with three-coordinate manganese(I) [LMn]₂ containing a reactive Mn-Mn bond has been successfully synthesized by reduction of the iodide [LMn(u-I)]₂.8 Herein, we report on easily available MnCl₂ as starting material and describe the synthesis and structural characterization of a series of neutral and ionic manganese(II) chlorides $LMn(\mu-Cl)_2Li(OEt_2)_2$ (3), $[LMn(\mu-$ Cl)]₂ (4), and $[LMnCl_2]^{-}[\{C(Me)N(iPr)\}_2CH]^{+}$ (6) supported by the same bulky ligand and the resulting organomanganese derivatives LMnCp(THF) (7), [LMn- $(\mu$ -Me)]₂ (8), and LMnPh (9). In addition, we also report on the first doubly carboxylato-bridged complex with

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four-coordinate manganese(II) of composition [LMn(µ-O₂CMe)]₂ (5).

Results and Discussion

Synthesis of Compounds 3–9. The β -diketiminate lithium salt LLi(OEt₂) (1) (L = HC(CMeNAr)₂, Ar = 2,6*i*Pr₂C₆H₃) has been reported previously and widely used as metathesis reagent.⁹ The reaction of 1 and anhydrous MnCl₂ in diethyl ether afforded the metalate complex $LMn(\mu-Cl)_2Li(OEt_2)_2$ (3) in high yield (Scheme 1). Attempts to remove the coordinated lithium salt from the manganese center were unsuccessful. According to the experiences of preparing manganese iodides free of lithium salt,^{7b} we investigated the reaction of MnCl₂ with the potassium salt LK (2) instead. As expected, the dimeric compound $[LMn(\mu-Cl)]_2$ (4) free of the coordinated salt was obtained in high yield (Scheme 2). Attempts to prepare the bis(β -diketiminate) complex by using 2 equiv of 1 or 2 were unsuccessful.

Dinuclear manganese complexes bridged by carboxylate groups have attracted great attention since such systems are known to exist at the active centers of some manganese-containing enzymes.¹⁰ So it is of interest to model the coordination environment of the manganese centers in such enzymes. The doubly carboxylatobridged complex $[LMn(\mu - O_2CMe)]_2$ (5) was prepared from 2 and Mn(O₂CMe)₂ in THF in good yield. Crystals of 5 suitable for X-ray structural analysis were obtained by recrystallization from THF.

N-Heterocyclic carbenes have been widely used as neutral and two-electron-donor ligands; however, the investigation of their basicities is rare.¹¹ We are interested in using the N-heterocyclic carbene as the acceptor for the proton of LH. The novel ionic compound $[LMnCl_2]^{-}[{C(Me)N(iPr)}_2CH]^+$ (6) was easily obtained as a yellow crystalline solid in high yield from the reaction of LH, $MnCl_2(THF)_{1.5}$, and $\{C(Me)N(iPr)\}_2C$ in





THF at room temperature. However, no reaction occurs when in either case LH and $\{C(Me)N(iPr)\}_2C$ or LH and $MnCl_2(THF)_{1.5}$ were mixed in THF at room temperature. Therefore we suppose that the process for the formation of 6 is a concerted one and may proceed through the intermediate 6a (Scheme 3).

The substitution reactions of 4 with some nucleophiles were investigated in order to prepare organomanganese(II) complexes. Treatment of 4 with CpNa, MeLi, and PhLi resulted in the formation of complexes LMnCp-(THF) (7), $[LMn(\mu-Me)]_2$ (8), and LMnPh (9), respectively. The monocyclopentadienyl manganese(II) compound 7 was readily prepared as yellow crystals from the reaction of **4** and 2 equiv of CpNa in THF in high yield. Compound 7 is a rare example of a half-sandwich manganese(II) complex with a metal center of 17 valence electrons.¹² Complexes 8 and 9 have been prepared from the reaction of $[LMn(\mu-I)]_2$ with MeLi and PhLi, respectively.^{7c} Compared with the substitution reactions of the iodide, the reactions of 4 with MeLi and PhLi are similar except the yields are a little lower. Complexes of manganese with variable oxidation states are of wide interest owing to their significance for biological systems.^{4c,13} Thus, the oxidation reaction of 4 was examined in order to obtain high oxidation state manganese complexes. However, the efforts to oxidize 4 with I₂, S, or O₂ all resulted in the decomposition of 4.

Complexes 3–7 are yellow crystalline solids and are soluble in THF. These complexes were characterized by

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Table 1. Crystallographic Data for Complexes 3-7

			-		
	3	¹ / ₂ 4	5	6	7
formula	C37H61Cl2LiMnN2O2	C ₂₉ H ₄₁ ClMnN ₂	C ₆₂ H ₈₈ Mn ₂ N ₄ O ₄	C40H62Cl2MnN4	C38H54MnN2O
fw	698.66	508.03	1063.24	724.78	609.77
<i>T</i> (K)	153(2)	200(2)	203(2)	150(2)	133(2)
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	C2/c	$P2_1/c$	$P2_12_12_1$	$P2_{1}2_{1}2_{1}$
a (Å)	12.053(2)	22.921(5)	17.32(3)	11.218(4)	10.007(2)
<i>b</i> (Å)	21.327(4)	14.8779(15)	15.210(17)	12.606(10)	16.985(3)
c (Å)	15.706(3)	16.291(2)	23.30(3)	28.93(2)	20.081(4)
α (deg)	90	90	90	90	90
β (deg)	100.11(3)	90.884(12)	101.94(6)	90	90
γ (deg)	90	90	90	90	90
$V(Å^3)$	3974.3(14)	5555.1(15)	6010(2)	4090(1)	3413.3(12)
Ζ	4	8	4	4	4
D_{calcd} (g cm ⁻³)	1.168	1.215	1.176	1.177	1.187
$\mu (\text{mm}^{-1})$	0.498	0.590	0.467	0.484	0.417
F(000)	1500	2168	2280	1556	1316
cryst size (mm)	$0.90\times0.60\times0.30$	$0.60 \times 0.40 \times 0.40$	$0.70 \times 0.40 \times 0.30$	$0.60 \times 0.50 \times 0.50$	$0.30 \times 0.30 \times 0.30$
2θ range (deg)	7.04 - 50.10	7.02 - 49.96	7.06 - 45.00	7.06 - 44.98	3.14 - 49.44
no. of rflns collected	10 312	7144	7382	3116	36 246
no. of indep rflns	6998 (R(int) = 0.0574)	4872 (R(int) = 0.0307)	7382 (R(int) = 0.0000)	2999 (R(int) = 0.0745)	5798 (R(int) = 0.0371)
no. of data/restraints/ params	6998/0/420	4872/0/308	7382/0/671	2999/0/449	5798/0/389
goodness-of-fit, F ²	1.026	1.024	1.013	1.089	1.064
$\tilde{R}1$, wR2 $[I > 2\sigma(I)]$	0.0505, 0.1213	0.0626, 0.1648	0.0815, 0.1843	0.0445, 0.1009	0.0255, 0.0617
R1, wR2 (all data)	0.0636, 0.1322	0.0821, 0.1817	0.1403, 0.2315	0.0653, 0.1136	0.0280, 0.0626
largest diff peak (e Å $^{-3}$)	0.562 to -0.634	0.400 to -1.366	0.579 to -0.721	0.533 to -0.505	0.305 to -0.291

elemental analyses, EI-MS, and IR. EI-MS of 3 shows that the molecular ion peak is silent, and [LMnCl]⁺ appears as the most intense ion at m/z 507 without the coordinated lithium salt. The molecular ion peaks of the dimeric complexes 4 and 5 in the mass spectrum are not observed, whereas half of the molecular mass $[1/2M]^+$ appeared at m/z 507 and 531 as the most intense peak, respectively. Interestingly, the ion [M – H]⁺ in the mass spectrum of **6** can be seen albeit with low intensity (m/z 723, 2%), followed by [LMnCl]⁺ m/z507 (43%) and $[{C(Me)N(iPr)}_2CH]^+$ 181 (52%). In the EI-MS of 7, [LMnCp]⁺ appears at m/z 537 as the most intense ion without the coordinated solvent, followed by $m/z 472 [M - Cp]^+$ (92%). The IR spectrum of 5 displays the prominent vibrations for the O-C-O part of the bridging acetate group $v_{as}(1602 \text{ cm}^{-1})$ and $v_s(1437 \text{ cm}^{-1})$.

X-ray Solid-State Structural Analysis. Complexes **3**–**7** were characterized by single-crystal X-ray diffraction. Crystallographic data are given in Table 1 and selected bond lengths and angles in Table 2.

The X-ray structural analyses reveal that LMn(µ- $Cl)_2Li(OEt_2)_2$ (3) is monomeric and $[LMn(\mu-Cl)]_2$ (4) dimeric in the solid state (Figures 1 and 2). [LMnCl₂]- $[{C(Me)N(iPr)}_2CH]$ (6) crystallizes as separated monomeric anions $[LMnCl_2]^-$ and cations $[{C(Me)N(iPr)}_2-$ CH]⁺. The structure of the anion is given in Figure 4. In these three compounds each manganese center is bound to two nitrogen atoms of the chelating ligand and two chlorine atoms in a distorted tetrahedral geometry. The backbone of the chelating ligand is nearly planar, and the manganese atoms in these compounds are always out of the C₃N₂ planes (0.45 Å in 3, 0.47 Å in 4, and 0.70 Å in 6). The N–Mn–N angle in 6 (91.6°) is a little smaller than the corresponding angles in 3 (92.2°) and 4 (92.8°), and the Mn-N bond lengths in 6 (av 2.11 Å) are longer than those in **3** (av 2.08 Å) and **4** (av 2.08 Å), which indicates that the metal center in 6 is more weakly bonded to the chelating ligand due to the two terminal Mn-Cl bonds. The average value of the terminal Mn–Cl distance (av 2.36 Å) in **6** is comparable to those of the bridging Mn–Cl distances in **3** (av 2.38 Å) and **4** (av 2.33 Å) due to the anion character of the $[LMnCl_2]^-$ in **6**. Accordingly, the Cl–Mn–Cl angle in **6** (112.0°) is significantly larger than those in **3** (96.2°) and **4** (90.5°).

The lithium atom in **3** is connected by two bridging chlorines and two oxygen atoms of two coordinated ether molecules in a distorted tetrahedral geometry. The structure is like that of the alkali metal adducts of the β -diketiminate metal complexes of general formula L'M(μ -X)₂Li(ether)₂ (L' = β -diketiminate ligand; X = Cl, I).^{5,7a,14} The Li–Cl and Li–O distances (av 2.38 and 1.96 Å, respectively) are similar to those found in LM(μ -Cl)₂Li(THF)₂ (M = Fe(II), Co(II)).^{5,14}

The central core of **4** contains an ideal planar fourmembered Mn_2Cl_2 ring, which bisects and is perpendicular (89.2°) to the two chelating ligands around them. The distance between two manganese atoms is 3.28 Å, which can be compared to that in $[LMn(\mu-I)]_2$ (3.62 Å)^{7b} and is out of the range of a Mn–Mn bond. The structure of the cation $[{C(Me)N(iPr)}_2CH]^+$ in **6** is similar to that in $[{C(Me)N(Me)}_2CH]^+$ [Ph₅C₅]^{-.11}

Compound **5** crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The structure of **5** is shown in Figure 3. The central manganese atoms are bonded to two nitrogen atoms each from the chelating ligands and two oxygen atoms from the two bridging acetates in a distorted tetrahedral fashion. To the best of our knowledge, compound **5** is the first example of a doubly carboxylato-bridged complex with four-coordinate manganese(II). Similar to complexes **3**, **4**, and **6**, the manganese atoms are out of the chelating ligand plane (av 0.64 Å). Complex **5** contains two peripheral six-membered C_3N_2Mn rings and one central eight-membered $C_2Mn_2O_4$ macrocycle.

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Figure 1. Molecular structure of **3** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds 3–7

Compound 3							
Mn(1)-N(1)	2.083(2)	N(1) - Mn(1) - N(2)	92.21(8)				
Mn(1) - N(2)	2.072(2)	N(1) - Mn(1) - Cl(1)	118.99(7)				
Mn(1) - Cl(1)	2.3688(11)	N(2) - Mn(1) - Cl(1)	116.72(7)				
Mn(1) - Cl(2)	2.3887(10)	Cl(1) - Mn(1) - Cl(2)	96.10(3)				
Li(1) - Cl(1)	2.371(5)	N(1) - Mn(1) - Cl(2)	115.29(6)				
Li(1) - Cl(2)	2.383(5)	N(2) - Mn(1) - Cl(2)	119.48(6)				
Li(1) - O(1)	1.948(6)	Cl(1) - Li(1) - Cl(2)	96.20(17)				
Li(1) - O(2)	1.975(6)	O(1)-Li(1)-O(2)	114.7(3)				
		- () - ()					
Compound 4							
Mn(1)-N(1)	2.0830(9)	N(1) - Mn(1) - N(2)	92.80(3)				
Mn(1)-N(2)	2.0819(10)	N(1) - Mn(1) - Cl(1)	117.09(3)				
Mn(1)-Cl(1)	2.3422(7)	N(2) - Mn(1) - Cl(1)	118.34(3)				
Mn(1)-Cl(1A)	2.3093(6)	Cl(1)-Mn(1)-Cl(1A)	90.49(2)				
Mn(1A)-Cl(1)	2.3093(6)	N(1)-Mn(1)-Cl(1A)	119.74(3)				
Mn(1)-Mn(1A)	3.275	N(2)-Mn(1)-Cl(1A)	120.93(3)				
Compound F							
$M_{\rm P}(1) = N(1)$	2.075(6)	N(1) = Mp(1) = N(2)	00.0 (2)				
Mn(1) = N(1) Mn(1) = N(2)	2.073(0)	N(1) = Mn(1) = N(2) N(1) = Mn(1) = O(1)	90.9(2)				
Mn(1) = N(2) Mn(1) = O(1)	2.077(0)	N(1) - Mn(1) - O(1) N(1) - Mn(1) - O(2)	110.9(3)				
Mn(1) = O(1)	2.014(7)	N(1) - Mn(1) - O(2)	115.6(3)				
Mn(1) - O(2)	1.991(7)	N(2) - Mn(1) - O(1)	110.9(3)				
Mn(2) - N(3)	2.082(6)	N(2) - Mn(1) - O(2)	112.3(3)				
Mn(2) - N(4)	2.086(6)	O(1) - Mn(1) - O(2)	114.1(3)				
Mn(2) - O(3)	2.012(7)	O(3) - Mn(2) - O(4)	117.8(3)				
Mn(2) - O(4)	2.031(7)	N(3) - Mn(2) - N(4)	92.0 (2)				
Mn(1)-Mn(2)	4.319						
Compound 6							
Mn(1) - N(1)	2.102(2)	N(1)-Mn(1)-N(2)	91.64(8)				
Mn(1) - N(2)	2.111(2)	N(1) - Mn(1) - Cl(1)	107.84(6)				
Mn(1) - Cl(1)	2.3890(11)	N(2) - Mn(1) - Cl(1)	109.42(7)				
Mn(1) - Cl(2)	2.3370(10)	Cl(1) - Mn(1) - Cl(2)	112.00(4)				
		(-)(-)(-)					
Compound 7							
Mn(1)-N(1)	2.1242(15)	N(1) - Mn(1) - N(2)	90.26(5)				
Mn(1)-N(2)	2.1306(15)	N(1)-Mn(1)-O(31)	97.69(5)				
Mn(1)-O(31)	2.2787(12)	N(2)-Mn(1)-O(31)	97.60(6)				
Mn(1) - C(6)	2.547(2)	N(1)-Mn(1)-C(6)	96.96(6)				
Mn(1) - C(7)	2.442(2)	N(2)-Mn(1)-C(6)	144.79(7)				
Mn(1)-C(8)	2.419(2)	O(31) - Mn(1) - C(6)	115.34(6)				
Mn(1)-C(9)	2.5088(19)	N(1)-Mn(1)-C(7)	120.33(7)				
Mn(1) - C(10)	2.5778(19)	N(2)-Mn(1)-C(7)	147.88(7)				

The six- and eight-membered rings are nearly orthogonal to each other, as shown by a dihedral angle of 85.8°.

The two acetates are in the bidentate $\mu_{1,3}$ syn-syn bridging mode, which is rare in the doubly carboxylatobridged manganese(II) complexes.¹⁰ The Mn-O distances (av 2.01 Å) for the acetato bridges in **5** compare well with those (2.00–2.24 Å) observed in the manganese complexes adopting the same $\mu_{1,3}$ mode.¹⁵ The



Figure 2. Molecular structure of **4** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.



Figure 3. Molecular structure of **5** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.



Figure 4. Crystal structure of the anion of **6** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

nonbonding intramolecular Mn–Mn distance is 4.32 Å, which is in the normal range (4.15–4.79 Å) of those found in comparable manganese(II) complexes.¹⁰ The Mn–N distance (av 2.08 Å) and the N–Mn–N angle (90.9°) in **5** can be compared with those observed in **3** and **4**.

Compound **7** is monomeric with a Cp coordinated to the manganese center and crystallizes in the ortho-

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Figure 5. Molecular structure of **7** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

rhombic space group $P2_12_12_1$. The metal center is of pseudotetrahedral geometry surrounded by the cyclopentadienyl ring, the oxygen atom of the coordinated THF, and two nitrogen atoms of the chelating ligand. The Mn–C distances (2.42–2.58 Å) are consistent with those found in [MeC₅H₄MnPEt₃(μ -X)]₂ (X = Cl, Br, I) (2.40–2.63 Å)¹² and CpMnTMEDA(η ¹-Cp) (2.44–2.57 Å).¹⁶ The Mn–N distance (av 2.13 Å) in 7 is the longest and the N–Mn–N angle (90.3)° is the smallest among those in complexes **3**–7, which is in agreement with the higher coordination number of manganese. The Cp, the ligand plane, and THF plane are nearly orthogonal to each other.

Conclusion

In summary, we have synthesized a series of neutral and ionic manganese(II) chlorides (**3**, **4**, and **6**) by using the bulky β -diketiminate ligand [HC(CMeNAr)₂]. The reactivity of compound **4** was investigated. The substitution reactions of **4** with CpNa, MeLi, and PhLi afforded organomanganese complexes **7**–**9**, respectively. In addition, we also report on the first doubly carboxylato-bridged complex (**5**) with four-coordinate manganese(II). Further studies on the chemistry of these complexes including oxidation reactions of **4** are in progress.

Experimental Section

General Procedures. All reactions were performed using standard Schlenk and drybox techniques. Solvents were appropriately dried and distilled under dinitrogen prior to use. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Mass spectra were obtained on a Finnigan Mat 8230. IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer as Nujol mulls between KBr plates. LH,¹⁷ LLi(OEt₂) (1),⁹ LK (2)^{7b} (L = HC(CMeNAr)₂, Ar = 2,6-*i*Pr₂C₆H₃), and {C-(Me)N(*i*Pr)}₂C¹⁸ were prepared by literature procedures. Mn-(O₂CMe)₂ was purchased from Aldrich and used without purification. Anhydrous MnCl₂ was obtained by dehydration of MnCl₂(H₂O)₄.¹⁹ MnCl₂(THF)_{1.5} was synthesized as described

(19) Horvath, B.; Moeseler, R.; Horvath, E. G. Z. Anorg. Allg. Chem. 1979, 450, 165. in the literature.²⁰ The syntheses of complexes **8** and **9** are similar to those of **7c**. NMR spectra of complexes 3-9 are not available due to the paramagnetic nature of manganese(II).

LMn(μ -**Cl**)₂**Li**(**OEt**₂)₂ (3). LLi(OEt₂) (1.0 g, 2 mmol) in diethyl ether (15 mL) was added to a suspension of MnCl₂ (0.25 g, 2 mmol) in diethyl ether (40 mL) at -78 °C. The mixture was warmed to room temperature and stirred for 14 h. The resulting precipitate was removed by filtration. The solution was concentrated to ca. 10 mL. Yellow crystals were obtained after 2 days at -26 °C. Yield: 1.13 g (81%). Mp: > 270 °C (dec). Anal. Calcd for C₃₇H₆₁Cl₂LiMnN₂O₂ (698.66): C, 63.55; H, 8.73; N, 4.01. Found: C, 63.13; H, 8.54; N, 4.47. EI-MS: m/z (%) 507 (100) [M - LiCl(OEt₂)₂]. IR (KBr, Nujol mull, cm⁻¹): $\tilde{\nu}$ 1624 (w), 1539 (w), 1523 (m), 1398 (m), 1366 (w), 1316 (m), 1262 (m), 1231 (w), 1176 (w), 1099 (m), 1056 (w), 1022 (m), 934 (w), 873 (w), 853 (w), 795 (m), 759 (w), 722 (w), 636 (w), 600 (w), 527 (w), 452 (w).

[LMn(μ -**Cl)**]₂ (4). LK (0.91 g, 2 mmol) in diethyl ether (15 mL) was added to a suspension of MnCl₂ (0.25 g, 2 mmol) in diethyl ether (40 mL) at -78 °C. The mixture was warmed to room temperature and stirred for 14 h. The resulting precipitate was removed by filtration. The solution was concentrated to ca. 10 mL. Yellow crystals were obtained after 1 day at -26 °C. Yield: 0.88 g (87%). Mp: >400 °C. Anal. Calcd for C₅₈H₈₂-Cl₂Mn₂N₄ (1016.06): C, 68.50; H, 8.07; N, 5.51. Found: C, 68.75; H, 8.23; N, 5.21. EI-MS: *m*/*z* (%) 507 (100) [1/2M]. IR (KBr, Nujol mull, cm⁻¹): $\tilde{\nu}$ 1656 (w), 1623 (w), 1592 (w), 1553 (w), 1528 (w), 1326 (w), 801 (m), 758 (w), 722 (w), 664 (w), 618 (w), 541 (w), 466 (w).

[LMn(\mu-O₂CMe)]₂ (5). LK (0.91 g, 2 mmol) in THF (10 mL) was added to a suspension of Mn(O₂CMe)₂ (0.35 g, 2 mmol) in THF (30 mL) at -78 °C. The mixture was warmed to room temperature and stirred for 12 h. The resulting precipitate was removed by filtration. The solution was concentrated to ca. 5 mL. Yellow crystals were obtained after 7 days at -26 °C. Mp: >330 °C (dec). Yield: 0.80 g (75%). Anal. Calcd for C₆₂H₈₈-Mn₂N₄O₄ (1063.24): C, 70.00; H, 8.28; N, 5.27. Found: C, 69.68; H, 8.19; N, 5.00. EI-MS: *m/z* (%) 531 (100) [1/2M]. IR (KBr, Nujol mull, cm⁻¹): $\tilde{\nu}$ 1602 (s), 1544 (m), 1519 (m), 1437 (s), 1380 (m), 1317(m), 1262 (w), 1177 (w), 1099 (w), 1021 (w), 933 (w), 851 (w), 793 (w), 759 (w), 643 (w).

[LMnCl₂][{C(Me)N(*i*Pr)}₂CH] (6). THF (40 mL) was added to a mixture of $MnCl_2(THF)_{1.5}$ (0.47 g, 2 mmol), LH (0.83 g, 2 mmol), and {C(Me)N(iPr)}2C (0.36 g, 2 mmol) at room temperature. The resulting suspension was stirred for 12 h, and a clear yellow solution was obtained. The solution was concentrated to ca. 10 mL and kept at 4 °C. Yellow crystals were obtained after 3 days. Yield: 1.23 g (85%). Mp: > 210 °C (dec). Anal. Calcd for C40H62Cl2MnN4 (724.78): C, 66.23; H, 8.55; N, 7.73. Found: C, 65.85; H, 8.75; N, 7.45. EI-MS: m/z (%) 723 (2) [M - H]+, 507 (43) [LMnCl], 181 (52) [{C(Me)- $N(iPr)_2$ CH]. IR (KBr, Nujol mull, cm⁻¹): $\tilde{\nu}$ 3126 (w), 3058 (w), 1663 (w), 1628 (w), 1551 (m), 1542 (m), 1516 (m), 1438 (s), 1400 (s), 1321 (s), 1263 (s), 1232 (m), 1193 (w), 1177 (m), 1143 (w), 1101 (s), 1056 (w), 1023 (s), 962 (w), 936 (m), 868 (w), 849 (w), 799 (s), 792 (s), 764 (m), 758 (m), 721 (w), 652 (w), 630 (w).

LMnCp(THF) (7). CpNa (0.6 mL, 2.0 M in THF, 1.2 mmol) was added to a solution of **4** (0.51 g, 0.5 mmol) in THF (20 mL) at -78 °C. The mixture was allowed to warm to room temperature and stirred for 14 h. All volatiles were removed in vacuum, and the residue was extracted with toluene (15 mL). The yellow solution was concentrated to ca. 10 mL and kept at room temperature for 2 days to give yellow crystals. The crystals were collected by filtration, and the filtrate was concentrated and kept at 4 °C for 7 days to give additional crystals. Total yield: 0.52 g (86%). Mp: 210–212 °C. Anal. Calcd for C₃₈H₅₄MnN₂O (609.77): C, 74.88; H, 8.87; N, 4.60.

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Found: C, 74.46; H, 8.76; N, 4.64. EI-MS: m/z (%) 537 (100) [M –THF], 472 (92) [LMn]. IR (KBr, Nujol mull, cm⁻¹): $\tilde{\nu}$ 1653 (w), 1542 (w), 1521 (m), 1401 (m), 1315 (m), 1262 (s), 1231 (w), 1172 (w), 1098 (s), 1056 (m), 1028 (s), 933 (w), 872 (w), 846 (w), 793 (s), 765 (w), 751 (m), 721 (m), 667 (w), 601 (w), 466 (w).

X-ray Crystallography. Crystallographic data for **3–6** were collected on a Stoe-Siemens-Huber four-circle diffractometer coupled to a Siemens CCD area detector and for **7** on a Stoe IPDS II-array detector system. In both cases graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å) was used. All structures were solved by direct methods (SHELXS-97)²¹ and refined against F^2 using SHELXL-97.²² All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically calculated positions and refined using a riding model. For compound **6**, Flack *x* parameter = -0.0229 with esd 0.0382. Expected values are 0 (within 3 esd's) for correct and +1 for the inverted absolute structure. The absolute structure of **7** could not be determined, and a twin refinement was done.

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Supporting Information Available: X-ray structural information for complexes **3**–**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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