Synthesis and Structural Characterization of Monomeric Manganese(II) *N*-Heterocyclic Carbene Complexes $[MnX_2(C\{N(iPr)C(Me)\}_2)_2]$ (X = Cl, I, and MeCOO)

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Reaction of $MnCl_2(THF)_{1.5}$, MnI_2, or $Mn(MeCOO)_2$ with two equivalents of *N*-heterocyclic carbene $[C(Me)N(iPr)]_2C$ (**1**) in THF at room temperature readily afforded the corresponding carbene adducts $[MnX_2(C\{N(iPr)C(Me)\}_2)_2]$ [X = Cl (**2**); X = I (**3**); X = MeCOO (**4**)] in good yield. Solid-state structural analysis of complexes **2**–**4** reveals that all complexes are monomeric. In complexes **2** and **3** the central manganese atoms are four coordinate and have a distorted tetrahedral geometry. The manganese atom in compound **4** has a coordination number of six and resides in a highly distorted octahedral geometry. The *N*-heterocyclic carbene ligands in these complexes are coordinated differently to the central metal atoms.

Introduction

The first carbenes were isolated in the late 1980s and early 1990s,[1] and since then there has been a revival of interest in carbene ligands,[2] which are formally neutral, two-electron donors. A major portion of the work has focused on *N*-heterocyclic carbenes due to their easy preparation and good thermal stability, which have been used to prepare a variety of main-group, transition metal, and lanthanide complexes.[2a,2c] A significant number of these complexes, especially the late transition metal complexes, have been shown to be effective catalysts in a number of organic reactions, such as hydrosilylation,[3] hydrogenation and hydroformylation of olefins or copolymerization of ethylene and CO.[2,4] In addition, palladium *N*-heterocyclic carbene complexes have been successfully applied in various C−C bond forming syntheses, in particular the Heck, Suzuki, and Kumada reactions.[2,5] Recently, iron(II) halides possessing *N*-heterocyclic carbenes of composition FeX_2L_2 [X = Cl, Br; L = $C\{N(iPr)C(Me)\}_2$] were found to be remarkably active and efficient catalysts for atom-transfer radical polymerization.[6]

Manganese(II) complexes bearing tertiary phosphane ligands have been extensively studied.[7] It seems that chelating bidentate phosphane ligands are necessary to prepare monomeric manganese dihalide adducts such as dmpe and diphos. The isolation of $[MnX_2(PPh_3)_2]$ has been questioned and it is likely that the complexes are $[MnX_2(OPPh_3)_2]$ instead.[8] Until now, only one monomeric manganese(II) dihalide with a nonchelating phosphane ligand of composition $[MnI_2(PEt_3)_2]$ has been unambiguously characterized.[8] *N*-Heterocyclic carbenes are considered to be analogues of tertiary phosphanes,[9] although they are stronger σ-donor ligands and therefore, in general, form more stable bonds to metals. Compared with tertiary phosphane ligands, *N*-heterocyclic carbene ligands have better thermal stability and oxidation resistance and a mobile steric effect upon changing the substituents at the nitrogen atoms.[2b] However, manganese *N*-heterocyclic carbene complexes are rare and have not attracted much attention to date.[2a] To the best of our knowledge, only a few manganese *N*-heterocyclic carbene complexes are known including $[Mn(MeC_5H_4)(CO)_2(C\{N(Me)CH_2\}_2)]$,[10] $[MnBr(CO)_3(C\{N(Me)CH_2\}_2)]$,[10] and $[Mn(CO)_5C\{N(BH_3)C(Me)C(Me)N(Me)\}]$[11] with a formal oxidation state of +1 at the manganese. Therefore, we became interested in the synthesis and structures of *N*-heterocyclic carbene complexes containing manganese(II). Recently, we reported the first structurally characterized manganese *N*-heterocyclic carbene complex of composition $[Mn(NHAr)\{HC(CMeNAr)_2\}(C\{N(iPr)C(Me)\}_2)]$ (Ar = 2,6-$iPr_2C_6H_3$), which shows that the Mn−C(carbene) bond length (2.27 Å) is in the range of an Mn−C single bond and that Mn→C(carbene) back-bonding is negligible.[12] For a better understanding of manganese *N*-heterocyclic carbene complexes and for comparison of *N*-heterocyclic carbenes with

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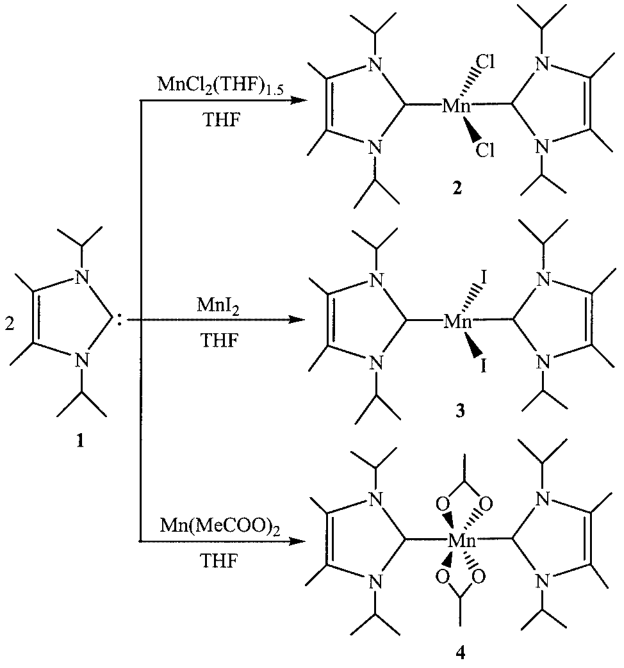
tertiary phosphane ligands, we describe herein the synthesis and structural characterization of several monomeric adducts of manganese(II) halides and acetate with *N*-heterocyclic carbenes $[MnX_2(C\{N(iPr)C(Me)\}_2)_2]$ [X = Cl (**2**); X = I (**3**); X = MeCOO (**4**)].

Results and Discussion

Synthesis of Compounds 2−4

The isolation of free stable *N*-heterocyclic carbenes enables the easy synthesis of a variety of carbene adducts that were previously inaccessible.[13] The reaction of $[MnCl_2(THF)_{1.5}]$, MnI_2, or $Mn(MeCOO)_2$ with two equivalents of $[C(Me)N(iPr)]_2C$ (**1**) in THF at room temperature readily afforded the corresponding carbene adducts in good yield (91% **2**, 77% **3**, and 81% **4**; Scheme 1). Compounds **2** and **4** are colorless solids and compound **3** is a light-orange solid. Compounds **2** and **3** are moderately air sensitive and can even be exposed to air for a short period of time when in the solid state, while compound **4** is much more sensitive to air. Compounds **2**−**4** are poorly soluble in non-polar solvents, although they are readily soluble in solvents such as CH_2Cl_2 and MeCN. Compound **4** has also a good solubility in THF, but **2** and **3** are sparingly soluble in THF. Complexes **2**−**4** have been characterized by mass spectrometry, IR spectroscopy, X-band EPR spectroscopy, microanalysis and single crystal X-ray structural analysis. The EI mass spectra of these compounds are similar: the molecular ion peak is not observed, but free carbene appears as the most intense signal at $m/z = 180$ (100%), which indicates the cleavage of the Mn−C(carbene) bond in these compounds under the experimental conditions. This is consistent with the results reported in the literature.[14] The IR spectrum of **4** displays two prominent vibrations for the O−C−O part of the acetate group ν_{as} (1599 cm^{-1}) and ν_s (1406 cm^{-1}). The absorption at about 1600 cm^{-1} is broad.



Scheme 1

X-ray Diffraction Analyses for Complexes 2−4

Compounds **2** and **3** are the first structurally characterized manganese halides possessing *N*-heterocyclic carbene ligands. Single crystals of **2** and **3** suitable for X-ray structural analysis were obtained by recrystallization from THF solutions at 4 °C. The molecular structures of **2** and **3** are shown in Figures 1 and 2, respectively; selected bond

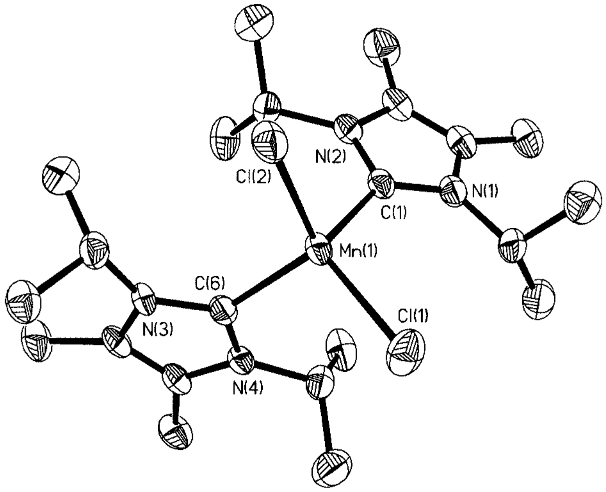


Figure 1. Molecular structure of **2** (50% probability ellipsoids); hydrogen atoms are omitted for clarity

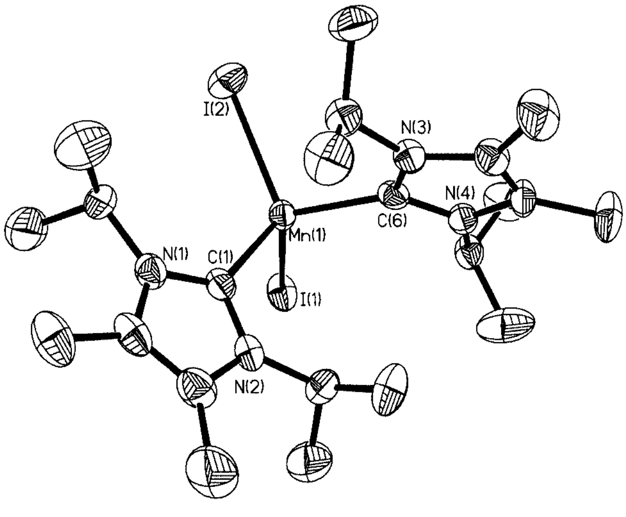


Figure 2. Molecular structure of **3** (50% probability ellipsoids); hydrogen atoms are omitted for clarity

Table 1. Selected bond lengths (Å) and bond angles (°) for compounds **2** and **3**

Compound **2**			
Mn(1)−Cl(1)	2.3535(11)	N(1)−C(1)	1.355(4)
Mn(1)−Cl(2)	2.3575(10)	N(2)−C(1)	1.355(4)
Mn(1)−C(1)	2.214(3)	N(3)−C(6)	1.355(4)
Mn(1)−C(6)	2.219(3)	N(4)−C(6)	1.359(4)
C(1)−Mn(1)−C(6)	103.02(12)	C(6)−Mn(1)−Cl(2)	114.64(9)
C(1)−Mn(1)−Cl(6)	112.77(9)	Cl(1)−Mn(1)−Cl(2)	111.47(4)
C(6)−Mn(1)−C1(1)	108.92(9)	N(1)−C(1)−N(2)	104.5(3)
C(1)−Mn(1)−Cl(2)	105.78(8)	N(3)−C(6)−N(4)	104.6(3)
N(1)−C(1)−Mn(1)	131.6(2)	N(2)−C(1)−Mn(1)	123.9(2)
N(3)−C(1)−Mn(1)	132.3(2)	N(4)−C(1)−Mn(1)	122.6(2)
Compound **3**			
Mn(1)−I(1)	2.7307(7)	N(1)−C(1)	1.356(5)
Mn(1)−I(2)	2.7114(8)	N(2)−C(1)	1.352(6)
Mn(1)−C(1)	2.210(4)	N(3)−C(6)	1.354(5)
Mn(1)−C(6)	2.204(4)	N(4)−C(6)	1.352(5)
C(1)−Mn(1)−C(6)	102.35(15)	C(6)−Mn(1)−I(2)	105.79(11)
C(1)−Mn(1)−I(1)	106.46(10)	I(1)−Mn(1)−I(2)	109.04(2)
C(6)−Mn(1)−I(1)	116.60(10)	N(1)−C(1)−N(2)	104.7(3)
C(1)−Mn(1)−I(2)	116.89(11)	N(3)−C(6)−N(4)	104.1(3)
N(1)−C(1)−Mn(1)	131.7(3)	N(2)−C(1)−Mn(1)	123.3(3)
N(3)−C(1)−Mn(1)	124.5(3)	N(4)−C(1)−Mn(1)	131.2(3)

lengths and angles are listed in Table 1. The manganese centers are four coordinate and have a distorted tetrahedral geometry in which each manganese is bonded to two halides and two carbene carbons. A crystallographic twofold axis passes through the metal center bisecting the angles X−Mn−X and C−Mn−C. There is a slight difference between the two structures due to the different ionic radius of Cl and I: the X−Mn−X (111.5°) and C−Mn−C (103.0°) angles in **2** are slightly larger than the corresponding ones in **3** (109.0° and 102.4°, respectively). The dihedral angle between the two carbene planes is 84.5° in **2** and 77.0° in **3**. These differences possibly result from the stronger repulsion between iodine and carbene in **3** than that between chlorine and carbene in **2**; this is also reflected in the EPR spectra.

The Mn−C(carbene) bond lengths (av. 2.21 Å) in **2** and **3** are in the expected range of Mn−C single bonds, but significantly shorter than the Mn−P bond lengths found in $[MnI_2(PEt_3)_2]$[8] (av. 2.53 Å) and $[MnI_2(PPhMe_2)]_n$ [15] (av. 2.67 Å). The Mn−I distances (av. 2.72 Å) in **3** are a little longer than those in $[MnI_2(PEt_3)_2]$ (av. 2.67 Å)[8] due to the different *trans* influence. However, the I−Mn−I (109.0°) and C−Mn−C (102.4°) angles in **3** are significantly smaller than the corresponding ones (120.1° and 115.1°, respectively) in $[MnI_2(PEt_3)_2]$.[8]

The N(1)−C(1)−Mn(1) (131.6°) and N(3)−C(6)−Mn(1) (132.3°) angles deviate significantly from their counterparts N(2)−C(1)−Mn(1) (123.9°) and N(4)−C(6)−Mn(1) (122.6°) in **2**, which implies that both the *N*-heterocyclic carbenes undergo *in-plane* bending.[16] However, *out-of-plane* bending is only observed for one *N*-heterocyclic carbene ligand [C(6), N(3), C(7), C(8) and N(4)] and the Mn(1)−C(6) bond lies out of the *N*-heterocyclic carbene plane by 6.4°. The other *N*-heterocyclic carbene and the central manganese atom are coplanar. In **3**, both the *N*-heterocyclic carbene ligands undergo *out-of-plane* bending, as shown by the Mn−C bond angles, which deviate from the corresponding *N*-heterocyclic carbene planes by 4.7° and 4.3°, respectively. These angles are in the normal range.[14]

Compound **4** is the first structurally characterized monomeric manganese complex containing two symmetric chelating acetate groups. Single crystals suitable for X-ray structural analysis were grown from THF solution at −26 °C. The molecular structure is shown in Figure 3; selected bond lengths and bond angles are listed in Table 2. Complex **4** crystallizes in the monoclinic space group *C*2/*c*. The central manganese atom is surrounded by four oxygen atoms from the two chelating carboxy groups and two carbene carbon atoms in a highly distorted octahedral geometry. The complex adopts a symmetric structure. A mirror plane passes through the manganese atom bisecting the two acetate groups and the two carbenes.

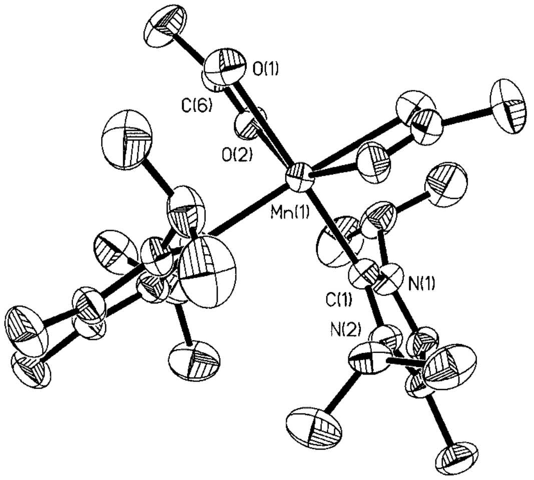


Figure 3. Molecular structure of **4** (50% probability ellipsoids); hydrogen atoms are omitted for clarity

The two acetate groups are symmetrically bonded, in a chelating fashion, to the manganese atom, resulting in the formation of two MnOCO four-membered rings. Both rings are planar and nearly orthogonal, as shown by a dihedral angle of 85.8°. Manganese complexes containing chelating carboxy groups are rare.[17] The Mn−O distances from the O *trans* to the *N*-heterocyclic carbene carbon (2.34 Å) are slightly longer than those (2.23 Å) from the O *cis* to the carbon, probably due to the strong donor property of the *N*-heterocyclic carbene. Accordingly, the shorter Mn−O bond is associated with a longer carboxy C−O bond. The average value (2.29 Å) of the Mn−O distance is significantly longer than that of the bridging carboxyl group in the $[Mn_2(\mu\text{-}MeCOO)_x]^{4-x}$ system (1.99−2.13 Å),[18] and is also longer than that (av. 2.07 Å) of the chelating acetate group in $[Mn(MeCOO)(CO)_2(PPh_3)_2]$.[19] The distance from

Table 2. Selected bond lengths (Å) and bond angles (°) for compound **4**

Mn(1)−O(1)	2.343(2)	Mn(1)−C(1A)	2.254(3)
Mn(1)−O(2)	2.233(2)	Mn(1)−C(6A)	2.612(3)
Mn(1)−O(1A)	2.343(2)	O(1)−C(6)	1.238(4)
Mn(1)−O(2A)	2.233(2)	O(2)−C(6)	1.258(4)
Mn(1)−C(1)	2.254(3)	N(1)−C(1)	1.364(3)
Mn(1)−C(6)	2.612(3)	N(2)−C(1)	1.356(3)
C(1)−Mn(1)−C(1A)	96.68(13)	O(1)−Mn(1)−C(1A)	87.69(9)
C(1)−Mn(1)−O(1)	161.79(9)	O(1)−Mn(1)−O(1A)	93.65(12)
C(1)−Mn(1)−O(1A)	87.69(9)	O(1)−Mn(1)−O(2A)	98.60(8)
C(1)−Mn(1)−O(2)	104.91(9)	O(1A)−Mn(1)−O(2A)	56.92(8)
C(1)−Mn(1)−O(2A)	97.34(8)	O(1A)−Mn(1)−C(1A)	161.79(9)
O(2)−Mn(1)−O(2A)	146.33(12)	O(2A)−Mn(1)−C(1A)	104.91(8)
O(2)−Mn(1)−C(1A)	97.34(8)	O(1)−C(6)−O(2)	122.0(3)
O(2)−Mn(1)−O(1)	56.92(8)	N(1)−C(1)−N(2)	104.0(2)
O(2)−Mn(1)−O(1A)	98.60(8)	N(2)−C(1)−Mn(1)	126.67(18)
N(1)−C(1)−Mn(1)	129.32(18)		

the manganese atom to the central carbon atom of the acetate group (2.61 Å) is in the non-bonding range.[19]

The C−Mn−C angle in **4** is 96.7°, which shows that the two *N*-heterocyclic carbenes are in a *cis* position. The Mn−C distance (2.25 Å) is in the range (2.20−2.27 Å) of the Mn−C(*N*-heterocyclic carbene) distances known and is slightly longer than those in **2** and **3**.

Interestingly, no *in-plane* or *out-of-plane* bending of the *N*-heterocyclic carbenes is found in **4**. The similar N(1)−C(1)−Mn(1) (129.3°) and N(2)−C(1)−Mn(1) (126.7°) angles do not support any *in-plane* bending of the *N*-heterocyclic carbenes.

Solid-State Powder EPR Measurements

Manganese(II) complexes give a great variety of EPR signals related to their structures.[20] The X-band EPR spectra of complexes **2**−**4** were recorded at ambient temperature for powder samples. As expected, a strong resonance in complexes **2** and **3** is observed near $g_{\mathrm{eff}} = 4.3$ due to their tetrahedral geometry.[21a] In addition, compound **2** exhibits two shoulders at lower field and several weaker bands at higher field, while the spectrum of **3** is much simpler: another strong resonance ($g_{\mathrm{eff}} = 2$) and a very weak one at high field. The spectrum of compound **4** exhibits a very strong band ($g_{\mathrm{eff}} = 2$) and a weaker one (near $g_{\mathrm{eff}} = 4.3$) and has shoulders at higher and lower field of the main line. The spectrum of **4** is very similar to that of [Mn(*o*-phen)$_2$(NCS)$_2$], which has a very small D value (near zero) and a large λ value (near 1/3) (D and λ are zero-field splitting parameters).[21b] The spectrum is consistent with the symmetric structure of **4** and the *cis* arrangement of the two carbene ligands.

Conclusion

In summary, we have shown that the *N*-heterocyclic carbene ligand [C(Me)N(*i*Pr)]$_2$C (**1**) forms stable adducts **2**−**4** with manganese(II) halides and acetate. The X-ray structural analyses show that complexes **2**−**4** are monomeric and the *N*-heterocyclic carbene ligands in these complexes are arranged differently at the central metal atoms. These results indicate that the *N*-heterocyclic carbene ligand is a better ligand to form monomeric adducts than the tertiary phosphane ligand.

Experimental Section

General: 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. The EPR spectra were recorded on a Bruker Elexsys E 500 X-band spectrometer. All samples were measured as crystalline powders in an argon atmosphere at room temperature with a modulation frequency of 100 kHz, 3−5 G modulation amplitude, about 9.42 GHz microwave frequency and microwave power in the range between 2 and 10 mW as spectrometer settings. [C(Me)N(*i*Pr)]$_2$C[22] (**1**) was prepared by the literature protocol.

Preparation of 2: THF (40 mL) was added to a mixture of **1** (0.72 g, 4 mmol) and [MnCl$_2$(THF)$_{1.5}$] (0.47 g, 2 mmol) at room temperature. The suspension was stirred for 13 h. The solvent was concentrated to about 3 mL and the colorless precipitate was collected by filtration. Yield: 0.88 g (91%). M.p. 268−270 °C. $C_{22}H_{40}Cl_2MnN_4$ (486.42): calcd. C 54.27, H 8.22, N 11.51; found C 54.32, H 8.23, N 11.52. IR (KBr, Nujol mull): $\tilde{\nu}$ = 1629 cm^{-1} (m), 1552 (w), 1401 (m), 1376 (s), 1360 (s), 1262 (vw), 1218 (m), 1168 (w), 1136 (m), 1107 (w), 1070 (m), 1023 (w), 968 (vw), 931 (vw), 905 (w), 885 (w), 803 (vw), 751 (m), 722 (m), 674 (vw), 544 (m), 412 (w).

Preparation of 3: The procedure is the same as that described for **2**. Yield: 1.03 g (77%). M.p. 273−283 °C. $C_{22}H_{40}I_2MnN_4$ (669.32): calcd. C 39.46, H 5.98, N 8.37; found C 39.54, H 6.00, N 8.34. IR (KBr, Nujol mull): $\tilde{\nu}$ = 1629 cm^{-1} (m), 1552 (w), 1398 (m), 1377 (s), 1364 (s), 1291 (vw), 1262 (vw), 1219 (m), 1191 (vw), 1168 (w), 1136 (m), 1109 (w), 1071 (m), 1023 (w), 968 (vw), 931 (vw), 905 (w), 886 (w), 848 (vw), 803 (vw), 750 (m), 722 (m).

Preparation of 4: THF (40 mL) was added to a mixture of **1** (0.72 g, 4 mmol) and Mn(MeCOO)$_2$ (0.34 g, 2 mmol) at room temperature. A clear solution was obtained immediately and stirred for 6 h. The solution was concentrated to about 5 mL and kept at −26 °C for 3 days to give colorless crystals. Yield: 0.86 g (81%). M.p. 156−158 °C. $C_{26}H_{46}MnN_4O_4$ (532.96): calcd. C 58.54, H 8.63, N 10.51; found C 58.58, H 8.67, N 10.14. IR (KBr, Nujol mull): $\tilde{\nu}$ = 1750 cm^{-1} (vw), 1695 (vw),1628 (s), 1599 (vs), 1573 (s), 1406 (s), 1323 (m), 1260 (m), 1238 (w), 1222 (m), 1195 (w), 1167 (vw), 1138 (m), 1112 (m), 1073 (w), 1048 (vw), 10231 (vw), 917 (w), 908 (w), 888 (vw), 804 (s), 751 (m), 722 (m), 658 (s), 648 (w), 616 (m), 544 (m), 483 (w), 457 (vw), 411 (vw).

X-ray Crystallography: Crystallographic data (see Table 3) for complexes **2**−**4** were collected on a Stoe−Siemens−Huber four-circle diffractometer coupled to a Siemens CCD area detector with graphite-monochromated Mo-K_{α} radiation (λ = 0.71073 Å). All structures were solved by direct methods (SHELXS-97)[23] and refined against F^2 using SHELXL-97.[24] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically calculated positions and refined using a riding model.

Table 3. Crystallographic data for compounds **2−4**

	2	**3**	**4**·THF
Empirical formula	$C_{22}H_{40}Cl_2MnN_4$	$C_{22}H_{40}I_2MnN_4$	$C_{30}H_{54}MnN_4O_5$
Molecular mass	486.42	669.32	605.71
Temperature (K)	200(2)	200(2)	203(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
Unit cell dimensions (Å)	a = 11.2852(17)	a = 11.2771(13)	a = 12.970(2)
	b = 14.867(3)	b = 16.054(3)	b = 14.374(3)
	c = 15.321(3)	c = 15.705(3)	c = 19.322(2)
	β = 90.24(2)°	β = 90.399(14)°	β = 106.070(10)°
Volume (Å^3)	2570.6(9)	2843.1(8)	3461.5(10)
Z	4	4	4
D (calcd. Mg·m^{-3})	1.257	1.564	1.162
Crystal size (mm^3)	1.00 × 0.30 × 0.20	0.80 × 0.60 × 0.30	0.90 × 0.70 × 0.70
Absorption coefficient (mm^{-1})	0.736	2.650	0.421
θ range for data collection (°)	3.54 to 22.53	3.61 to 25.01	3.54 to 24.94
F(000)	1036	1324	1308
Reflections collected	3570	6010	3231
Independent reflections	3348 (R_{int} = 0.0671)	4994 (R_{int} = 0.0660)	3028 (R_{int} = 0.0717)
Data/restraints/parameters	3348/0/274	4994/0/274	3028/0/174
Goodness-of-fit on F^2	1.081	1.065	1.015
Final R indices [$I > 2\sigma(I)$]	0.0460, 0.1150	0.0411, 0.1077	0.0595, 0.1597
R (all data)	0.0544, 0.1233	0.0440, 0.1111	0.0670, 0.1701
Largest diff. peak/hole (e·Å^{-3})	0.673/−0.854	1.161/−1.433	0.762/−0.834

CCDC-222956 (for **2**), -222955 (for **3**), and -222954 (for **4**) 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: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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