Organometallics **2004,** *23,* 1177−1179 1177

Structurally Characterized Neutral Monoalkyl and -aryl Complexes of Manganese(II)[†]

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Received October 28, 2003

*Summary: The synthesis and X-ray crystal structures of the monomethyl and -phenyl manganese complexes [LMn(μ-Me)]$_2$ (**2**) and LMnPh (**3**) (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) are reported. These complexes represent the first structurally characterized neutral dimeric manganese(II) monoalkyl complexes and monomeric manganese(II) monoaryl complexes. Furthermore, compound **3** shows an interesting coplanar arrangement of the phenyl group and the chelating ligand.*

There is widespread interest in organomanganese(II) complexes, especially alkyl and aryl derivatives, since such complexes have extensive applications in organic synthesis.[1,2] Manganese(II) alkyl and aryl complexes have been proved to be excellent reagents in C−C coupling reactions and can be compared to other organo-transition-metal complexes such as the widely used organocopper reagents.[3] Moreover, they also show good thermal stability, high chemoselectivity, and excellent functional group tolerance.[1d,3] Some neutral and ionic dialkyl and diaryl derivatives of Mn(II) of composition MnR$_2$,[4] MnR$_2$B$_x$,[1d,4a,5] LiMnR$_3$,[3] and Li$_2$MnR$_4$[4a,6] (R = alkyl, aryl; B = Lewis base, x = 1−4) have been synthesized and characterized. Recently ionic manganese(II) monoalkyl and -aryl complexes Mn(acacen)(R)-Li(DME) (acacen = *N*,*N*′-ethylenebis(acetylacetiminato) dianion; R = Me, Ph, Mes) were reported as bifunctional carriers of polar organometallics.[7] However, neutral monoalkyl and -aryl derivatives of Mn(II) are rare. Compounds of composition RMnX (X = halide) have only been used as intermediates without isolation.[2] To the best of our knowledge, only two compounds of this class, [Mn(*n*Bu)(NPEt$_3$)]$_4$ and [Mn(Me)(NPEt$_3$)]$_4$, have been structurally characterized containing a heterocubane structure.[8] There is no structural investigation known of lower aggregated complexes (monomer or dimer). Keeping this in mind and the recent interesting results[9] obtained by taking advantage of β-diketiminato ligands on the basis of their unique electronic and steric effects to stabilize unusual complexes such as the monomeric iron(II) monomethyl complex {HC(C*t*BuNAr)$_2$}FeMe (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$),[10] we set out to synthesize low aggregated manganese(II) monoalkyl and -aryl complexes using such ligands. Herein we report the preparation and molecular structure of the dimeric compound [LMn(μ-Me)]$_2$ (**2**) and the monomeric compound LMnPh (**3**) (L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$).

The addition of MeLi and PhLi, respectively, to [LMn(μ-I)]$_2$ [11] (**1**) in toluene at low temperature smoothly provided the dimeric **2** and the monomeric **3** in moderate yield.[12] However, the successful isolation of pure **2** and **3** was not easy, due to the difficulties in removing small amounts of unreacted starting material **1**. This requires

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[†] Dedicated to Professor Edgar Niecke on the occasion of his 65th birthday.

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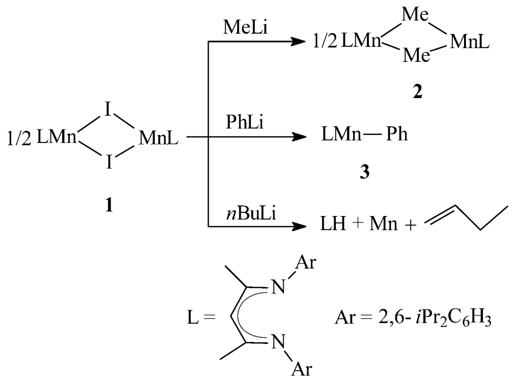
(12) Selected data for **2**: yield 52%; mp 190−192 °C; EI-MS *m*/*z* (%) 487 (6) [LMnMe]$^+$, 472 (100) [LMn]$^+$. Anal. Calcd for C$_{60}$H$_{88}$Mn$_2$N$_4$ (975.22): C, 73.83; H, 9.02; N, 5.74. Found: C, 73.31; H, 8.76; N, 5.64. Selected data for **3**: yield 65%; mp 230−232 °C; EI-MS *m*/*z* (%) 549 (3) [M]$^+$, 471 (100) [M − C$_6$H$_6$]$^+$. Anal. Calcd for C$_{35}$H$_{46}$MnN$_2$ (549.68): C, 76.41; H, 8.37; N, 5.09. Found: C, 75.72; H, 8.13; N, 4.86. NMR spectroscopic data for **2** and **3** are not available, due to the paramagnetism of Mn(II).

10.1021/om030645i CCC: $27.50
Publication on Web 02/07/2004

Scheme 1



a number of precautions. The RLi reagents should be in excess, according to the stoichiometric amounts given in Scheme 1. Sometimes it is necessary to recrystallize the product from pentane several times. The reaction of **1** with *n*BuLi, however, resulted in the formation of a manganese mirror and LH, which was confirmed by EI-MS and ^{1}H NMR. The proposed mechanism for this reaction is obviously the direct intramolecular elimination of the alkyl group and the chelating ligand. A similar decomposition pathway was suggested for various dialkyl Mn(II) species.[13]

Complexes **2** and **3** are both yellow crystalline solids, which are highly sensitive to air and moisture and were handled in a glovebox under purified nitrogen. Below the corresponding melting points of **2** and **3** (190−192 °C for **2** and 230−232 °C for **3**), no decomposition was observed. In the EI-MS of **2** the molecular ion peak M^+ was silent; however, half of the molecular mass $[LMnMe]^+$ was observed (*m*/*z* 487, 6%) and the most intense peak (*m*/*z* 472, 100%) was assigned to $[LMn]^+$. For **3**, M^+ was observed at *m*/*z* 549 (3%), followed by $[M - C_6H_6]^+$ (*m*/*z* 471) as the most intense peak.

Compound **2** is the first structurally characterized manganese alkyl complex containing bridging methyl groups.[14] The solid-state structure of **2** (Figure 1) shows that the manganese centers have a distorted-tetrahedral geometry. The backbone of the chelating ligand is nearly planar, and the manganese atom is out of this plane (0.56 Å). The central core contains an ideal planar four-membered $Mn_2(\mu\text{-}Me)_2$ ring, which bisects and is perpendicular (89.5°) to the two chelating ligands around them. The distance between two manganese atoms (2.809(1) Å) indicates that there is some weak interaction rather than a strong Mn−Mn bond.[3,4a,5h] The distance is comparable to those of Mn_2C_2 four-membered rings reported in the literature such as those in $Mn_2(CH_2C_6H_4NMe_2)_4$ (2.810(3) Å),[5h] $Mn_2(CH_2SiMe_3)_4(PMe_3)_2$ (2.772(1) Å),[5i] and $Mn_2(CH_2CMe_2Ph)_4$ (2.719 Å).[4a] The Mn−C(methyl) bond length (average 2.273(7) Å) is in the normal range of those (2.22(6)−2.28(1) Å) in the manganates $[Li(TMEDA)]_2[MnR_4]$ (R = Me, Et, Bu, CH_2SiMe_3)[4a,6] and, as expected, slightly longer than those (2.060(11)−2.249(4) Å) of terminal Mn−methyl bonds.

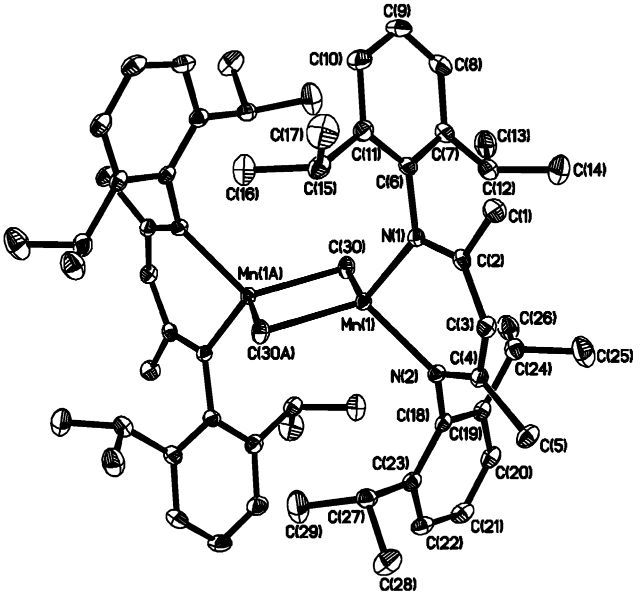


Figure 1. ORTEP drawing for complex **2** (35% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Mn(1)−N(1) = 2.125(2), Mn(1)−N(2) = 2.129(2), Mn(1)−C(30) = 2.241(2), Mn(1)−C(30A) = 2.306(2), Mn(1)−Mn(1A) = 2.809(1); N(1)−Mn(1)−N(2) = 89.68(6), N(1)−Mn(1)−C(30) = 117.53(8), N(2)−Mn(1)−C(30) = 117.18(8), N(1)−Mn(1)−C(30A) = 114.41(7), N(2)−Mn(1)−C(30A) = 114.72(8), C(30)−Mn(1)−C(30A) = 103.71(7).

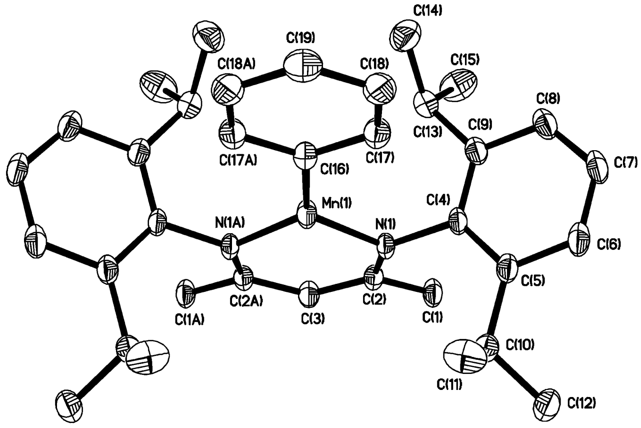


Figure 2. ORTEP drawing for complex **3** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Mn(1)−N(1) = 2.041(3), Mn(1)−N(1A) = 2.041(3), Mn(1)−C(16) = 2.077(6); N(1)−Mn(1)−N(1A) = 91.31(16), N(1)−Mn(1)−C(16) = 134.27(8), N(1A)−Mn(1)−C(16) = 134.28(8).

Single crystals suitable for X-ray structural analysis of **3** were obtained by recrystallization from diethyl ether. The X-ray structural analysis reveals a mononuclear three-coordinate manganese center with a terminal phenyl group (Figure 2). Complexes with three-coordinate manganese are rare.[15] The sum of the angles

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[14] Crystal data for $^1/_2$ **2**: $C_{30}H_{44}MnN_2$, M_r = 487.61, monoclinic, space group *C*2/*c*, a = 22.612(5) Å, b = 14.880(3) Å, c = 16.481(3) Å, β = 90.05(3)°, V = 5545.2(19) Å^3, Z = 8, ρ_{calcd} = 1.168 Mg m^{-3}, $F(000)$ = 2104, μ(Mo Kα) = 0.495 mm^{-1}. The total number of reflections was 20 857 in the range $3.28 \leq 2\theta \leq 49.42°$, of which 4662 were unique. Final *R* indices: R1 = 0.0327 ($I > 2\sigma(I)$) and wR2 = 0.0772 (all data). The maximum/minimum residual electron density was 0.257/−0.260 e Å^{-3}. Crystal data for **3**: $C_{35}H_{46}MnN_2$, M_r = 549.68, orthorhombic, space group *Pnma*, a = 16.6103(13) Å, b = 20.943(2) Å, c = 9.2785(13) Å, β = 90°, V = 3227.8(6) Å^3, Z = 4, ρ_{calcd} = 1.131 Mg m^{-3}, $F(000)$ = 1180, μ(Mo Kα) = 0.433 mm^{-1}. The total number of reflections was 8044 in the range $3.88 \leq 2\theta \leq 45.98°$, of which 2191 were unique. Final *R* indices: R1 = 0.0514 ($I > 2\sigma(I)$) and wR2 = 0.1296 (all data). The maximum/minimum residual electron density was 0.199/−0.408 e Å^{-3}.

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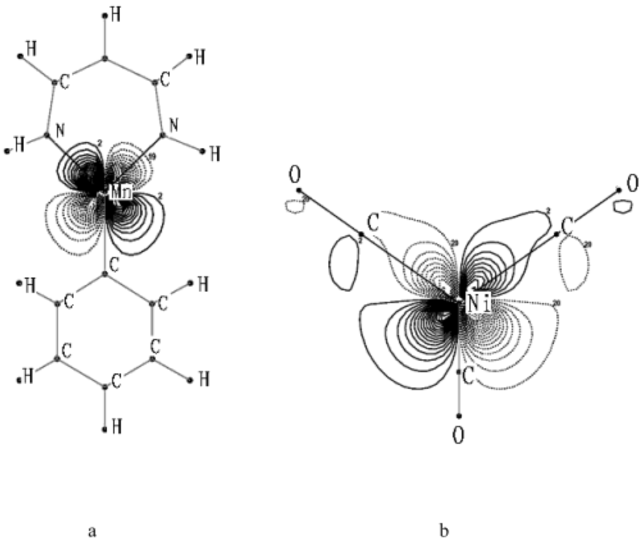

Figure 3. The most extended d orbital of Mn in compound **3** (a) and of Ni in $Ni(CO)_4$ (b).

at the metal center is 359.87(76)°, which shows that the manganese center is of planar-trigonal geometry. The six-membered MnN_2C_3 ring is essentially planar, which is in addition coplanar with the terminal phenyl ring with a mean deviation of $\Delta = 0.02$ Å. The Mn−C bond length in **3** is 2.077(6) Å, which is particularly short compared to those (2.089(8)−2.1858(4) Å) in the other terminal manganese aryl derivatives.

The order of the corresponding N−Mn−N angles is **1** (average 94.585(14)°) > **3** (91.31(16)°) > **2** (average 89.68(6)°), while the order of the Mn−N bond lengths is **3** (average 2.041(3) Å) < **1** (average 2.067(2) Å) < **2** (average 2.127(2) Å). The unexpectedly short Mn−N bond lengths in **3** are probably due to the low-coordinate metal center, which is consistent with the theoretical calculated results.

DFT calculations were carried out to get further insight into the geometry and electronic structure of compound **3**. RI-BP86 (TZVP for Mn, SV(P) for the other atoms) in Turbomole 5.5[16] was used throughout the calculation, except for the localized orbital in Figure 3, where B3LYP (6-311g(d) for Mn and 6-31g(d) for other atoms) in Gaussian 98[17] was applied. The reliability of RI-BP86 was tested by comparing the optimized geometry with the experimental structure of compound **3**. The maximum deviation in bond length is less than 0.03 Å, and the bond angle is less than 4°. These results show that RI-BP86 gives reliable results for compound **3**.

One task of the theoretical study is to find a reason for the coplanarity of the Ph ring and the chelating ligand. The result distinctly shows that the two rings in vertical positions are less stable than the coplanar arrangement by 2.9 kcal/mol. However, if the Ar groups of the chelating ligand are replaced by H atoms, the two rings in vertical positions are more stable than the coplanar arrangement by 57.4 kcal/mol, which indicates that the coplanar arrangement of the two rings results from the influence of the Ar groups, not the conjugation between the two rings. The role of the Ar groups can be attributed to two aspects: one is steric repulsion, which is the major factor in the coplanar arrangement. If the two rings are forced into vertical positions, several short H(Ph)···H(*i*Pr) distances can be found; the other is a phenyl−phenyl interaction. In **3** the terminal Ph and Ar groups are nearly in their optimized positions for this kind of interaction (dihedral angle 83.9°).[18] The shortest C···H distance between the phenyl rings is 3.345 Å. The crystal packing analysis shows that there is no close interaction with neighboring molecules.

The calculated results do not support the existence of significant Mn−C and Mn−N d−π conjugation in **3**. This is demonstrated if the terminal Ph is replaced by a CH_3 group, where the Mn−C d−π conjugation is impossible, while the Mn−C bond length almost does not change significantly (2.047−2.059 Å). Compound **3** was calculated by the B3LYP method (the ligand is replaced by $C_3H_5N_2$) and the molecular orbitals were localized by Boys methods;[19] the most extended d orbital of Mn was drawn by the MOLDEN 3.8 program[20] (Figure 3) and compared with that of Ni in $Ni(CO)_4$. The d orbital is well localized around Mn in **3**, while in $Ni(CO)_4$ the d orbitals are deformed and overlap with other atoms. These results indicate that the Mn−C and Mn−N bonds are of pure σ character, and the rather short Mn−C and Mn−N distances are attributed to the low coordination number of the central metal.

In summary, monomethyl and -phenyl complexes of Mn(II) have been successfully synthesized and characterized by using bulky β-diketiminato ligands. Research on the application of these complexes to C−C coupling reactions is in progress.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Göttinger Akademie der Wissenschaften for support of this work.

Supporting Information Available: Text and tables giving experimental, spectroscopic, and crystallographic details and details of the calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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