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Use of Manganese(II)−Schiff Base Complexes for Carrying Polar Organometallics and Inorganic Ion Pairs

Emma Gallo,[†] Euro Solari,[†] Carlo Floriani,[*,†] Angiola Chiesi-Villa,[‡] and Corrado Rizzoli[‡]

Institut de Chimie Minérale et Analytique, BCH, Université de Lausanne,
CH-1015 Lausanne, Switzerland, and Dipartimento di Chimica, Università di Parma,
I-43100 Parma, Italy

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This report concerns the carrier properties of [Mn(acacen)]-derived compounds toward polar organometallics, inorganic ion pairs, and salts. Such properties are the consequence of Mn(II) behaving as a Lewis acid and the $\mathrm{O}\frown\mathrm{O}$ bite of the bidentate Schiff base ligand toward alkali cations. The starting compounds, which occur in a dimeric form, [Mn(acac-L-en)]$_2$ [$\mathrm{L}' = \mathrm{CH_2CH_2}$ (**1**); $\mathrm{L}'' = \mathrm{C_6H_{10}}$ (**2**); $\mathrm{L}''' = \mathrm{R,R\text{-}C_6H_{10}}$ (**3**)] have been synthesized either *via* a metathesis reaction from MnCl$_2$ or using [Mn$_3$Mes$_6$]. The reaction of **1**−**3** with lithium organometallics allowed the isolation of [Mn(acac-L-en)(R)Li(DME)] [R = Me, L = L′ (**4**); R = Ph, L = L′ (**5**); R = Mes, L = L′ (**6**); R = Me, L = L″ (**7**); R = Me, L = L‴ (**8**)] as metalated forms, where the alkyl or aryl group is σ-bonded to Mn(II), while the lithium cation is anchored to the Schiff base ligand. The metalated forms **4**−**8** react with PhCHO to give the corresponding lithium alkoxide, which remains bound in its ion-pair form to the [Mn(acacen)] skeleton in [Mn$_2$(acac-L′-en)$_2$Li$_2$(OCH(Ph)Me)$_2$]$_n$ (**9**). The use of **8**, which has a chiral bridge across two nitrogen atoms, did not lead to a significant asymmetric induction in the reaction with PhCHO, because of the long separation between the lithium cation and the stereogenic center. The metalated form **4** was able to transfer the methyl group to the nitrile function to give the corresponding lithium−imide which then remains bonded to [Mn(acacen)] as the ion pair in a dimeric structure, as revealed for [Mn$_2$(acac-L′-en)$_2$Li$_2$(DME){N═C(Ph)Me}$_2$]$_n$ (**10**). Their reaction with **1** appears to depend on the steric bulkiness of the alkyl group in NaOR, resulting in either monomeric adducts, i.e. in [Mn(acac-L′-en)(2,6-Bu$^t_2$C$_6$H$_3$O)Na(DME)$_2$] (**11**·2DME), or polymeric structures, like in [Mn(acac-L′-en)Na(DME)(μ-OEt)]$_n$ (**13**). All the dimeric units reported in this paper show a slight antiferromagnetic coupling between the two Mn(II) assisted by bridging alkoxo groups.

Introduction

The concept of a "carrier" has been largely developed in recent years for achieving the dissolution of salts in hydrocarbon solvents using crown-ether type compounds.[1] Although the carrier properties of transition metal complexes interacting with small molecules have also been addressed,[2] the idea of using carriers for polar organometallics and their reaction products is less familiar.[3] In the latter case the most synthetically valuable approach was the use of copper(I) salts for carrying lithium organometallics in the so-called cuprate methodology.[4] The use of homoleptic alkyl or aryl compounds converted into the corresponding metalated form[5] [MR$_n$Li$_m$] has been less successful for a number of technical reasons, including the waste of rather expensive M−C functionalities. A particularly interesting prospect is the idea of a carrier−catalyst, which would be particularly appealing in designing catalysts in a number of fields such as the metal-assisted alkylation using polar organometallics,[4] the metal-controlled aldol condensation reaction,[6] or the reduction using alkali hydrides.[7] The target carrier compound we have chosen is [Mn(acacen)] [acacen = *N,N′*-

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[*] To whom correspondence should be addressed.

[†] University of Lausanne.

[‡] University of Parma.

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acetylacetone iminato dianion) and its substituted derivatives. This choice has been determined by a number of factors:[8−11] (i) The bifunctional nature of a tetradentate Schiff base-metal complex is determined by the Lewis acidity of the unsaturated transition metal, as is the case for Mn, and the binding (basic) ability of the $O\frown O$ bite toward organic or inorganic cations. (ii) There is remarkable solubility of [Mn(acacen)] and their derivatives in aromatic hydrocarbons. (iii) The acacen ligand is easily modified into a chiral form.[11]

We report here the formation of ion-pair adducts between LiR and [Mn(acacen)] derivatives and their reactivity in Mn-assisted alkyl transfer reactions, including the formation of alkoxo polymetallic aggregates. Significant examples in a quite related field have been reported by Pecoraro in the use of metallacrowns complexing alkali salts.[1c,12] Some preliminary results in the reaction of LiR with [Mn(acacen)] have been communicated.[13]

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The synthesis of $[Mn_3Mes_6]\cdot$toluene has been performed as reported.[14] ^{1}H NMR, IR, UV−vis, and EPR spectra were recorded on 200-AC Bruker, Perkin-Elmer 883, Hewlett Packard 8452A, and Bruker ESP 300E instruments, respectively.

Synthesis of 1. NaH (3.27 g, 136 mmol) was slowly added (*ca.* 3 min) to an unstirred yellow THF (500 mL) solution of acacenH_2 (15.28 g, 68.20 mmol). Gas evolution was immediately observed with the concomitant formation of a white suspension. The mixture was stirred at room temperature until gas evolution stopped (*ca.* 10 min) and refluxed for 3 h, and then $[MnCl_2(thf)_{1.5}]_n$ (15.9 g, 68.0 mmol) was added. The resulting yellow suspension was refluxed overnight and then evaporated to dryness, and the residue was extracted with toluene (300 mL) to eliminate NaCl. The yellow crystalline solid was collected by filtration and dried *in vacuo* (70%). Recrystallization from toluene gave crystals suitable for X-ray analysis. Anal. Calcd for $C_{12}H_{18}MnN_2O_2$, **1**: C, 51.99; H, 6.54; N, 10.10. Found: C, 51.94; H, 6.39; N, 10.03. IR (Nujol, ν_{max}/cm^{-1}): 1603 (s), 1537 (s), 1507 (s), 1413 (s), 1393 (s), 1273 (m), 1251 (m), 1214 (m), 933 (m), 742 (m). MW (cryoscopy in benzene): Found 570; calcd 554.

Synthesis of 2. $[Mn_3Mes_6]\cdot$toluene[14] (2.33 g, 2.40 mmol) was added to a THF (250 mL) solution of acacyhH_2 (2.00 g, 7.19 mmol). After 10 min the orange solution changed to yellow and was then refluxed for 12 h and concentrated to $^1/_3$ of its volume; Et_2O (100 mL) was then added. The resulting yellow solid was collected by filtration and dried *in vacuo* (75%). Anal. Calcd for $C_{16}H_{24}MnN_2O_2$, **2**: C, 58.00; H, 7.30; N, 8.46. Found: C, 58.26; H, 7.40; N, 8.20. IR (Nujol, ν_{max}/cm^{-1}): 1580 (s), 1500 (s), 1401 (s), 1354 (m), 1254 (m), 1235 (m), 1139 (w), 1093 (w), 1067 (w), 1009 (m), 931 (m), 760 (m), 670 (w), 443 (w). MW (cryoscopy in benzene): Found 680; calcd 662.

Synthesis of 3. $[Mn_3Mes_6]\cdot$toluene[14] (8.21 g, 8.45 mmol) was added to a THF (300 mL) solution of acacyh(*R*,*R*)H_2 (7.00 g, 25.18 mmol). After 10 min the orange solution changed to yellow and was then refluxed for 12 h and concentrated to $^1/_3$ of its volume; Et_2O (100 mL) was then added. The resulting yellow solid was collected by filtration and dried *in vacuo* (84%). Anal. Calcd for $C_{16}H_{24}MnN_2O_2$, **3**: C, 58.00; H, 7.30; N, 8.46. Found: C, 58.52; H, 7.59; N, 8.21.

Synthesis of 4. A solution of MeLi in Et_2O (1.74 M, 36.10 mmol) was added dropwise to an orange suspension of **1** (10.01 g, 18.07 mmol) in DME (250 mL) at −40 °C. A red solution was obtained, which was stirred at room temperature for 12 h and then evaporated to dryness; Et_2O (150 mL) was then added. The orange product was collected and dried *in vacuo* (76%). Recrystallization from Et_2O/DME (3:2) gave crystals suitable for X-ray analysis. Anal. Calcd for **4**, $C_{17}H_{31}LiMnN_2O_4$: C, 52.45; H, 8.03; N, 7.20. Found: C, 52.52; H 8.15; N 7.27. IR (Nujol, ν_{max}/cm^{-1}): 1608 (s), 1531 (s), 1427 (s), 1224 (m), 1078 (s), 939 (m), 870 (m), 764 (m), 508 (m), 435 (m). $\mu = 5.85\ \mu_B$ at 295 K.

Synthesis of 5. A solution of PhLi in THF (0.34 M, 14.10 mmol) was added dropwise to an orange suspension of **1** (3.90 g, 7.04 mmol) in DME (200 mL) at −60 °C. A red solution was obtained, which was stirred at room temperature for 12 h; then the volume reduced *in vacuo* to 25 mL and Et_2O (150 mL) added. The orange product was collected and dried *in vacuo* (60%). Anal. Calcd for **5**, $C_{22}H_{33}LiMnN_2O_4$: C, 58.54; H, 7.37; N, 6.21. Found: C, 58.01; H, 7.45; N, 6.93. IR (Nujol, ν_{max}/cm^{-1}): 1601 (s), 1521 (s), 1423 (s), 1342 (w), 1269 (m), 1227 (m), 1193 (w), 1119 (w), 1081 (s), 1018 (w), 938 (m), 869 (m), 758 (m), 703 (m). $\mu = 5.83\ \mu_B$ at 295 K.

Synthesis of 6. A solution of MesLi in THF (0.12 M, 16.00 mmol) was added dropwise to an orange suspension of **1** (4.40 g, 7.94 mmol) in DME (150 mL) at −60 °C. The resulting orange solution was stirred at room temperature for 12 h; then the volume was reduced *in vacuo* to 25 mL and Et_2O (150 mL) added. The orange product was collected and dried *in vacuo* (69%). Recrystallization from Et_2O/DME (4:1) gave crystals suitable for X-ray analysis. Anal. Calcd for **6**, $C_{25}H_{39}LiMnN_2O_4$: C, 60.85; H, 7.97; N, 5.68. Found: C, 60.86; H, 8.01; N, 6.13. IR (Nujol, ν_{max}/cm^{-1}): 1601 (s), 1522 (s), 1422 (s), 1364 (m), 1341 (w), 1273 (w), 1225 (m), 1123 (m), 1084 (s), 1022 (m), 1004 (m), 939 (m), 874 (m), 838 (m), 760 (s). $\mu = 5.74\ \mu_B$ at 295 K.

Synthesis of 7. An ethereal solution of MeLi (0.68 M, 4.62 mmol) was added dropwise to an orange suspension of **2** (1.53 g, 4.60 mmol) in DME (150 mL) at −40 °C. The orange solution was stirred at room temperature for 12 h; then the resulting yellow suspension was concentrated to $^1/_3$ of its volume and Et_2O (200 mL) added. The yellow product was collected and dried *in vacuo* (88%). Anal. Calcd for **7**, $C_{21}H_{37}LiMnN_2O_4$: C, 56.88; H, 8.41; N, 6.32. Found: C, 56.33; H, 8.26; N, 6.82. IR (Nujol, ν_{max}/cm^{-1}): 1621 (s), 1603 (s), 1535 (s), 1414 (s), 1235 (m), 1221 (m), 1192 (w), 1120 (m), 1084 (s), 933 (m), 869 (m), 751 (m), 515 (m), 428 (m).

Synthesis of 8. A MeLi solution in Et_2O (0.47 M, 8.40 mmol) was added dropwise to an orange suspension of **3** (2.79 g, 8.40 mmol) in

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DME (200 mL) at −60 °C. The orange solution was stirred at room temperature for 12 h, and the resulting yellow suspension was then concentrated to $^1/_3$ of its volume and Et_2O (200 mL) added. The yellow product was collected and dried *in vacuo* (55%). Anal. Calcd for **8**, $C_{21}H_{37}LiMnN_2O_4$: C, 56.88; H, 8.41; N, 6.32. Found: C, 57.09; H, 8.05; N, 6.75.

Synthesis of 9. A toluene solution (100 mL) of **4** (1.58 g, 4.06 mmol) was cooled to −70 °C and then reacted with a toluene solution (50 mL) of PhCHO (0.41 mL, 4.06 mmol); the resulting yellow solution was stirred for 12 h at room temperature. The solvent was evaporated to dryness, the residue treated with *n*-hexane (100 mL), and the yellow solid collected and dried *in vacuo* (79%). Anal. Calcd for **9**, $C_{40}H_{54}Li_2Mn_2N_4O_6$: C, 59.27; H, 6.71; N, 6.91. Found: C, 58.65; H, 6.91; N, 7.18. IR (Nujol, ν_{max}/cm^{-1}): 1602 (s), 1518 (s), 1426 (s), 1410 (s), 1365 (m), 1339 (w), 1270 (w), 1225 (w), 1009 (m), 938 (m), 754 (m), 698 (w), 418 (m). A $CHCl_3$ solution (50 mL) of **9** (0.5 g, 0.6 mmol) was quenched with dilute HCl, and the organic phase was washed with water, dried (Na_2SO_4), and evaporated to dryness. Flash chromatography (*n*-hexane/EtOAc = 8/2) provided pure HOCH(CH_3)(Ph). The product was identified by NMR and GC-MS. ^{1}H NMR (CD_2Cl_2, 298 K) (*δ*, ppm): 7.42−7.30 (m, 5H); 4.92−4.89 (m, 1H); 2.34 (s, 1H); 1.52 (d, 3H).

Reaction of Complex 8 with PhCHO. A toluene suspension (100 mL) of **8** (1.8 g, 4.06 mmol) was cooled to −70 °C and then reacted with a toluene solution (50 mL) of PhCHO (0.41 mL, 4.06 mmol); the resulting yellow solution was analyzed by TLC (*n*-hexane/EtOAc = 8/2), at −70 °C, to control the alcohol formation. The mixture was stirred for 12 h at −70 °C and then quenched with dilute HCl. The organic phase was washed with water, dried (Na_2SO_4), and then evaporated to dryness. Flash chromatography (*n*-hexane/EtOAc = 8/2) provided the racemic mixture of HOCH(CH_3)(Ph). $[\alpha]_D^{25} = 0.007$.

Reaction of Complex 4 with 2-Phenylpropanal. To an orange toluene (150 mL) solution of **4** (2.28 g, 5.86 mmol) was added, in a dropwise manner and at −70 °C, a toluene (50 mL) solution of 2-phenylpropanal (0.78 mL, 5.86 mmol). The resulting yellow solution was stirred at −70 °C for 12 h. The mixture was quenched with dilute HCl, and the organic phase was washed with water, dried (Na_2SO_4), and then evaporated to dryness. Flash chromatography (*n*-hexane/EtOAc = 8/2) provided pure 3-phenyl-2-butanol. The product was identified by NMR, and the diastereomeric *ratio* is 88:13 (*anti*:*syn*). ^{1}H NMR ($CDCl_3$, 298 K) (*δ*, ppm): 7.44−7.28 (m, 5H); 3.93 (q, 1H); 2.78 (q, 1H); 2.64 (s, 1H); 1.44 (d, 3H); 1.17 (d, 3H). ^{13}C NMR ($CDCl_3$, 298 K) (*δ*, ppm): (Cram) 144.3, 128.1, 127.9, 126.3, 72, 47.1, 20.9, 16.3; (*anti*-Cram) 143.5, 127.6, 127.0, 125.2, 72, 47.4, 20.1, 17.2.

Reaction of Complex 4 with 2-Cyclohexen-1-one. To an orange toluene (100 mL) solution of **4** (1.90 g, 4.88 mmol) at −50 °C was added dropwise a toluene (100 mL) solution of freshly distilled 2-cyclohexen-1-one (0.47 mL, 4.88 mmol). The resulting yellow suspension was stirred at room temperature for 12 h. The solvent was evaporated to dryness, the residue treated with *n*-hexane (100 mL), and then the yellow solid collected and dried *in vacuo* (80%). Anal. Calcd for [Mn(acacen)CH_3Li(OPh)], $C_{19}H_{28}LiMnN_3O_3$: C, 57.87; H, 7.16; N, 7.10. Found: C, 58.78; H, 7.16; N, 7.20. IR (Nujol, ν_{max}/cm^{-1}): 1706 (s), 1599 (s), 1510 (s), 1410 (s), 1338 (m), 1270 (m), 1223 (m), 1093 (w), 1009 (m), 937 (m), 751 (w), 417 (m). A $CHCl_3$ solution (50 mL) of [Mn(acacen)CH_3Li(OPh)] (0.7 g, 1.71 mmol) was quenched with dilute HCl and the organic phase washed with water and dried (Na_2SO_4); GC-MS analysis shows the 3-methyl-2-cyclohexenone and the *β*-reductive dimerization product $(C_6H_{11}O)_2$ of 2-cyclohexen-1-one in the ratio 1:3.

Synthesis of 10. A toluene solution (100 mL) of **4** (1.81 g, 4.65 mmol) was cooled to −70 °C and then reacted with a toluene solution (50 mL) of freshly distilled PhCN (0.52 mL, 4.65 mmol). The resulting yellow suspension was stirred for 12 h at room temperature. The solvent was removed *in vacuo*, the residue treated with *n*-hexane (100 mL), and then the yellow solid collected and dried *in vacuo* (65%). Anal. Calcd for **10**, $C_{44}H_{62}Li_2Mn_2N_6O_6$: C, 59.06; H, 6.98; N, 9.39. Found: C, 59.09; H, 7.18; N, 10.1. IR (Nujol, ν_{max}/cm^{-1}): 1610 (s), 1518 (s), 1411 (s), 1365 (s), 1338 (m), 1270 (m), 1224 (m), 1010 (w), 938 (m), 758 (m), 464 (w), 417 (m). A $CHCl_3$ solution (50 mL) of **10** (1.1 g, 1.23 mmol) was quenched with dilute HCl, and the organic phase was washed with water, dried (Na_2SO_4), and evaporated to dryness. Flash chromatography (*n*-hexane/Et_2O = 6/4) provided pure CH_3COPh as determined by ^{1}H NMR and GC-MS. ^{1}H NMR (CD_2Cl_2, 298 K) (*δ*, ppm): 7.97−7.93 (m, 2H); 7.55−7.47 (m, 3H); 2.58 (s, 3H).

Synthesis of 11. 2,6-(Bu^t)$_2$PhONa (1.79 g, 7.84 mmol) was added at room temperature to a THF (250 mL) solution of **1** (2.13 g, 3.84 mmol). The resulting orange solution was stirred for 12 h; then the solvent was removed *in vacuo* and the residue treated with Et_2O (100 mL). The yellow solid was collected and dried *in vacuo* (73%). Recrystallization from DME gave crystals suitable for X-ray analysis. During the drying procedure the crystallization solvent was lost. Anal. Calcd for **11**, $C_{26}H_{39}MnN_4NaO_3$: C, 61.77; H, 7.78; N, 5.52. Found: C, 62.45; H, 7.98; N, 5.37. IR (Nujol, ν_{max}/cm^{-1}): 1620 (m), 1597 (m), 1528 (s), 1410 (s), 1306 (m), 1226 (w), 1096 (w), 1005 (w), 935 (w), 865 (w), 755 (m), 639 (w).

Synthesis of 12. MeONa (0.35 g, 6.48 mmol) was added at room temperature to a THF solution (200 mL) of **1** (1.77 g, 3.19 mmol). The resulting orange suspension was stirred for 12 h, and then the solvent was removed *in vacuo* and the residue treated with DME (100 mL). The yellow solid was collected and dried *in vacuo* (52%). Anal. Calcd for **12**, $C_{13}H_{21}MnN_2O_3$: C, 47.14; H, 6.39; N, 8.46. Found: C, 46.88; H, 6.45; N, 8.07. IR (Nujol, ν_{max}/cm^{-1}): 1591 (s), 1508 (s), 1429 (s), 1349 (s), 1272 (s), 1228 (m), 1042 (m), 935 (m), 752 (m), 563 (w).

Synthesis of 13. EtONa (0.38 g, 5.59 mmol) was added at room temperature to a THF solution (200 mL) of **1** (2.98 g, 5.38 mmol). The resulting orange suspension was stirred for 12 h, and then the solvent was removed *in vacuo* and the residue treated with DME (150 mL). The yellow solid was collected and dried *in vacuo* (84%). Recrystallization from DME gave crystals suitable for X-ray analysis. Anal. Calcd for **13**, $[C_{30}H_{51}Mn_2N_4NaO_7]_n$: C, 50.56; H, 7.21; N, 7.86. Found: C, 49.70; H, 7.19; N, 7.53. IR (Nujol, ν_{max}/cm^{-1}): 1594 (s), 1503 (s), 1418 (s), 1339 (m), 1271 (m), 1224 (m), 1100 (m), 1049 (w), 932 (w), 739 (m), 425 (m).

Magnetic Measurements. Magnetic susceptibility measurements were made on a with a MPMS5 SQUID susceptometer (Quantum Design Inc.) operating at a magnetic field strength of 3 kG. Corrections were applied for diamagnetism calculated from the Pascal constants. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_{Mn}T)^{1/2}$, where χ_{Mn} is the magnetic susceptibility per manganese atom. A detailed magnetic analysis was performed only on the dimeric compounds **1**, **9**, **10**, and **13**. Magnetic susceptibility data were collected in the temperature range 80−300 K, and the temperature dependence of the magnetic moments is typical of weakly coupled Mn(II) dimers. The effective magnetic moments observed at room temperature fall around 5.9 μ_B, as expected for weakly interacting Mn(II) centers. The data were fitted with the simple theoretical equation[15] obtained by the Heisenberg spin Hamiltonian $H_{ex} = -2J\hat{S}_1\hat{S}_2$, with $S_1 = S_2 = {}^5/_2$. A good fit to the collected data was obtained for the following: $g = 1.96$, $J = -0.72$ cm^{-1} (complex **1**); $g = 2.03$, $J = -6.5$ cm^{-1} (complex **9**); $g = 2.06$, $J = -3.5$ cm^{-1} (complex **10**); $g = 2.01$, $J = -8.1$ cm^{-1} (complex **13**).

X-ray Crystallography for Complexes 1, 4, 6, and 13. Suitable crystals were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[16] Crystal data and details associated with data collection are given in Tables 1 and S1 (Supporting Information). Intensity data were collected on a single-crystal diffractometer (Philips PW1100 for **1**, Enraf-Nonius CAD4 for **4**, Rigaku AFC6S for **6** and **13**) at 295 K for **1**, **4**, and **13** and at 143 K for **6**. For intensities and background, individual reflection profiles were analyzed.[17] The structure amplitudes were obtained after the usual Lorentz and polarization corrections,[18] and the absolute scale was established by the Wilson method.[19] The crystal quality was tested by

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Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes **1**, **4**, **6**, and **13**

	complex			
	1	**4**	**6**	**13**
formula	$C_{24}H_{36}Mn_2N_4O_4$	$C_{17}H_{31}LiMnN_2O_4$	$C_{25}H_{39}LiMnN_2O_4$	$C_{30}H_{51}Mn_2N_4NaO_7$
a, Å	8.606(3)	27.485(4)	11.004(5)	17.651(1)
b, Å	11.600(3)	11.785(3)	13.286(4)	12.546(1)
c, Å	7.390(3)	15.136(3)	9.883(2)	16.803(1)
α, deg	95.84(4)	90	103.50(2)	90
β, deg	114.00(4)	119.86(3)	95.08(3)	99.13(1)
γ, deg	90.70(4)	90	70.36(2)	90
V, Å^3	669.3(5)	4252(2)	1323.2(8)	3673.9(4)
Z	1	8	2	4
fw	554.4	389.3	493.5	712.6
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
t, °C	22	22	−130	22
λ, Å	0.710 69	0.710 69	1.541 78	1.541 78
ρ_{calc}, g cm^{-3}	1.376	1.216	1.239	1.288
μ, cm^{-1}	9.39	6.15	43.08	61.14
transm coeff	0.741−1.000	0.896−1.000	0.824−1.000	0.678−1.000
R^a	0.061	0.072	0.043	0.058
w$R2^a$	0.152	0.223	0.127	0.175

[a] $R = \sum|\Delta F|/\sum|F_o|$ calculated on the unique observed data. $wR2 = [\sum w|\Delta F^2|^2/\sum w|F_o^2|^2]^{1/2}$ calculated on the unique total data excluding those with $I \leq 0$.

ψ scans showing that crystal absorption effects could not be neglected. Data were then corrected for absorption using the program ABSORB[20] for **4** and a semiempirical method[21] for **1**, **6**, and **13**. Anomalous scattering corrections were included in all structure factor calculations.[22b] Scattering factors for neutral atoms were taken from ref 22a for non-hydrogen atoms and from ref 23 for H.

The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map[24] using the observed reflections [$F_o^2 > 2\sigma(F_o^2)$]. The function minimized during the least-squares refinements was $\sum w(\Delta F^2)^2$.[25] For complexes **4**, **6**, and **13** all the unique total data but those having $I \leq 0$ were considered in the refinement. In the last stage of refinement the weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ (with $P = (F_o^2 + 2F_c^2)/3$) was applied with a resulting in values of 0.1140, 0.1168, 0.0689, and 0.0865 for **1**, **4**, **6**, and **13**, respectively.

Refinement of all complexes was carried out first isotropically and then anisotropically for all the non-H atoms. The hydrogen atoms were located from difference maps for **1**, **4**, and **6** and put in geometrically calculated positions for **13**. They were introduced prior to the final refinements as fixed atom contributions with isotropic U's fixed at 0.08 Å^2 for **6**, 0.10 Å^2 for **1** and **13**, and 0.12 Å^2 for **4**. The final difference maps showed no peaks having chemical meaning above the general background.

Final atomic coordinates are listed in Tables S2−S5 for non-H atoms and in Tables S6−S9 for hydrogens. Thermal parameters are given in Tables S10−S13, and bond distances and angles in Tables S14−S17.[26]

Results and Discussion

The synthesis of the parent compound **1** has been performed *via* a metathesis reaction from the corresponding $MnCl_2$ under strictly anhydrous and anaerobic conditions according to Scheme 1 (pathway *a*). In the case of the ligand-modified complexes **2** and **3** we preferred the organometallic approach pathway *b*, leading to higher yield. This is particularly appropriate in the case of expensive and/or elaborate ligands.

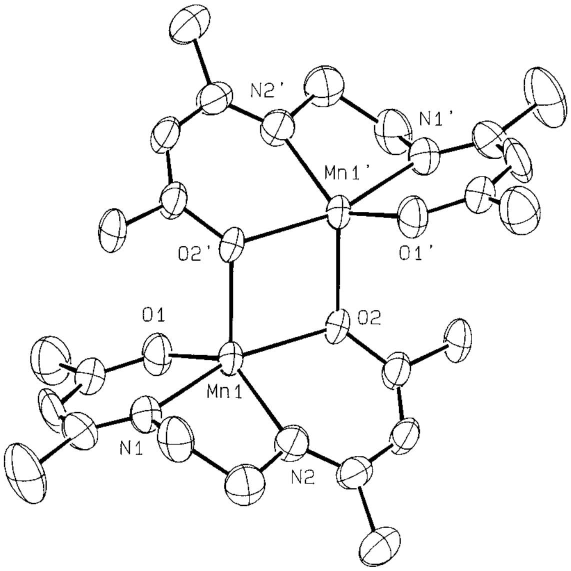
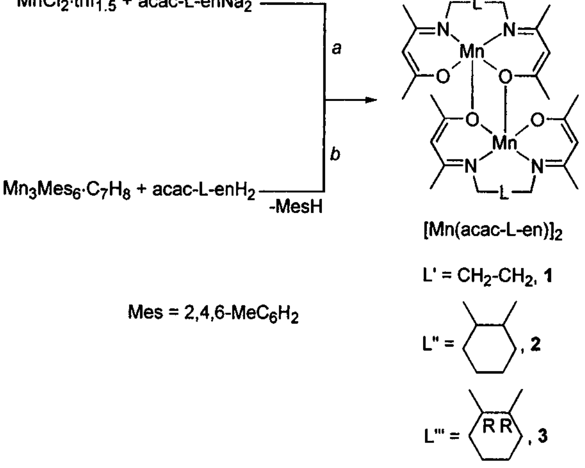


Figure 1. ORTEP drawing of complex **1** (50% probability ellipsoids). Prime denotes a transformation of $-x$, $-y$, $-z$.

Scheme 1



A molecular weight determination of **1** in benzene confirms the persistence of the dimeric form in solution (MW, found 570, theoretical 554). The magnetic measurements show a weak

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(26) See the paragraph at the end of the paper regarding the Supporting Information.

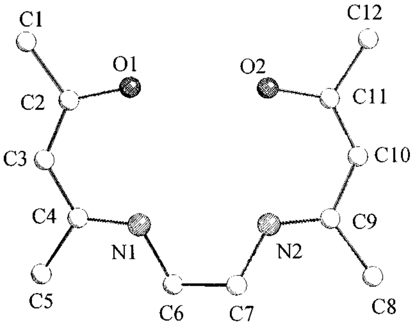

Figure 2. Labeling scheme adopted.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **1**[a]

Mn1−O1	2.050(5)	N1−C6	1.439(9)
Mn1−O2	2.139(5)	N2−C7	1.476(9)
Mn1−O2′	2.140(6)	N2−C9	1.314(10)
Mn1−N1	2.155(6)	C2−C3	1.391(10)
Mn1−N2	2.192(5)	C3−C4	1.404(11)
O1−C2	1.286(8)	C6−C7	1.530(13)
O2−C11	1.338(9)	C9−C10	1.438(10)
N1−C4	1.306(10)	C10−C11	1.341(8)
O2′−Mn1−N2	121.5(2)	Mn1′−O2−C11	125.5(4)
O2−Mn1−N1	160.7(2)	Mn1−O2−C11	125.6(4)
O1−Mn1−N2	137.9(2)	Mn1−N1−C6	109.0(5)
O1−Mn1−O2′	100.3(2)	Mn1−N1−C4	127.4(5)
O1−Mn1−O2	109.8(2)	C4−N1−C6	123.3(6)
N1−Mn1−N2	76.8(2)	Mn1−N2−C9	125.0(5)
Mn1−O1−C2	129.3(5)	Mn1−N2−C7	113.0(4)
Mn1−O2−Mn1′	100.8(2)	C7−N2−C9	118.6(6)

[a] Primes denote a transformation of −*x*, −*y*, −*z*.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **4**

Mn1−O1	2.162(6)	O3−C15	1.375(16)
Mn1−O2	2.144(6)	O4−C16	1.357(13)
Mn1−N1	2.182(9)	O4−C17	1.357(19)
Mn1−N2	2.187(7)	N1−C4	1.274(17)
Mn1−C13	2.173(10)	N1−C6	1.483(12)
Li1−O1	1.883(16)	N2−C7	1.445(14)
Li1−O2	1.866(17)	N2−C9	1.279(13)
Li1−O3	2.002(15)	C2−C3	1.356(14)
Li1−O4	2.027(19)	C3−C4	1.432(13)
O1−C2	1.297(13)	C6−C7	1.39(2)
O2−C11	1.299(11)	C9−C10	1.438(12)
O3−C14	1.39(2)	C10−C11	1.337(11)
N1−Mn1−N2	75.6(3)	Mn1−O2−Li1	93.4(5)
O2−Mn1−N2	83.6(3)	Li1−O2−C11	138.0(7)
O2−Mn1−N1	132.8(3)	Mn1−O2−C11	126.9(5)
O1−Mn1−N2	129.9(3)	Mn1−N1−C6	106.1(7)
O1−Mn1−N1	83.9(3)	Mn1−N1−C4	130.5(8)
O1−Mn1−O2	77.9(2)	C4−N1−C6	123.1(10)
Mn1−O1−Li1	92.4(5)	Mn1−N2−C9	129.5(6)
Li1−O1−C2	137.8(7)	Mn1−N2−C7	112.5(7)
Mn1−O1−C2	127.0(5)	C7−N2−C9	116.9(9)

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex **6**

Mn1−O1	2.155(2)	O3−C32	1.423(4)
Mn1−O2	2.174(2)	O4−C33	1.427(5)
Mn1−N1	2.184(2)	O4−C34	1.446(6)
Mn1−N2	2.221(2)	N1−C4	1.294(4)
Mn1−C21	2.180(4)	N1−C6	1.463(4)
Li1−O1	1.884(5)	N2−C7	1.464(3)
Li1−O2	1.894(6)	N2−C9	1.303(4)
Li1−O3	2.002(7)	C2−C3	1.370(3)
Li1−O4	1.952(6)	C3−C4	1.451(4)
O1−C2	1.298(4)	C6−C7	1.523(5)
O2−C11	1.302(4)	C9−C10	1.438(4)
O3−C31	1.424(6)	C10−C11	1.362(4)
N1−Mn1−N2	75.8(1)	Mn1−O2−Li1	92.2(2)
O2−Mn1−N2	83.3(1)	Li1−O2−C11	140.0(3)
O2−Mn1−N1	136.3(1)	Mn1−O2−C11	126.2(2)
O1−Mn1−N2	123.8(1)	Mn1−N1−C6	106.0(2)
O1−Mn1−N1	82.6(1)	Mn1−N1−C4	131.7(2)
O1−Mn1−O2	77.8(1)	C4−N1−C6	122.4(3)
Mn1−O1−Li1	93.1(2)	Mn1−N2−C9	127.5(2)
Li1−O1−C2	139.3(3)	Mn1−N2−C7	113.2(2)
Mn1−O1−C2	127.6(2)	C7−N2−C9	118.4(3)

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex **13**[a]

	mol. A	mol. B		
Mn1−O1	2.091(5)	2.097(6)	Na1−O1A	2.322(6)
Mn1−O2	2.110(5)	2.098(3)	Na1−O2A	2.337(5)
Mn1−O3	2.030(5)	2.032(5)	Na1−O1B′	2.277(6)
Mn1−N1	2.170(6)	2.161(5)	Na1−O2B′	2.400(5)
Mn1−N2	2.161(6)	2.187(6)	Na1−O4	2.517(7)
O1−C2	1.295(10)	1.278(9)		
O2−C11	1.311(9)	1.281(8)		
N1−C4	1.314(11)	1.284(9)		
N1−C6	1.462(9)	1.465(11)		
N2−C7	1.436(9)	1.446(10)		
N2−C9	1.307(10)	1.287(9)		
C2−C3	1.356(12)	1.358(12)		
C3−C4	1.408(11)	1.447(13)		
C6−C7	1.501(12)	1.474(12)		
C9−C10	1.430(10)	1.419(11)		
C10−C11	1.344(11)	1.379(11)		

	mol. A	mol. B		mol. A	mol. B
N1−Mn1−N2	77.3(2)	77.3(2)	Na1−O1−C2	124.4(4)	127.5(5)
O3−Mn1−N2	104.3(2)	116.1(2)	Mn1−O1−C2	125.7(5)	128.7(4)
O3−Mn1−N1	116.5(2)	106.0(2)	Mn1−O2−Na1	95.5(2)	
O2−Mn1−N2	84.0(2)	85.3(2)	Na1−O2−C11	131.7(4)	
O2−Mn1−N1	131.8(2)	146.3(2)	Mn1−O2−C11	125.9(4)	
O2−Mn1−O3	111.1(1)	107.6(2)	Mn1−N1−C6	113.5(4)	106.0(4)
O1−Mn1−N2	145.3(2)	134.0(2)	Mn1−N1−C4	126.1(5)	130.2(5)
O1−Mn1−N1	84.9(2)	84.1(2)	C4−N1−C6	120.1(6)	123.5(6)
O1−Mn1−O3	110.3(2)	109.3(2)	Mn1−N2−C9	128.6(4)	126.9(5)
O1−Mn1−O2	86.0(2)	87.7(2)	Mn1−N2−C7	107.4(4)	112.6(5)
Mn1−O1−Na1	96.5(2)		C7−N2−C9	123.4(6)	120.3(6)
Mn1A−O3-Mn1B	125.5(2)				

[a] Primes denote a transformation of *x*, 0.5 − *y*, 0.5 + *z*.

antiferromagnetic coupling between the two Mn(II) due to the sharing of the oxygens from the acacen ligand [$g = 1.96$; $J = -0.72$ cm^{-1}]. The structure of the centrosymmetric dimer **1** is shown in Figure 1. The labeling scheme adopted is given in Figure 2.

Selected bond distances and angles are listed in Tables 2−5 for complexes **1**, **4**, **6**, and **13**, respectively. In Table 6 the most relevant conformational parameters for the four complexes are compared. The planarity of the N_2O_2 core in complex **1** is completely lost (Table 6), and the coordination polyhedron could be better described as a trigonal bipyramid with the O1, N2, and O2′ atoms defining the equatorial plane and the N1 and O2 atoms occupying the apices (′ = −*x*, −*y*, −*z*). The Mn_2O_2 inner fragment is square planar for symmetry requirements; the two bridging Mn−O2 distances are not significantly different from each other [Mn−O2, 2.139(5), Mn−O2′, 2.140(6) Å]. They are significantly longer than the Mn1−O1 bond distance [2.050(5) Å] not involved in dimerization. Small but significant lengthening is also observed for the Mn−N2 and O2−C11 bond distances with respect to Mn−N1 and O1−C2 (Table 2). The Mn···Mn separation is 3.296(2) Å. The [Mn(acacen)] unit exhibits an *umbrella* conformation.[27] As a consequence of dimerization, the conformations of the two six-membered

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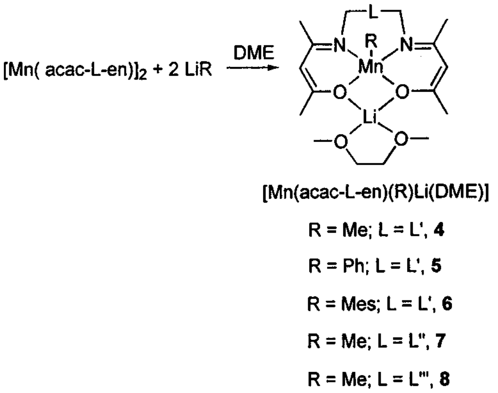
Table 6. Comparison of Relevant Structural Parameters within the Mn(acacen) Units for Complexes **1**, **4**, **6**, and **13**

				13	
	1	**4**	**6**	mol. A	mol. B
dist of atoms from the N_2O_2 core (Å)					
O1	0.207(5)	0.019(6)	0.111(3)	0.113(5)	0.094(5)
O2	−0.211(5)	−0.019(6)	−0.109(3)	−0.066(4)	−0.082(5)
N1	−0.401(6)	−0.038(9)	−0.111(3)	−0.160(6)	−0.116(5)
N2	0.406(6)	0.035(8)	0.109(3)	0.137(6)	0.143(6)
Mn1	−0.390(2)	−0.893(2)	−0.920(2)	0.756(1)	−0.709(1)
folding[a] along the N1··O1 line (deg)	1.7(3)	9.6(3)	14.4(1)	20.3(2)	13.8(3)
folding along the N2··O2 line (deg)	22.5(2)	12.7(3)	18.2(1)	19.7(2)	12.2(2)
angle between the Mn1−N1−O1 and Mn1−N2−O2 planes (deg)	38.4(2)	67.1(3)	69.2(1)	57.5(2)	55.0(2)
angle between the mean OC_3N planes (deg)	57.0(3)	45.0(3)	37.2(1)	19.8(2)	29.7(3)
torsion angle N1−C6−C7−N2 (deg)	48.3(8)	28.3(16)	44.2(4)	−43.9(8)	40.2(9)
dist of atoms from the Mn1−N1−N2 plane (Å)					
C6	0.730(9)	0.786(14)	0.859(4)	0.198(8)	0.776(9)
C7	0.130(9)	0.482(13)	0.326(4)	0.717(7)	0.316(9)

[a] The folding is defined as the dihedral angle between the Mn,N,O and OC_3N planes of a six-membered chelation ring.

Scheme 2



chelation rings are different: The O1,C2,C3,C4,N1,Mn ring is nearly planar [Mn is displaced by 0.047(2) Å from the plane through the other five atoms], while the O2,C11,C10,C9,N2 ring is folded along the N···O line, the metal being displaced by 0.612(2) Å from the mean OC_3N plane. The five-membered chelate ring is asymmetrically folded with respect to the N···N line with the C6 and C7 carbons upward on the same side (Table 6). The trend of the C−C and C−N bond distances (Table 6) indicates a π delocalization within the O1···N1 ring and significant double bond localization on the C10−C11 bond [1.341(8) Å] within the O2···N2 ring in agreement with the observed lengthening of the O2−C11 bond distances and the almost single-bond character of the C9−C10 bond distance [1.438(10) Å].

Despite the dimeric form, complexes **1**−**3** behave as monomers in their reactions with ion-pair species. The first class of reactions we explored involved the lithium−organometallics and is outlined in Scheme 2.

A suspension of **1** in DME dissolves upon addition of LiR giving a solution which contains the adducts **4**, **5**, and **6**, while **2** and **3** give **7** and **8**. All of them have been isolated in good yield as crystalline solids. The nature of **4**−**8** has been clarified, in addition to the conventional analysis, by an X-ray structure determination on **4** and **6**. Before discussing the structural features of such adducts, we should stress the peculiarities of the reactions in Scheme 2, which represent a straightforward entry into Mn(II)−carbon bond chemistry.[28] Although Mn(II) homoleptic alkyls or aryls exist, they usually have a limited stability and very high reactivity.[14,28,29] They have been isolated in a rather stable form as metalated derivatives $[MnR_n]^{(n-2)-}$, which has never been identified in the ion-pair form.[10] The Mn(II)−alkyls in their neutral or metalated form have found application as alkylating agents in a variety of reactions, but they normally deliver a single alkyl group, though they consume two or more LiR for their synthesis. Complexes **4**−**8** have the appropriate form for delivering a single alkyl group, with the minimum consumption of the expensive lithium organometallics. In such a way, complexes **1**−**3** can function as carrier catalysts in metal-assisted reactions of LiR with substrates. A structural peculiarity of **4**−**8** is the rather close geometrical relationship between the cation Li^+ and the anion (R^-) of the starting ion pair, both having an important role in bifunctional systems. Such a distance can be tuned by varying the metal−Schiff base fragment. In the case of **4**−**8** the structural parameters concerning the bifunctional unit can be obtained from the X-ray analysis of **4** and **6**, whose structure has been briefly reported in the preliminary communication[13] (see Figures 3 and 4, respectively).

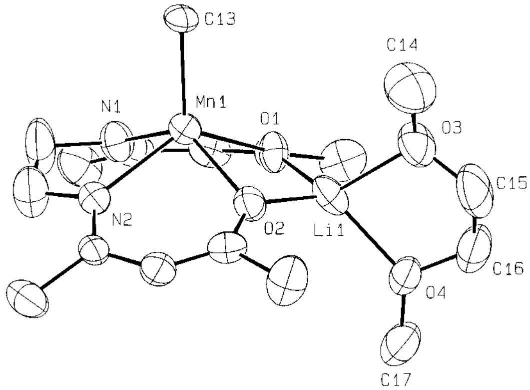


Figure 3. ORTEP drawing of complex **4** (30% probability ellipsoids).

The structure consists of dinuclear neutral molecules of [Mn(R)(acacen)Li(DME)] (R = Me, Mes), where a $\{Mn(R)(acacen)\}^-$ anion acts as a bidentate oxygen-donor ligand toward a $Li(DME)^+$ cation. The coordination polyhedron around the manganese atom is square pyramidal with the metal displaced by 0.893(2), **4**, and 0.920(2) Å, **6**, from the N_2O_2 mean plane toward the apical carbon atom. This results in an umbrella conformation of the [Mn(acacen)] moiety which is clearly

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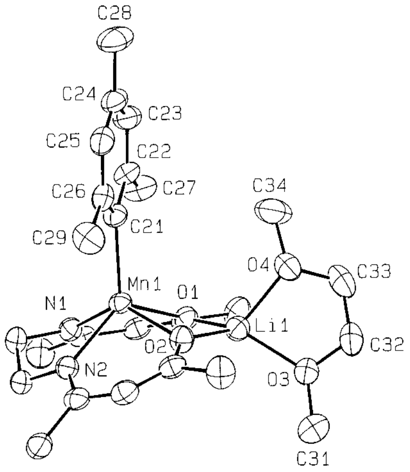


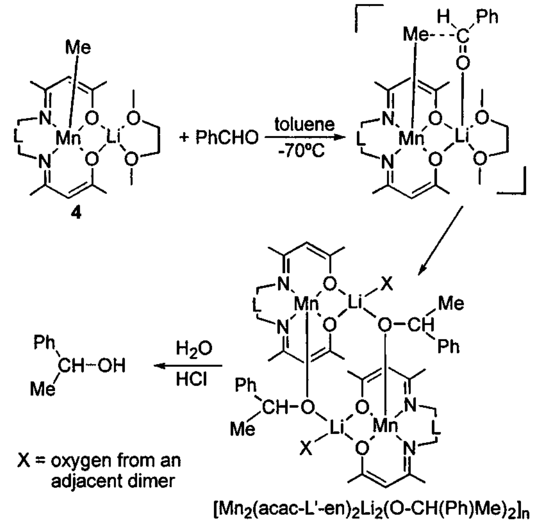
Figure 4. ORTEP drawing of complex **6** (60% probability ellipsoids).

indicated by the dihedral angle between the two O−Mn−N planes (Table 6). The N_2O_2 core shows small tetrahedral distortions ranging from −0.038(9) to 0.035(8) Å. The direction of the Mn1−C13 bond and Mn−C21 form angles of 1.8(2)°, **4**, and 8.5(1)°, **6**, with respect to the normal to the coordination plane. The six-membered chelate rings are folded along the N···O lines, the metal being displaced by 0.278(2), 0.366(1) Å, **4**, and 0.407(2), 0.515(1) Å, **6**, from the mean planes through O1,C2,C3,C4,N1 and N2,C9,C10,C11,O2, respectively. The five-membered chelate ring is asymmetrically folded with respect to the N···N line with the C6 and C7 carbons upward on the same side as a consequence of the downward folding of the six-membered chelate ring. The O···O bite of the Schiff base and the O1−Mn1−O2 angle [77.9(2)°, **4**, and 77.8(1) Å, **6**] are strongly affected by the binding to the alkali cation [109.8(2) Å in **1**]. The *umbrella* conformation of the [Mn(acacen)] moiety, which is almost typical for five-coordinated Schiff base metal complexes, is similar to that observed in *e.g.* [Ti(acacen)(Mes)],[30] though the distance of the metal atom from the N_2O_2 core is remarkably longer (Table 6) than the values observed in other acacen organometallic derivatives [*e.g.* 0.499(4) and 0.421(1) Å in [Ti(acacen)(Mes)] and [V(acacen)(Ph)],[30] respectively]. The Mn−C bond distances [Mn−C13, 2.173(10), in **4**; Mn−C21, 2.180(4) Å, in **6**] are remarkably longer than the unique value found in the literature for five-coordinated Mn complexes [2.046 Å for bis(2-((dimethylamino)methyl)phenyl)methylmanganese].[31] The other structural parameters do not deserve any special comment except the Mn−O distances, which are longer (Tables 3 and 4) than the unbridged ones in **1** and are attributed to the interaction with the lithium cation.

The reaction of alkylating agents with transition metal Schiff base complexes led usually to (i) the alkylation of the metal *via* metathesis of a metal−halogen bond (see cobalt(III)−alkyl chemistry based on macrocycles),[27,32] (ii) the reduction of the metal (*vide infra*), and (iii) the alkylation of the imino carbons in the case of electrophilic metals.[33]

In the present case we report the binding of the alkylating agent in its intact form to the metal−Schiff base moiety. Note that in the case of [Mn(acac-L-en)] derivatives, as is true in many other cases, the highest oxidation state compatible with the alkyl or aryl groups at the metal is +2. When we tried, as in cobalt(III) chemistry,[32] to carry out the alkylation of [Mn(acac-L-en)](Cl)] [L = CH_2CH_2], the ultimate result was the reduction of Mn(III) to Mn(II), independent of the alkylating agent.[34]

Scheme 3



9

The reactivity of the alkylated forms **4**−**8** has been explored using **4** as a model compound and PhCHO as a model substrate (see Scheme 3).

In Scheme 3 we propose a preliminary coordination of PhCHO to the lithium cation, followed by the intramolecular transfer of the methyl from Mn to the carbonyl group. The resulting alkoxo derivative rearranges to a dimeric structure. The suggested dimeric form of the resulting alkoxo derivative is supported by the structural results on the alkoxo−Mn(acacen) derivatives obtained from a direct synthesis (see the following section). Further support for the dimeric structure of **9** comes from its magnetic properties, which are typical for an alkoxo-bridged Mn(II) dimer [$g = 2.03$, $J = -6.5$ cm^{-1}].

The key role of Li^+ in binding benzaldehyde in the preliminary stage (Scheme 3) is indirectly supported by observing that the reaction rate decreases by a factor of 6:1 when carried out in the presence of 12-crown-4, which saturates the coordination environment of the lithium cation. The use of **7** in the reaction with PhCHO showed that an increase in the steric hindrance around Mn ensured by the cyclohexenyl substituent does not affect the rate of the reaction, supporting the hypothesis that the Li cation is essentially involved in the preliminary activation of the carbonyl group. The rather poor asymmetric induction in the reaction of **8** with benzaldehyde (Scheme 4) is a consequence of the rather long separation between the

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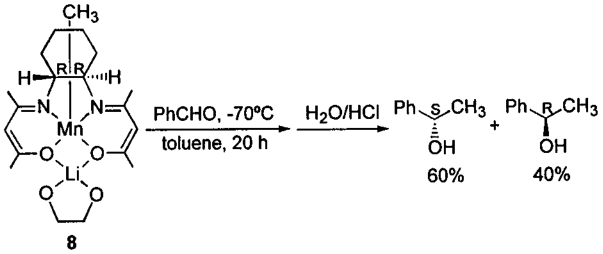
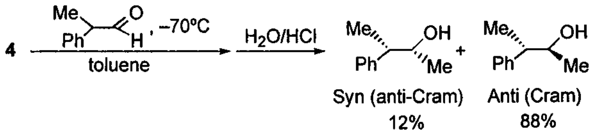
Scheme 4

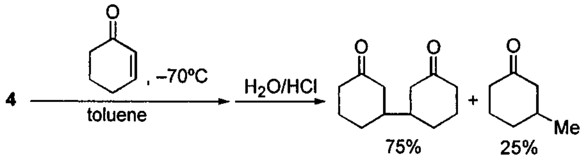


8

Scheme 5



Scheme 6



stereogenic and the reactive centers. An appropriate strategy would force the stereogenic centers closer to lithium cation.

We examined if our model complex **4** would cause any diastereoselection in its reaction with an aldehyde having a stereocenter in the α-position[35] and found that the the predominant compound is the *anti*-diastereoisomer (88%) as expected from the Cram rule. The reaction of **4** with 2-cyclohexen-1-one gave the results shown in Scheme 6.

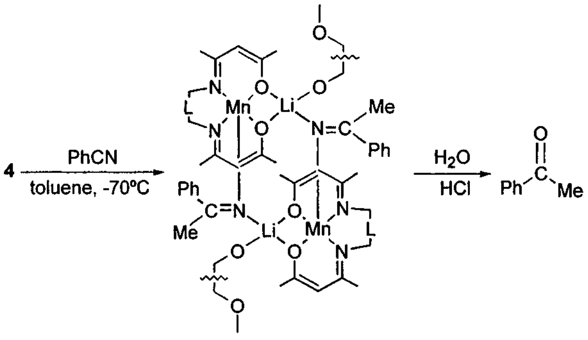
This reaction allows us to compare the same substrate using either a typical cuprate or a Mn(II)−organometallic derivative. In the former case the 1,4-addition is almost exclusively observed,[36] while in the latter the result of the reaction depends on the form of the Mn(II)−organometallic derivative [RMnX (1,2-addition),[37] R_2Mn (1,4-addition),[38] R_3MnLi (β-reductive dimerization)].[39] In the present case, **4** drives the reaction, as expected, by behaving essentially as a metalated form.

The Mn-assisted alkylation has been extended to functionalities other than the carbonylic one, and this is exemplified by the reaction of **4** with PhCN in Scheme 7.

The reaction led to a Mn−Li imido dimer, where the Li−imido is complexed in its ion-pair form. The dimeric complexity of **10** is essentially supported by its magnetic properties [$g = 2.06$, $J = -3.5$ cm^{-1}] and by analogy with the structure of the corresponding alkoxo derivatives, which are shown in Scheme 7 as polymers of dimeric nonmagnetically interacting units. The alkylation of PhCN was then proved by hydrolyzing **10** to give, quantitatively, acetophenone.

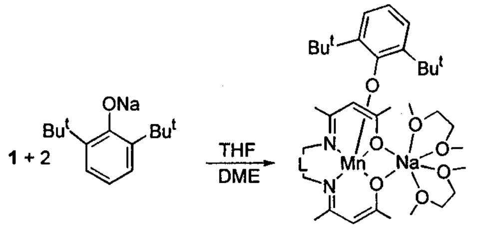
[Mn(acacen)]$_2$-Carrying Alkali-Metal Alkoxides: Toward the Synthesis of Polynuclear Mn(II) Complexes. As in the case of polar organometallics, alkali-metal alkoxides are carried in their ion-pair separated forms by **1** (Scheme 8).

Scheme 7



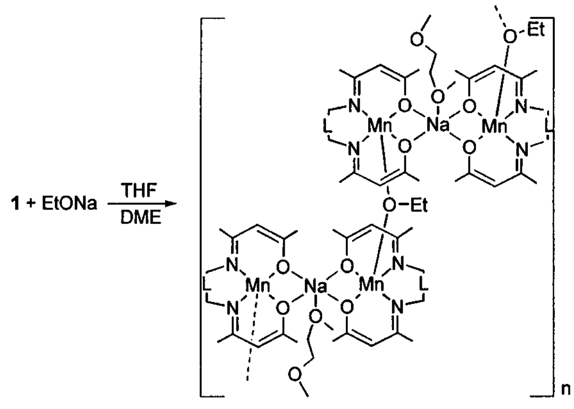
$[Mn_2(acac\text{-}L'\text{-}en)_2Li_2(DME)\{N{=}C(Ph)Me\}_2]_n$
10

Scheme 8



$[Mn(acac\text{-}L'\text{-}en)(2,6\text{-}Bu^t{}_2C_6H_3O)Na(DME)_2]$
11·2DME

Scheme 9



$[Mn_2(acac\text{-}L'\text{-}en)Na(DME)(\mu\text{-}OEt)]_n$
13

The choice of an *o*-sterically hindered phenolate was made in order to isolate a mononuclear species like **11**·2DME. The structure of complex **11**·2DME has been confirmed by an X-ray analysis, which is not included in the present paper.[40] Unlike the alkyl group, which usually displays a terminal bonding mode, the alkoxo anion can function as a bridging ligand, where sterically permitted. Therefore the reaction in Scheme 8 can be applied for assembling Mn(II) in polynuclear polymeric structures taking advantage of the bonding properties of [Mn(acac-L_1-en)]$_2$ (Scheme 9).

As revealed by an X-ray analysis, the aggregate **13** is, in fact, the polymeric form of a dimeric unit. The related magnetic properties are those of a dimer where the two Mn(II) are connected by an alkoxo group [$g = 2.01$, $J = -8.1$ cm^{-1}], with the polymerization being achieved by sharing the sodium cation. The repeating unit of **13** is shown pictorially in Figure 5.

The structure of **13** consists of $[\{Mn(acacen\}_2(\mu\text{-}OEt)]^-$ dimeric anions and $[Na(DME)]^+$ cations linked in *zigzag* infinite polymeric chains running parallel to the crystallographic [010] axis (Figure 5). The dimer takes origin from the presence of

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(40) Due to the absence of any peculiar structural interest, this structure is not reported.

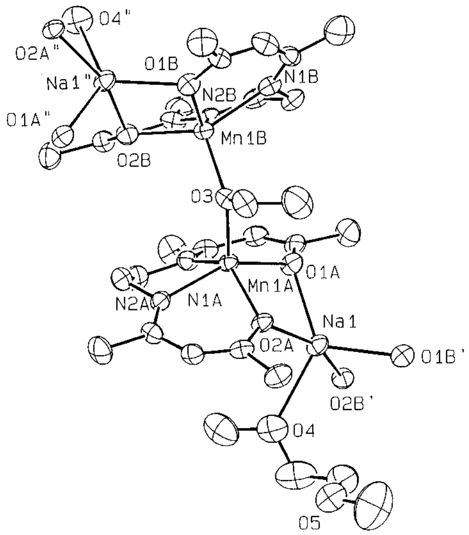

Figure 5. ORTEP drawing of complex **13** (30% probability ellipsoids). Prime and double prime denote transformations of x, $0.5 - y$, $0.5 + z$ and x, $0.5 - y$, $-0.5 + z$, respectively.

an ethoxide anion bridging two independent [Mn(acacen)] units through the O3 oxygen atom. The alkali metals are anchored to the oxygen atoms of dimers related by the screw axis giving rise to the chains. Coordination around the sodium cation is completed to distorted trigonal bipyramidal by an oxygen atom of a DME molecule acting as a monodentate ligand. In each dimer the two independent manganese atoms show square pyramidal coordination involving the donor atoms of the acacen ligand in the base and the O3 oxygen atom at the apex, so that the two coordination polyhedra share a vertex. The Mn−O3 lines form dihedral angles of 2.9(2) and 3.2(1)° with the normal to the mean N_2O_2 planes of moieties A and B, respectively. The N_2O_2 core shows significant tetrahedral distortions, the manganese cations being remarkably displaced toward the ethoxy oxygen (Table 6). The six-membered chelate rings are folded along the N···O lines, the metal being displaced by 0.554(1) [0.709(1)] and 0.541(1) [0.379(1)] Å from the mean planes through O1,C2,C3,C4,N1 and N2,C9,C10,C11,O2, respectively. Values in brackets refer to molecule B. The five membered chelate ring is asymmetrically folded with respect to the N···N line with the C6 and C7 carbons upward on the same side as a consequence of the downward folding of the six-membered chelaten ring. The [Mn(acacen)] units show the *umbrella* conformation. The Mn−O bond distances involving the oxygen atoms of the Schiff bases are not significantly different from each other (Table 5) and are significantly shorter than those observed in **4** and **6**. The Mn−O3 bond distances are close to the value of 2.050(5) Å found in **1** for the Mn−O1 distance.

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Supporting Information Available: Tables giving crystal data and details of the structure determination, positional and thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (18 pages). Ordering information is given on any current masthead page.

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