

Synthesis and Reaction of Mn^{II} Iodides Bearing the β -Diketiminato Ligand: the First Divalent Manganese N-Heterocyclic Carbene Complexes $[\{HC(CMeNAr)_2\}MnI\{C[N(iPr)CMe]_2\}]$ and $[\{HC(CMeNAr)_2\}MnNHAr\{C[N(iPr)CMe]_2\}]$ (Ar = 2,6-*i*Pr₂C₆H₃)

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Keywords: Manganese / Iodine / N ligands / Heterocycles / Carbene ligands

The manganese mono-iodide $[HC(CMeNAr)_2]MnI(THF)$ (Ar = 2,6-*i*Pr₂C₆H₃) (**3**) was prepared in good yield from the reaction of $[HC(CMeNAr)_2]K$ with MnI_2 in THF. Treatment of **3** under reflux in toluene and removing all the volatiles in vacuo afforded the dimeric compound $[\{HC(CMeNAr)_2\}Mn]_2(\mu-I)_2$ (**4**). Displacement of the coordinated THF in **3** by a strong Lewis base $C[N(iPr)CMe]_2$ or by adding $C[N(iPr)CMe]_2$ to the toluene solution of **4** readily gave the N-heterocyclic carbene adduct $[\{HC(CMeNAr)_2\}MnI\{C[N(iPr)CMe]_2\}]$ (**5**). Reduction of **5** with sodium/potassium alloy at room temperature unexpectedly resulted in the formation of the monomeric compound

$[\{HC(CMeNAr)_2\}MnNHAr\{C[N(iPr)CMe]_2\}]$ (**6**). Alternatively **6** was obtained by the salt elimination reaction of **5** with $LiNHAr$. Compounds **5** and **6** are the first examples of divalent manganese N-heterocyclic carbene adducts and the first manganese non-carbonyl carbene complexes. The single crystal X-ray structural analyses reveal that compounds **3** and **6** are monomeric and compound **4** is dimeric in the solid state. The manganese centers in these compounds exhibit a distorted tetrahedral geometry.

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Introduction

Manganese carbene complexes are important due to their applications in organic synthesis, synthetic methodology and theoretical implications and have been studied extensively.^[1–4] N-Heterocyclic carbenes have attracted great attention in ligand design and homogeneous catalysis since Arduengo et al. reported the first stable crystalline N-heterocyclic carbene in 1991.^[5–8] A variety of transition metal N-heterocyclic carbene complexes have been synthesized and isolated and some of them have been successfully applied as catalysts in a number of organic reactions such as iridium-catalyzed transfer hydrogenation,^[6] ruthenium-catalyzed olefin metathesis, and especially palladium-catalyzed C–C coupling reactions: the Heck, Suzuki and Kumada reactions.^[7,9] However, manganese N-heterocyclic carbene complexes are rare and have not attracted much attention to date.^[9a] To the best of our knowledge, only a few monovalent manganese N-heterocyclic carbene complexes are known, including $[MeC_5H_4(CO)_2MnC(NMeCH_2)_2]$,^[10] $[(CO)_3MnBr\{C(NMeCH_2)_2\}_2]$ ^[10] and $[(CO)_5MnC\{N(BH_3)CMeCMeNMe\}]$ ^[11] and so far no higher oxidation state manganese N-heterocyclic carbene complexes have

been reported. Furthermore, no X-ray structural data of manganese N-heterocyclic carbene complexes are available.

Organometallic iodide complexes have unique chemical properties due to their labile M–I bond compared to the M–Cl congener.^[12] Recent results in our group proved that aluminum diiodide bearing a β -diketiminato ligand $[AlI_2\{HC(CMeNAr)_2\}]$ (Ar = 2,6-*i*Pr₂C₆H₃) is a good starting material for some interesting reactions such as reduction and hydrolysis. For instance, we reported the monomeric $[Al\{HC(CMeNAr)_2\}]$ as a stable carbene analogue by reduction of $[AlI_2\{HC(CMeNAr)_2\}]$ with potassium.^[13a] Furthermore, the aluminum dihydroxide complex $[Al(OH)_2\{HC(CMeNAr)_2\}]$, with terminal OH groups, was obtained by hydrolysis of $[AlI_2\{HC(CMeNAr)_2\}]$ using a liquid NH₃/toluene two-phase system.^[13b] Consequently we became interested in transition metals and investigated the behavior of Mn iodides bearing a β -diketiminato ligand. However, our efforts to reduce $[\{HC(CMeNAr)_2\}Mn(\mu-I)_2Li(OEt)_2]$ were unsuccessful with sodium or potassium due maybe to the existence of the stable lithium salt.^[14] Herein we report the preparation of manganese iodides bearing β -diketiminato ligand free of lithium salt of composition $[LMnI(THF)]$ (**3**), $[(LMn)_2(\mu-I)_2]$ (**4**) and $[LMnI\{C[N(iPr)CMe]_2\}]$ (**5**) [L = HC(CMeNAr)₂, Ar = 2,6-*i*Pr₂C₆H₃] and the derivative $[LMnNHAr\{C[N(iPr)CMe]_2\}]$ (**6**), in which compounds **5** and **6** are the

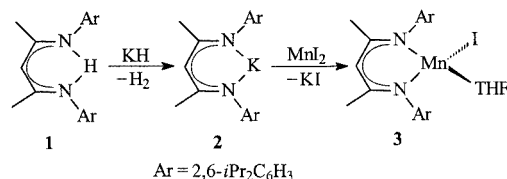
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first examples of divalent manganese N-heterocyclic carbene adducts and the first manganese non-carbonyl carbene complexes. Compound **6** is the first structurally characterized manganese N-heterocyclic carbene complex.

Results and Discussion

Synthesis of Compounds 2–6

KL (**2**) was prepared from the reaction of HL (**1**) with KN(SiMe₃)₂ in relatively low yield (27%).^[15] Herein we report that this compound can be conveniently obtained as a crystalline solid in good yield (87%) by the reaction of HL with KH in diethyl ether at room temperature (Scheme 1). The ¹H NMR spectrum and elemental analysis are identical with those of the literature.^[15] Compound **2** is stable under an inert atmosphere and can be kept for a long time without obvious decomposition.



Scheme 1

The reaction of MnI₂ with one equiv. of [LiL(Et₂O)] in diethyl ether afforded the heterobimetallic complex [LMn(μ-I)₂Li(OEt₂)₂].^[14] Attempts to remove the coordinated lithium salt from the manganese center were unsuccessful. However, the reaction of MnI₂ with one equiv. of **2** in THF easily gave the monomeric compound [LMnI(THF)] (**3**) in high yield (87%) with a coordinated THF at the metal center. EI-MS of **3** exhibits [LMnI]⁺ (*m/z* = 599, 100%) without the coordinated THF. The formula of **3** was confirmed by the crystal structure (Figure 1).

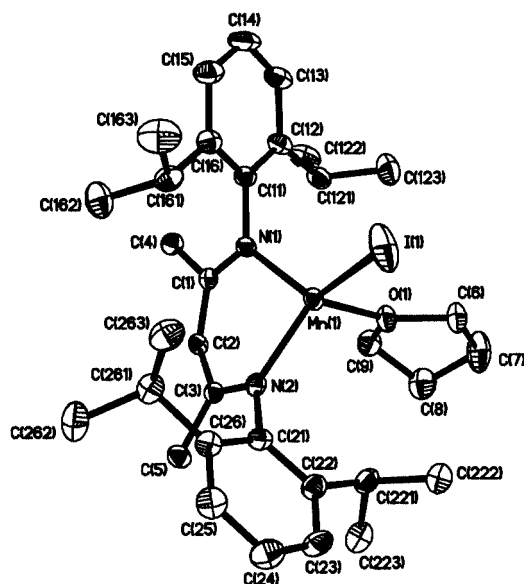
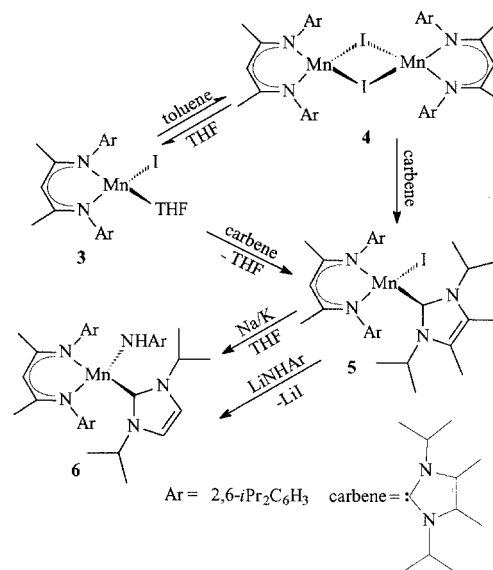


Figure 1. Molecular structure of **3** (30% probability thermal ellipsoids); hydrogen atoms are omitted for clarity

Attempts to prepare the di-β-diketiminato complex by using two equiv. of **2** were unsuccessful.

Refluxing of **3** in toluene for 0.5 h and removing all the volatiles in vacuo afforded the dimeric compound [LMn]₂(μ-I)₂ (**4**). Crystals suitable for X-ray analysis were obtained by recrystallization from toluene. EI-MS of **4** did not give the molecular ion peak M⁺ whereas half of the molecular mass [LMnI]⁺ is observed at *m/z* = 599 (100%), which shows that **4** is monomeric in the gas phase, and no indication of fragments containing a Mn–Mn species, which is consistent with the X-ray structural analysis. Compound **3** can easily be obtained by dissolving **4** in THF (Scheme 2).



Scheme 2

Compound **3** can be considered as an adduct of a Lewis acid LMnI and a weak Lewis base THF. Displacement of the THF by a strong Lewis base [C{N(*i*Pr)CMe₂}₂] readily afforded the N-heterocyclic carbene adduct [LMnI{C{N(*i*Pr)CMe₂}₂}] (**5**), which can also be obtained by adding [C{N(*i*Pr)CMe₂}₂] to a solution of **4** in toluene. On the other hand we were not able to prepare **4** by removing the carbene in **5**, which shows that the N-heterocyclic carbene is a much stronger σ-donor ligand. Compounds **3**, **4**, and **5** are all soluble in polar solvents such as THF and CH₂Cl₂ and have poor solubility in hydrocarbon solvents.

The chemistry of organometallic dinuclear complexes containing a metal-metal bond is a burgeoning field.^[16] We are interested in preparing L'MML' (L' = ligands, M = metal) type compounds by reduction of L'MX (X = halide). The first three-coordinate dinuclear manganese(I) compound LMnMnL [L = HC(CMeNAr)₂, Ar = 2,6-*i*Pr₂C₆H₃] has been successfully synthesized by reduction of **4** with sodium/potassium alloy.^[17] However, further reduction of **5** by sodium/potassium alloy at room temperature, unexpectedly resulted in the formation of the monomeric compound [LMnNHAr{C{N(*i*Pr)CMe₂}₂}] (**6**) in low yield. The efforts to identify other species were unsuccessful. Given that Mn^{II} complexes are used as radical initiators

for radical polymerisation processes,^[18] it is tempting to propose that the formation of compound **6** is due to the partial decomposition of the intermediate radical $[\text{LMnC}\{\text{N}(\text{iPr})\text{CMe}_2\}_2]$, which cannot aggregate due to the presence of the bulky N-heterocyclic carbene. In the mass spectrum, $[\text{LMnNHAr}]^+$ was observed at $m/z = 648$ (52%), followed by $[\text{LMn}]^+$ ($m/z = 472$, 100%). The elemental analyses are consistent with the solid-state structure. Compound **6** can also be prepared in good yield (76%) by the reaction of **5** with LiNHAr .

X-ray Diffraction Analyses for **3**, **4**, and **6**

The single-crystal X-ray diffraction analyses for compounds **3**, **4**, and **6** have been undertaken. For **3** and **4**, there are two molecules in the unit cell, one of which is shown in Figures 1 and 2, respectively. The structure of **6** is presented in Figure 3. Crystallographic data for **3**, **4**, and **6** are given in Table 1 and selected bond lengths and angles in Table 2.

The X-ray structural analyses reveal that the $[\text{LMnI}(\text{THF})]$ (**3**), $[\text{LMnNHAr}\{\text{C}[\text{N}(\text{iPr})\text{CMe}_2\}_2]$ (**6**) are monomeric and $[(\text{LMn})_2(\mu\text{-I})_2]$ (**4**) is dimeric in the solid state (Figures 1–3). In all three compounds the manganese centers are four-coordinate and display a distorted tetrahedral geometry. The backbone of the chelating ligand is nearly planar and the manganese atom in all the reported compounds is out of the C_3N_2 plane (0.62 Å in **3**, 0.43 Å in **4**, 0.78 Å in **6**). The $\text{N}(1)\text{--Mn}(1)\text{--N}(2)$ angle in **6** [$88.94(7)^\circ$] is significantly smaller than the corresponding angles in **3** [$93.56(13)^\circ$] and **4** [$95.57(14)^\circ$], while the $\text{Mn}(1)\text{--N}(1)$ and $\text{Mn}(1)\text{--N}(2)$ bond lengths in **6** [2.166(2) and 2.133(2) Å] are obviously longer than those in **3** [2.079(3) and 2.070(3) Å] and **4** [2.067(2) and 2.067(2) Å], which indicates that the metal center in **6** is more weakly bonded to the chelating ligand possibly due to the different substituents that cause a stronger trans effect.

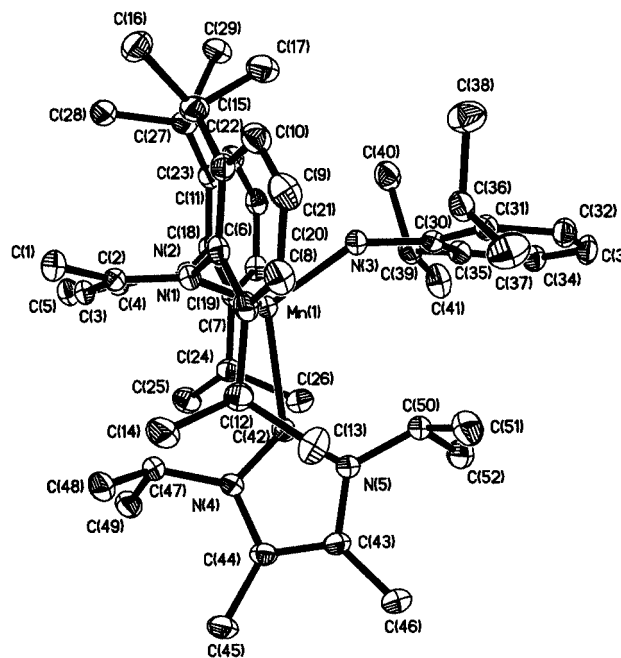


Figure 3. Molecular structure of **6** (30% probability thermal ellipsoids); hydrogen atoms are omitted for clarity

The terminal $\text{Mn}(1)\text{--I}(1)$ distance [2.6272(8) Å] in **3** is similar to the reported values for the terminal $\text{Mn}\text{--I}$ bond such as those in $[\text{MnI}(\text{sim})_2]$ [2.6233(6) Å] [$\text{sim} = \text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{N}(\text{SiMe}_3)$]^[19] and $[\text{MnI}_2(\text{PET}_3)_2]$ [av. 2.666(2) Å].^[20] which is significantly shorter than the bridging $\text{Mn}\text{--I}$ bond length in **4** [2.7688(7) and 2.7484(8) Å] and $[\text{LMn}(\mu\text{-I})_2\text{Li}(\text{OEt}_2)_2]$ [2.716(9) and 2.733(9) Å].^[14] The two manganese atoms are bridged by two iodine atoms in **4** and the distance between two manganese atoms is 3.615 Å, which is out of the range of a $\text{Mn}\text{--Mn}$ bond. The Mn_2I_2

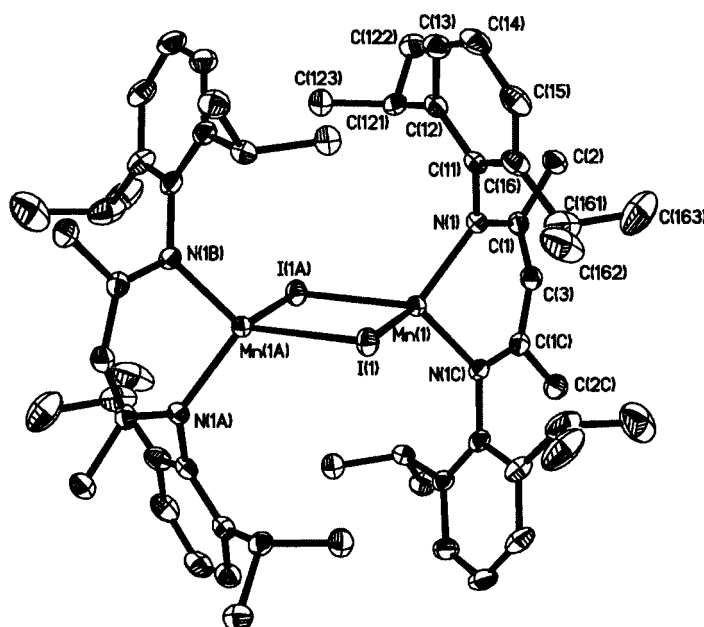


Figure 2. Molecular structure of **4** (30% probability thermal ellipsoids); hydrogen atoms are omitted for clarity

Table 1. Crystallographic data for compounds **3**, **4**, and **6**

	3	1/2 4 incl. toluene	6
Empirical formula	C ₃₃ H ₄₉ IMnN ₂ O	C ₃₆ H ₄₉ IMnN ₂	C ₅₂ H ₇₉ MnN ₅
Molecular weight	671.58	691.61	829.14
Temperature (K)	203(2)	203(2)	133(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>m</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions (<i>a</i> , <i>b</i> , <i>c</i> = Å, α , β , γ = °)	<i>a</i> = 16.752(2) <i>b</i> = 20.290(6) <i>c</i> = 19.620(3) α = 90 β = 91.317(14) γ = 90	<i>a</i> = 19.188(3) <i>b</i> = 21.000(4) <i>c</i> = 16.5839(13) α = 90 β = 100.053(8) γ = 90	<i>a</i> = 11.694(2) <i>b</i> = 19.388(4) <i>c</i> = 22.168(4) α = 90 β = 102.59(3) γ = 90
Volume (Å ³)	6670(1)	6580.0(16)	4905.3(17)
<i>Z</i>	8	8	4
Absorption coefficient (mm ⁻¹)	1.348	1.366	0.307
θ range for data collection	3.52 to 25.03°	3.57 to 25.00°	1.78 to 24.72°
<i>F</i> (000)	2776	2856	1804
Reflections collected	14274	7832	34511
Independent reflections	11722 (<i>R</i> _{int} = 0.0616)	5952 (<i>R</i> _{int} = 0.0425)	8269 (<i>R</i> _{int} = 0.0717)
Data/restraints/parameters	11722/0/705	5952/0/374	8269/0/543
Goodness-of-fit on <i>F</i> ²	1.053	1.018	0.932
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0534, 0.1296	0.0349, 0.0900	0.0422, 0.0983
<i>R</i> (all data)	0.0714, 0.1457	0.0388, 0.0936	0.0616, 0.1044
Largest diff. peak/hole (e ⁻ Å ⁻³)	0.971 /-1.279	0.977/-0.788	0.431/-0.469

Table 2. Selected bond lengths (Å) and bond angles (deg) for compounds **3**, **4**, and **6**

Compound 3			
Mn(1)–N(1)	2.079(3)	N(2)–Mn(1)–O(1)	104.28(12)
Mn(1)–N(2)	2.070(3)	N(1)–Mn(1)–O(1)	101.90(1)
Mn(1)–O(1)	2.155(3)	N(2)–Mn(1)–I(1)	124.79(9)
Mn(1)–I(1)	2.6272(8)	N(1)–Mn(1)–I(1)	124.12(9)
N(2)–Mn(1)–N(1)	93.56(13)	I(1)–Mn(1)–O(1)	104.96(8)
Compound 4			
Mn(1)–N(1)	2.067(2)	N(1)–Mn(1)–I(1)	119.04(7)
Mn(1)–N(1C)	2.067(2)	N(1C)–Mn(1)–I(1)	119.04(7)
Mn(1)–I(1)	2.7484(8)	N(1)–Mn(1)–I(1A)	113.02(7)
Mn(1)–I(1A)	2.7688(7)	I(1)–Mn(1)–I(1A)	98.14(2)
Mn(1A)–I(1)	2.7688(7)	Mn(1)–I(1)–Mn(1A)	81.86(2)
N(1)–Mn(1)–N(1C)	95.57(14)		
Compound 6			
Mn(1)–N(1)	2.166(2)	N(3)–Mn(1)–N(1)	99.25(7)
Mn(1)–N(2)	2.133(2)	N(2)–Mn(1)–N(1)	88.94(7)
Mn(1)–N(3)	2.055(2)	N(3)–Mn(1)–C(42)	117.46(8)
Mn(1)–C(42)	2.270(2)	N(2)–Mn(1)–C(42)	111.68(8)
N(3)–Mn(1)–N(2)	123.25(7)	N(1)–Mn(1)–C(42)	109.83(7)

four-membered ring is exactly planar, bisecting and perpendicular to the two chelating ligands around them.

[LMnNHAr{C[N(*i*Pr)CMe]₂}] (**6**) is, to the best of our knowledge, the first structurally characterized manganese N-heterocyclic carbene complex. The Mn–C(carbene) distance [2.270(2) Å] is in the normal range of those in the manganates [Li(TMEDA)]₂[MnR₄] [2.22(6)–2.28(1) Å]

(R = Me, Et, Bu or CH₂SiMe₃, TMEDA = tetramethylethylenediamine).^[21] However, it is significantly longer than the Mn–C (carbene) distance in extensively studied manganese carbonyl carbene complexes [CpMn(CO)₂CXY] [X = Y = Me, 1.872(10) Å;^[22] X = Y = Ph, 1.885(2) Å;^[23] X = F, Y = Ph, 1.830(5) Å;^[24] X = OEt, Y = Ph, 1.865(14) Å^[25]]. This could result from two reasons: one is the steric repulsion between the bulky substituents; the other is the very weak Mn→C back bonding in **6** due to the relatively high energy of the formal empty p(π) orbital of the N-heterocyclic carbene carbon, which is increased by the N→C bond.^[9a,26] In this respect N-heterocyclic carbenes are different from the usual carbenes, which have rather strong M→C(carbene) back bonding.^[25,27] The manganese atom in **6** is out of the carbene plane (0.41 Å) and the dihedral angle between the carbene plane and the chelating ligand plane is 108.8°. The Mn(1)–N(3) bond length in **6** is 2.055(2) Å, which is close to that reported in Mn^{II} amide.^[28]

Conclusion

As an extension of our previous work, manganese iodides bearing β-diketimate ligand free of lithium salt, and their derivatives, were successfully synthesized and characterized. Compounds **5** and **6** are the first examples of divalent manganese N-heterocyclic carbene adducts and the first manganese non-carbonyl carbene complexes. The structure of **6** shows that the Mn–C (carbene) bond length in **6** is significantly longer than that of a “real” manganese carbene bond and π-backbonding is considered to be negligible in this system.

Experimental Section

General: All reactions were performed using standard Schlenk and dry box 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. HL (**1**) [$L = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$]^[29] and $\text{C}[\text{N}(\text{iPr})\text{CMe}]_2$ ^[30] were prepared by literature procedures.

KL (2): A suspension of KH (0.18 g, 4.5 mmol) and **1** (1.67 g, 4 mmol) in diethyl ether (50 mL) was stirred at room temperature for 3 days. After filtration the light yellow filtrate was concentrated to ca. 10 mL and kept at -26°C for 24 h to afford crystalline solid. Yield: 1.59 g (87%). The ^1H NMR spectrum and elemental analyses are identical with those of the literature.^[15]

[LMnI(THF)] (3): A solution of **2** (0.91 g, 2 mmol) in THF (10 mL) was added to a suspension of MnI_2 (0.62 g, 2 mmol) in THF (35 mL) at -78°C . The mixture was allowed to warm to room temperature and stirred for 14 h. The precipitate was removed by filtration. The yellow filtrate was concentrated to ca. 5 mL and kept at -26°C for 24 h to give yellow crystals. Yield: 1.17 g (87%). M.p. $379\text{--}381^\circ\text{C}$. $\text{C}_{33}\text{H}_{49}\text{IMnN}_2\text{O}$ (670.84): calcd. C 59.03, H 7.30, N 4.17; found C 58.95, H 7.24, N 4.16. EI-MS: m/z (%) = 599 (100) $[\text{LMnI}]^+$. IR (KBr, Nujol mull): $\tilde{\nu} = 1624\text{ cm}^{-1}$ (w), 1552 (w), 1520.62 (m), 1314 (m), 1262 (m), 1174 (w), 1100 (w), 1024 (m), 935 (w), 870 (w), 852 (w), 794 (m), 757 (w), 721 (w), 600 (vw), 524 (w), 468 (vw).

[LMnI₂(μ-I)₂] (4): A solution of **3** (1.34 g, 2 mmol) in toluene (40 mL) was refluxed for 0.5 h. All volatiles were removed in vacuo and bright yellow micro crystals were obtained. Yield: 1.15 g (96%). M.p. $271\text{--}273^\circ\text{C}$ (dec). $\text{C}_{58}\text{H}_{82}\text{I}_2\text{Mn}_2\text{N}_4$ (1197.68): calcd. C 58.11, H 6.84, N 4.67; found C 58.34, H 6.92, N 4.85. EI-MS: m/z (%) = 599 (100) $[\text{LMnI}]^+$. IR (KBr, Nujol mull): $\tilde{\nu} = 1657\text{ cm}^{-1}$ (w), 1625 (w), 1552 (w), 1262 (m), 1097 (m), 1023 (m), 875 (w), 800 (m), 722 (w), 659 (vw), 536 (w), 468 (w).

[LMnI{C[N(iPr)CMe]₂}] (5): A solution of $\text{C}[\text{N}(\text{iPr})\text{CMe}]_2$ (0.18 g, 1 mmol) in THF (10 mL) was added to a THF (20 mL) solution of **3** (0.67 g, 1 mmol) at room temperature. The resulting mixture was stirred for 1 h. After removal of all volatiles in vacuo, a yellow solid was obtained. Yield: 0.76 g (98%). M.p. 271°C (dec). $\text{C}_{40}\text{H}_{61}\text{IMnN}_4$ (778.8): calcd. C 61.63, H 7.83, N 7.19; found C 61.78, H 8.02, N 7.20. EI-MS: m/z (%) = 599 (100) $[\text{LMnI}]^+$. IR (KBr, Nujol mull): $\tilde{\nu} = 1625\text{ cm}^{-1}$ (m), 1552 (s), 1505 (m), 1318 (m), 1261 (s), 1232 (w), 1218 (vw), 1190 (vw), 1171 (m), 1105 (m), 1071 (vw), 1020 (m), 936 (w), 929 (w), 793 (s), 763 (m), 758 (m), 722 (m).

[LMnNHAr{C[N(iPr)CMe]₂}] (6). Method a: A solution of **5** (0.78 g, 1 mmol) in THF (20 mL) was added to a suspension of sodium/potassium alloy (Na, 0.01 g, 0.5 mmol; K 0.04 g, 1 mmol) in THF (10 mL). The mixture was stirred for 6 days at room temperature. All volatiles were removed in vacuo and the residue was extracted with *n*-hexane (10 mL). Yellow crystals were obtained after cooling for one week at 4°C . The crystals were collected by filtration and the mother liquor was concentrated to ca. 4 mL and kept at 4°C for 4 days to give yellow crystals. Total yield: 0.19 g (23%). M.p. $170\text{--}172^\circ\text{C}$. $\text{C}_{52}\text{H}_{79}\text{MnN}_5$ (829.14): calcd. C 75.26, H 9.53, N 8.44; found C 74.84, H 9.92, N 8.85. EI-MS: m/z (%) = 472 (100) $[\text{LMn}]^+$, 648 (52) $[\text{LMnNHAr}]^+$. IR (KBr, Nujol mull):

$\tilde{\nu} = 3173\text{ cm}^{-1}$ (vw), 1633 (w), 1588 (w), 1543 (w), 1512 (m), 1420 (s), 1406 (m), 1316 (m), 1261 (m), 1169 (m), 1102 (w), 1019 (w), 929 (w), 886 (vw), 841 (w), 794 (m), 758 (w), 737 (m), 722 (m), 600 (vw), 565 (vw), 543 (vw).

Method b: A THF (10 mL) solution of LiNHAr (0.18 g, 1 mmol) was added to a THF (20 mL) solution of **5** (0.78 g, 1 mmol) at -78°C . The mixture was allowed to warm to room temperature and stirred for 14 h. After removal of all volatiles in vacuo, the residue was extracted with diethyl ether (10 mL). After filtration, the yellow filtrate was concentrated to ca. 5 mL and stored at -26°C for 3 days to give yellow crystals. Yield: 0.63 g (76%). The spectroscopic characterization of the compound is identical to that of the compound prepared by method a.

X-ray Crystallography: Crystallographic data for **3** and **4** were collected on a Stoe–Siemens–Huber four-circle diffractometer coupled to a Siemens CCD area detector and for **6** on a Stoe IPDS II-array detector system. In both cases graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) was used. All structures were solved by direct methods (SHELXS-97)^[31] and refined against F^2 using SHELXL-97.^[32] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically calculated positions and refined using a riding model. Atomic coordinates, thermal parameters, bond lengths and angles. CCDC-207299 (**3**), -207298 (**4**), and -207297 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and Ciba company. We thank Dr. Frauendorf (Institut für organische Chemie, Universität Göttingen) for MS(DCI) and helpful discussions.

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Received May 15, 2003

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Published Online October 10, 2003