Complexes of Manganese, Iron, Zinc, and Molybdenum with a Superbasic Tris(guanidine) Derivative of Tris(2-ethylamino)amine (Tren) as a Tripod Ligand

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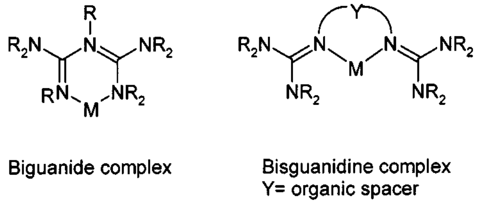
Dedicated to Professor Herbert Roesky on the occasion of his 65th birthday

Keywords: Ligand design / N ligands / Tripodal ligands / Coordination chemistry / Manganese / Iron / Zinc / Molybdenum

The synthesis of the novel tripod ligand $N[CH_2CH_2N{=}C(NMe_2)_2]_3$, based on the tris(2-ethylamino)amine (tren) backbone and having a set of three superbasic tetramethylguanidine (TMG) donor atoms instead of the primary amine functionalities, is described. This ligand has been prepared by treating tren with the Vilsmeyer salt $[(Me_2N)_2CCl]Cl$ in the presence of triethylamine as an auxiliary base and NaOH. Complexes of manganese(II), iron(II), and zinc(II) as biologically relevant transition metal ions as well as of molybdenum(0) have been synthesized and spectroscopically and structurally characterized. The electrochemical properties of selected complexes have been studied.

Introduction

Peralkylguanidines belong to the strongest neutral organic bases known.[1] They are several orders of magnitude more basic than tertiary amines due to the excellent stabilization of the positive charge over their resonance-stabilized cations.[2] This trend is illustrated by the $pK_{BH}{}^{+}$ values (MeCN) of the 1,2,2,6,6-pentamethylpiperidinium cation (18.62), the parent guanidinium cation (23.00), and the pentamethylguanidinium cation (25.00).[2c] Therefore, in aqueous media, guanidines exist almost exclusively in the protonated form.[3] Guanidines are currently attracting attention as anion receptors,[4] both in enzymes and in model systems. Due to their hydrophilic nature, they also play an important role in the mediation of solubility of natural products[5] and in the stabilization of protein conformations through hydrogen bonding.[5−7] However, surprisingly little is known about the coordination chemistry of guanidines. There is some indication that the guanidine functionality of arginine may play a role as a neutral donor towards various metal cations in the hydrophobic domains of cytochrome *c* enzymes and other such systems.[2,5,6,8] There have been a few reports on coordination compounds of monoguanidines $HN{=}C(NRR')_2$.[5,6,8,9] The first complexes of chelating bis(guanidine)s have recently been reported by Kuhn[10] and ourselves.[11a] We became interested in the coordination chemistry of bis-, tris-, and oligoguanidines because of the marked tendency of biguanides to stabilize unusually high oxidation states of metals, e.g. in Ag^{III} [12] and Ni^{III} [13] complexes (Scheme 1).



Scheme 1. Guanidine-based complexes

The focus of this investigation is the evaluation of the donor capabilities of tetradentate pentaalkylguanidine derivatives. The basicities of these neutral ligands are intermediate between those of tertiary amines and amido ligands, but the question remains as to how well they interact with Lewis acids. Indeed, the question arises as to whether, in addition to their strong σ-donor interaction $sp^2\text{-N}\rightarrow M$, guanidines may also be π-acidic like Schiff bases or π-basic like amido ligands. Various aspects of guanidine coordination chemistry remain unexplored, such as the fine tuning of the basicity, donor strength, steric demand, and control of the solubility by variation of the substituents at the guanidine function. Following our study on guanidine derivatives of the tmeda and tame backbones,[11a] we wish to report our first results on the synthesis and coordination chemistry of guanidine derivatives of the tren ligand family (Scheme 2). The target molecule 1,1,1-tris{2-[N^2-(1,1,3,3-tetramethylguanidino)]ethyl}amine (**1**) (TMG_3tren) is structurally related to known Schiff bases,[14] tris(pyridylmethyl)amine (tmpa),[15] and other tripodal ligands[16] based on the well-known tren backbone (Scheme 2).

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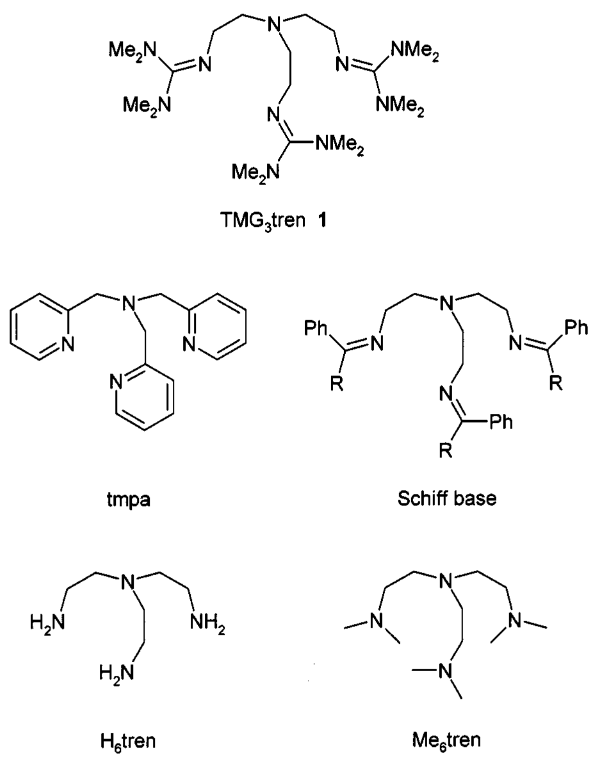
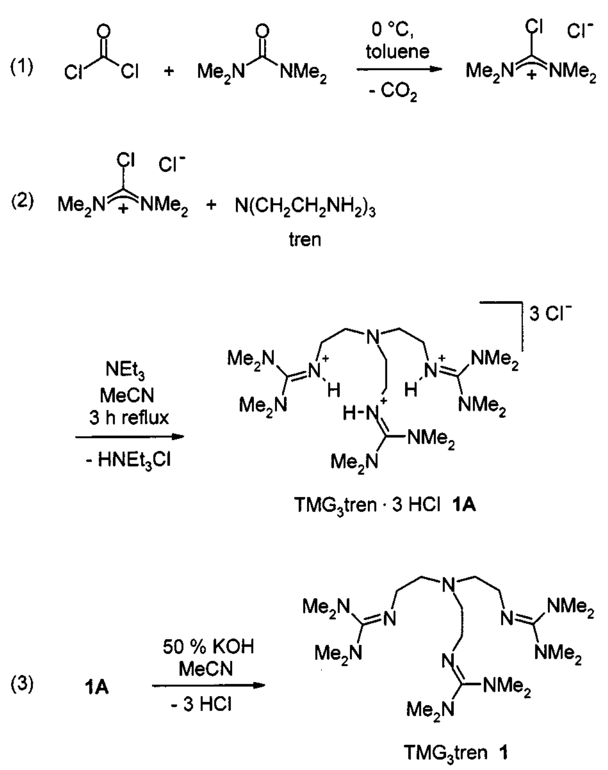


Scheme 2. Structural relationship between the target ligand **1** and known tripods of the tren ligand family



Scheme 3. Preparation of peralkylated oligoguanidines

Results and Discussion

Ligand Synthesis

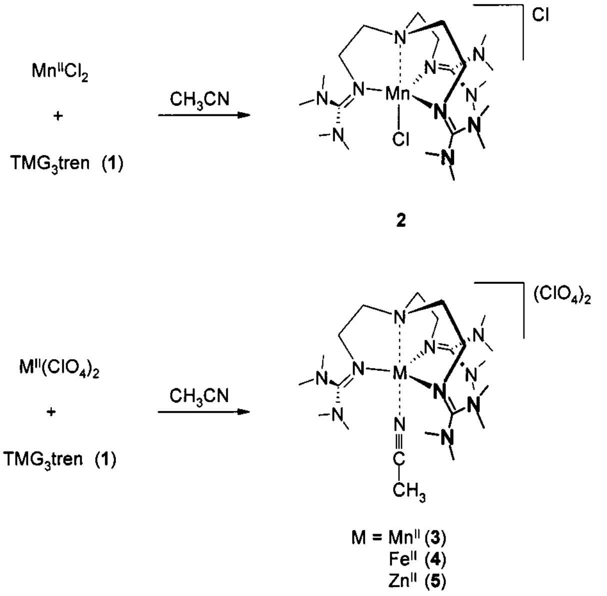
The synthesis of the target ligand **1** was accomplished following our general procedure that allows the transformation of primary bis-, tris-, or polyamines into the corresponding tetramethylguanidino derivatives.[11] The main problem associated with this synthesis is that polyguanidines as well as their hydrochlorides are extremely hygroscopic. Typically, they cannot be distilled/sublimed without decomposition and may not be purified by column chromatography on polar phases (SiO_2, Al_2O_3). Because of these purification difficulties, it was imperative that the synthesis involved selective reactions. A nearly quantitative transformation of a primary amine functionality into the guanidine may be accomplished by reaction with the Vilsmeyer salt $[(Me_2N)_2CCl]Cl$, a method first described by Eilingsfeld and Seefelder[17] and later improved by Kantlehner et al.[18] for *mono*guanidines. The Vilsmeyer salt is obtained by reaction of tetramethylurea with phosgene[19] or oxalyl chloride in toluene.[20] Reaction of the latter with tren in the presence of triethylamine as an auxiliary base leads to the corresponding hydrochloride **1A** (Scheme 3). Separation from the by-product Et_3NHCl is accomplished by adding 1 equiv. of NaOH per guanidine functionality and removing the resulting Et_3N and NaCl by crystallization from acetonitrile/diethyl ether. In the present case, the free base **1** was obtained in an overall yield of up to 86% by deprotonation of the tris(hydrochloride) using a two-phase system of MeCN/50% aqueous KOH.

The spectroscopic features of the protonated ligand **1A** are very similar to those of the free guanidine base **1**. A difference can be seen in the IR spectra, where TMG_3tren shows a single absorption at $\nu(C=N) = 1620\ cm^{-1}$ while the corresponding absorption of the tris(hydrochloride) is split into two separate bands at 1627 and 1584 cm^{-1}. This splitting is a typical feature due the decreased molecular symmetry in guanidinium cations. It is also observed for the hexamethylguanidinium cation.[21] In order to avoid steric interactions, the Me_2N substituents adopt a mutually twisted propeller-like conformation[21,22] rather than a coplanar one. The UV/Vis spectrum of **1** in MeCN shows an absorption at 216 nm with a molar extinction coefficient ε of approximately $1 \cdot 10^4$ for each guanidinium unit, attributable to the $\pi \rightarrow \pi^*$ transition of the C=N bond.[23] The ^1H NMR spectrum of **1** features only one signal due to the methyl groups, while the ^{13}C NMR spectrum reveals the presence of two chemically non-equivalent methyl groups. It is known from the literature that the barrier to rotation about the C=N double bond of pentaalkylguanidines (Scheme 4) leading to a *syn-anti* isomerization[2b,24] is markedly lowered by protonation or by increased steric demand of the alkyl groups. The bulkiness of the tren backbone leads to a lower barrier, which is manifested in the equivalence seen in the ^1H NMR spectrum.

Scheme 4. The *syn-anti* isomerization of pentasubstituted guanidines

Synthesis of the Metal Complexes

The free guanidine base **1** is moderately stable in D_2O. Due to slow hydrolysis, tetramethylurea is formed over a period of several days by decomposition of the guanidinium hydroxide. In contrast, the hydrochloride **1A** is perfectly stable in D_2O. In order to avoid side reactions due to hydrolysis of the ligand and of the metal salts, the latter were dehydrated by the orthoester method[25] prior to complexation. The complexes were synthesized in good yields by combining the dehydrated metal salts with 1.05 equiv. of TMG_3tren (**1**) in dry acetonitrile and stirring for 30 min (Scheme 5). The resulting ionic complexes **2**−**5** proved to be soluble in polar aprotic media such as MeCN, CH_2Cl_2, or acetone, but insoluble in diethyl ether and hydrocarbons.

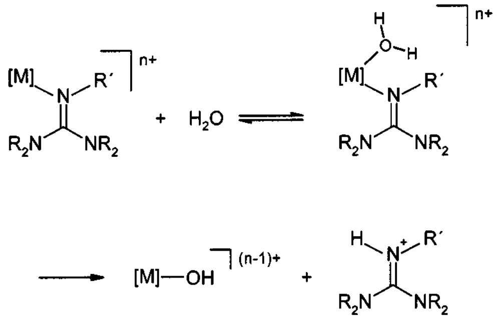


Scheme 5. Complexation of M^{2+} salts with TMG_3tren

The spectroscopic properties of the complexes resemble those of the protonated ligand (**1A**). For example, two IR absorptions are seen in the 1600 cm^{-1} region due to ν(C=N). The UV/Vis maxima are shifted 5−10 nm to lower wavelengths. While the zinc(II) complex (**5**) is diamagnetic, the manganese(II) (**2**, **3**) and iron(II) (**4**) complexes are paramagnetic with spin-only values of the order expected for d^5 and d^6 high-spin complexes[26] comparable to those of known complexes: μ_{eff}[Mn(Me$_6$tren)Br]Br: 6.01 B.M.; μ_{eff}[Fe(Me$_6$tren)Br]Br: 5.34 B.M.;[27] μ_{eff}[Mn(ntb)Cl]Cl [ntb = tris(2-benzimidazolylmethyl)amine]: 5.83 B.M.[28] Their magnetic susceptibilities, μ_{eff}(**2**): 5.9 B.M.; μ_{eff}(**3**): 5.8 B.M.; μ_{eff}(**4**): 5.4 B.M., all with an uncertainty of ±0.1, were determined by the Evans method.[29]

Attempts to prepare well-defined complexes of **1** with Fe^{III} and Mn^{III} salts have hitherto proved unsuccessful. It seems that, due to steric repulsion, the bite of the ligand is better matched with larger ions than with smaller, highly charged ions. This interpretation is in accordance with the electrochemical results discussed below, which reveal the rapid decomposition of the oxidized iron species.

The stabilities of compounds **2**−**5** towards hydrolysis were examined. All the complexes were found to be sensitive to air and moisture, despite the extreme steric shielding provided by the ligand. In general, it was observed that metal hydroxides along with the protonated ligand were formed when **2**−**5** were exposed to aqueous solvent mixtures. These findings may be explained by the extremely high proton affinity of guanidines. Deprotonation of an aqua ligand irreversibly induces the hydrolytic cleavage of the metal−nitrogen bond, a pattern that is also typical for amido complexes (Scheme 6).



Scheme 6. Hydrolytic cleavage of the metal−nitrogen bond

Structural Characterization

Single crystals of all the ionic complexes suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into acetonitrile solutions. The results of the structure analyses are presented in Figures 1−6, while selected bond lengths and angles are collected in Table 1 and parameters relating to the data collection and refinement are listed in Tables 7 and 8. Complexes **2** (Figures 1 and 2), **3** (Figure 3), **4** (Figure 4), and **5** (Figure 5) each possess a nearly C_3-symmetrical trigonal-bipyramidal molecular geometry, with the amine nitrogen atom located in one of the axial positions, and *N*-coordinated acetonitrile (**3**, **4**, **5**) or chloride ion (**2**) occupying the other.

The imino nitrogen atoms of the guanidine groups define the equatorial plane. The metal atom is slightly axially distorted from the equatorial plane towards the acetonitrile molecule. As is evident from Table 2, this deviation is accompanied by a change in the ionic radius of the metal center. It also has an effect on the bond lengths between the amine and guanidine nitrogen atoms and the metal ion, whereas the distance to the acetonitrile nitrogen atom remains essentially the same. Other compounds containing Mn, Fe, and Zn in similar tren ligand coordination spheres are included in the table in order to correlate our results.

Table 1. Selected bond lengths [pm] and bond angles [°] in complexes **2**−**6**, with standard deviations in parentheses

		[$Mn^{II}(TMG_3tren)Cl]Cl$ (**2**)			
Mn(1)−N(1)	218.2(2)	Mn(1)−N(4)	217.7(1)	Mn(1)−N(7)	219.1(2)
Mn(1)−N(10)	237.8(1)	Mn(1)−Cl(1)	243.0(1)		
av.(N_{eq}−Mn−N_{eq})	114.63(6)	av.(N_{ax}−Mn−N_{eq})	76.38(5)	N(10)−Mn(1)−Cl(1)	177.57(4)
		[$Mn^{II}(TMG_3tren)NCMe](ClO_4)_2$ (**3**)			
Mn(1)−N(2)	212.7(3)	Mn(1)−N(5)	214.8(3)	Mn(1)−N(8)	213.1(3)
Mn(1)−N(1)	232.8(3)	Mn(1)−N(11)	221.5(3)		
av.(N_{eq}−Mn−N_{eq})	115.79(11)	av.(N_{ax}−Mn−N_{eq})	78.00(10)	N(1)−Mn(1)−N(11)	175.64(11)
		[$Fe^{II}(TMG_3tren)NCMe](ClO_4)_2$ (**4**)			
Fe(1)−N(2)	207.3(3)	Fe(1)−N(5)	206.1(4)	Fe(1)−N(8)	208.4(4)
Fe(1)−N(1)	225.4(3)	Fe(1)−N(11)	215.1(4)		
av.(N_{eq}−Fe−N_{eq})	116.95(14)	av.(N_{ax}−Fe−N_{eq})	79.85(14)	N(1)−Fe(1)−N(11)	176.62(14)
		[$Zn^{II}(TMG_3tren)NCMe](ClO_4)_2$ (**5**)			
Zn(1)−N(2)	203.4(2)	Zn(1)−N(5)	203.4(2)	Zn(1)−N(8)	205.1(3)
Zn(1)−N(1)	226.9(2)	Zn(1)−N(11)	218.7(3)		
av.(N_{eq}−Zn−N_{eq})	117.46(10)	av.(N_{ax}−Zn−N_{eq})	80.74(9)	N(1)−Zn(1)−N(11)	177.25(9)
		[$Mo^0(TMG_3tren)(CO)_3$] (**6**)			
Mo(1)−N(1)	235.4(2)	Mo(1)−N(2)	233.6(2)	Mo(1)−N(5)	231.9(2)
Mo(1)−C(22)	193.0(3)	Mo(1)−C(23)	192.4(3)	Mo(1)−C(24)	192.4(3)
N(2)−C(3)	131.7(3)	C(3)−N(3)	136.4(4)	C(3)−N(4)	137.7(4)
N(5)−C(10)	131.1(3)	C(10)−N(6)	137.2(4)	C(10)−N(7)	137.2(4)
N(8)−C(17)	127.6(4)	C(17)−N(9)	139.6(4)	C(17)−N(10)	137.8(4)
N(1)−Mo(1)−C(23)	175.64(10)	N(2)−Mo(1)−C(24)	174.64(10)	N(5)−Mo(1)−C(22)	167.41(10)

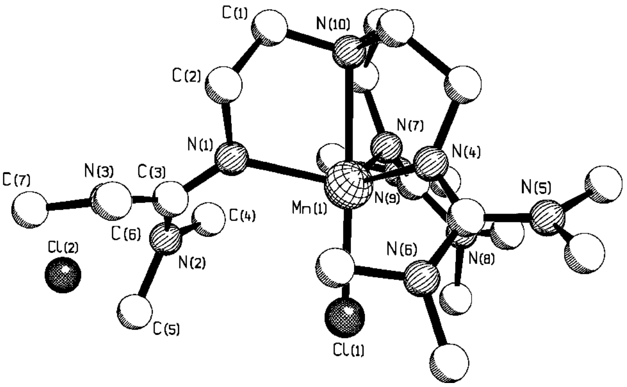


Figure 1. Molecular structure of **2**[44]

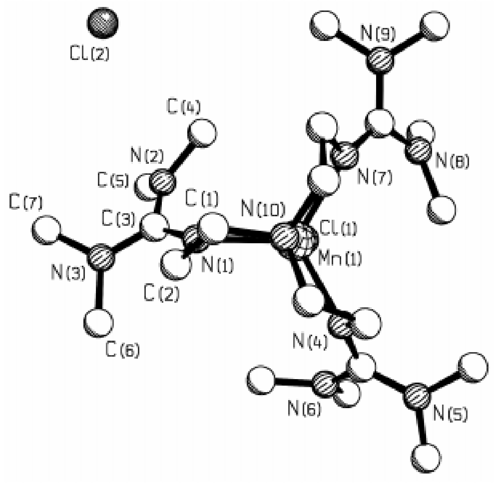


Figure 2. Molecular structure of [$Mn^{II}(TMG_3tren)Cl]Cl$ (**2**); SCHAKAL plot of a projection along the local C_3 axis[44]

However, an absolute comparison remains difficult because the ligand properties differ significantly, e.g. in terms of steric hindrance or considering the different neutral and anionic coligands, which lead to different effective charges at the metal atoms and hence to different bond lengths to the equatorial nitrogen atoms.[30]

Comparing complex **2**, which bears an anionic chloro ligand, with dicationic **3**, which has a neutral acetonitrile ligand instead, the increased contraction of the TMG_3tren ligand can be directly attributed to the higher effective charge at the metal center. As expected, the axial distortion decreases with decreasing ion radius of the central atom.

A comparison of **2** with [$Mn^{II}(Me_6tren)Br]Br$ [48] (**A**) as regards the relative donor abilities of the amine and guanidine ligands is made difficult by the different steric requirements of the two ligand regimes. In the case of **1**, steric repulsion is greatest at the periphery. Since donor ability incorporates both basicity and steric hindrance, the TMG_3tren ligand can be estimated to be superior to Me_6tren in its donor ability. The guanidine sp^2-nitrogen atom is much more basic than the amine sp^3-nitrogen atom of Me_6tren and is also sterically less hindered. The net result is that the average bond length between the equatorial guanidine nitrogen atoms and the metal center is much smaller (218 pm) than the corresponding amine−metal distance in [$Mn^{II}Br(Me_6tren)]Br$ (**A**) (227 pm). A stronger donor component of the equatorial guanidines is also consistent with the longer distance to the axial amine in **2** (238 pm) compared to that in the corresponding Me_6tren

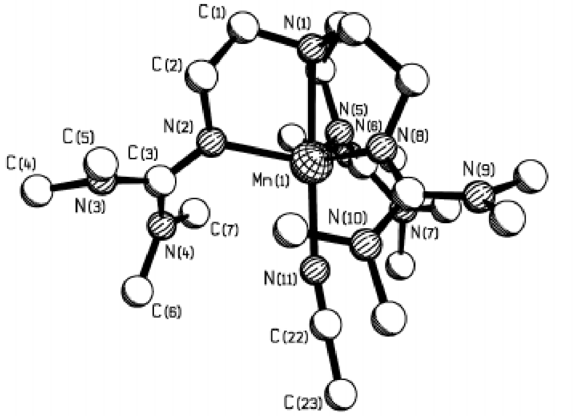


Figure 3. Molecular structure of **3**[44]

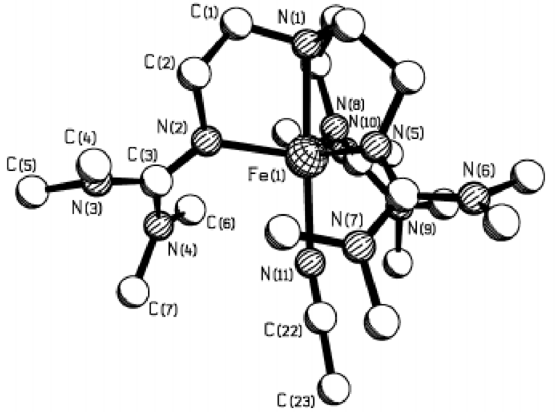


Figure 4. Molecular structure of **4**[44]

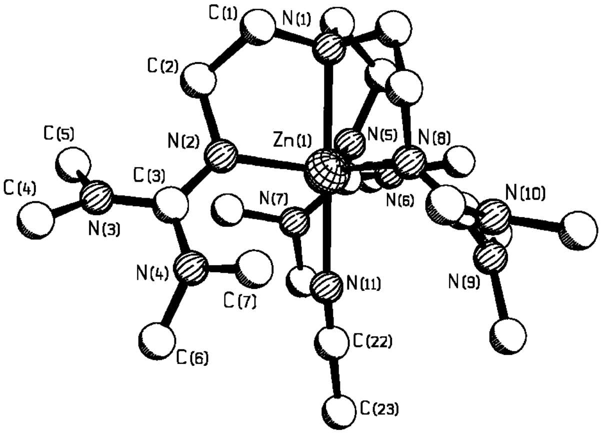


Figure 5. Molecular structure of **5**[44]

complex **A** (219 pm). In the latter donor−acceptor complex, the axial amine has to provide more electron density towards the overall charge compensation. As a consequence, the displacement of the manganese cation out of the equatorial plane is significantly greater in **2** (51 pm) compared to that in $[Mn^{II}(Me_6tren)Br]Br$ (**A**) (36 pm).

A characteristic structural feature of all the complexes **2−5** is shown in Figure 2. In order to reduce steric repulsion, the guanidine dimethylamino units are twisted by approximately 40° into a propeller-like conformation. The dimethylamino groups are not coplanar within the planar guanidine CN_3 unit but show out-of-plane torsion angles of 20−45° (Table 3). A similar distortion has been found for the hexamethylguanidinium cation in its ground state.[31]

In spite of these steric limitations to perfect π-conjugation in the outer ligand sphere, the superbasic tripod **1** efficiently stabilizes dicationic complexes by delocalizing the charge over the three perfectly planar guanidinium cations (sum of angles in representative **2**: see Table 5).

According to a CCDC search,[32] no structurally characterized complexes of iron and manganese with pentacoordination by five neutral N donor ligands have hitherto been reported. On the other hand, for d^{10} Zn^{2+},[33] Cd^{2+},[34] Ag^{+},[35] and d^9 Cu^{2+},[36] this coordination mode is more common. Just a few representatives involving the tren ligand or its *N*-methyl derivatives and an anionic ligand have been reported, for example the halide complexes of Di Vaira et al.[48] and Templeton et al.,[50] and the pseudohalide (OCN^- and SCN^-) complexes investigated by Laskowski and co-workers.[37]

The Question of π-Bonding Contributions of Guanidine Ligands

Because the C=N valence vibrations of coordinated guanidines do not seem to give a reliable measure of the donor and acceptor qualities of TMG_3tren, we set out to synthesize a complex containing CO as an indicator ligand for electronic interactions of the coligands. The tris(acetonitrile) complex $[Mo(CH_3CN)_3(CO)_3]$ was found to react cleanly with **1** to give compound **6** in 79% yield (Scheme 7). The IR spectrum of **6** features more than two ν(C=N) absorptions in the region 1515−1580 cm^{-1}, while in the ^{13}C NMR spectrum two resonances due to guanidine CN_3 moieties are observed. Complex **6** proved to be stable under atmospheric conditions for a short period of time, but ultimately turned from yellow to brown. It showed a similar sensitivity to oxidation in solution. While the TMG_3tren ligand is able to displace even an anionic chloro ligand from **2**, it is incapable of displacing more than three carbon monoxide ligands from $[Mo(CO)_6]$ or derivatives thereof. It bonds in a facial manner, leaving one guanidine functionality as a dangling arm. This may be taken as an indication that **1** is not a good π-acceptor, and furthermore that it is a ligand of constrained geometry, not being able to stabilize geometries other than trigonal-bipyramidal in its tripodal coordination mode. Figure 6 shows the results of an X-ray analysis of single crystals of **6** obtained from acetonitrile/diethyl ether.

The molecule of **6** exhibits local C_s symmetry in the crystalline state with a mirror plane defined by Mo, N(1), C(23), and C(24). The molybdenum atom is coordinated in a distorted octahedral manner. The inner ligand core is defined by three facial carbonyl ligands, one amine, and two guanidine ligands. One dangling guanidine arm points away from the inner core. The amine is bonded with a slightly longer Mo−N(1) distance [235.4(2) pm] than the two guanidines Mo−N(2) [233.6(2) pm] and Mo(1)−N(5) [231.9(2) pm]. However, this difference in bonding is not reflected in specific bonding differences of the *trans*-CO ligands. On the

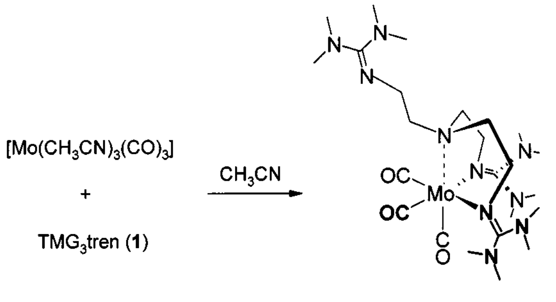
Table 2. Ionic radii of Mn, Fe, and Zn; structural features of complexes **2−5** and literature counterparts

Complex	Metal atom	Ion radius[47] [pm]	Axial distortion[a] [pm]	d(M−N$_{ax}$) [pm]	d(M−N$_{eq}$)[b] [pm]	d(M−L$_{ax}$) [pm]
A	$[L^1Mn^{II}-Br]^+$ [48]	89	36	219	227	249
A′	$[L^2Mn^{II}-Cl]^+$ [28]	89	63	252	216	236
B	$[L^1Fe^{II}-Br]^+$ [48]	85	32	221	215	248
C	$[L^1Zn^{II}-Br]^+$ [48]	82	27	219	211	245
C′	$[L^2Zn^{II}-Cl]^+$ [49]	82	64	248	205	225
C′′	$[L^3Zn^{II}-Cl]^+$ [50]	82	39	232	206	231
2	$[(\mathbf{1})Mn^{II}-Cl]^+$	89	51	237.8(1)	218.3(2)	243.0(1)
3	$[(\mathbf{1})Mn^{II}(NCMe)]^{++}$	89	44	232.8(3)	213.5(3)	221.5(3)
4	$[(\mathbf{1})Fe^{II}(NCMe)]^{++}$	85[c]	37	225.4(3)	207.3(4)	215.1(4)
5	$[(\mathbf{1})Zn^{II}(NCMe)]^{++}$	82	33	226.9(2)	204.0(2)	218.7(3)

[a] Distance of M from the equatorial plane defined by the three equatorial nitrogen atoms. − [b] Average distance of the three equatorial nitrogen atoms from the metal center. − [c] Average radius of Fe^{2+} for coordination numbers of 4 and 6 (high spin).[47] Standard deviations in parentheses. L^1 = Me$_6$tren, L^2 = tris(2-benzimidazolylmethyl)amine (ntb), L^3 = $_6$tren.

Table 3. Torsion angles [°] in complex $[Mn^{II}(TMG_3tren)Cl]Cl$ (**2**)

Mn(1)−N(1)−C(3)−N(2/3)	−42.7/140.3
N(1)−C(3)−N(2)−C(4/5)	−22.4/139.9
N(1)−C(3)−N(3)−C(6/7)	−40.6/147.2



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Scheme 7. Facial coordination of TMG$_3$tren to [Mo(CO)$_3$] in **6**

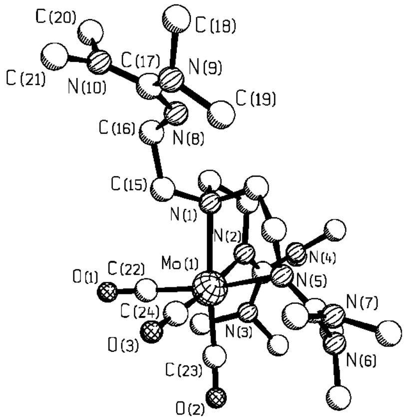

Figure 6. Molecular structure of **6**[48]

other hand, a comparison of the structural parameters of the closely related complexes **6** and [Mo(CO)$_3$(dien)],[38] in which *cis*-diethylenetriamine (dien) acts as a pure σ-donor, indicates slightly stronger donation by the guanidine ligand. Back-donation in **6** is slightly stronger; the Mo−C bonds tend to be shorter and the C−O bonds tend to be slightly longer as compared to those in the amine complex [Mo(CO)$_3$(dien)] (Table 4).

Table 4. Comparison of bond lengths in **6** and [Mo(CO)$_3$(dien)]; dien = *cis*-diethylenetriamine

	6	[Mo(CO)$_3$(dien)][38]
av.(Mo−N$_{amine}$) [pm]	235.4	232.3
av.(Mo−N$_{imine}$) [pm]	232.7	−
av.(Mo−C) [pm]	192.6	194.3
av.(C−O) [pm]	117.8	115.3
av.(C−Mo−C) [°]	84.8	85.3

Carbonyl stretching frequencies are often used as an additional criterion for evaluating the donor/acceptor qualities of coligands. There is no clear trend when guanidine **6** (1883 cm^{-1}) is compared to complexes of amines that act as pure σ-donors such as [Mo(CO)$_3$(tacn)] (1850 cm^{-1})[39] or [Mo(CO)$_3$(dien)] (1887 cm^{-1}).[38] On the basis of structural and IR spectroscopic evidence, it appears that there is no π-interaction between the metal center and ligand **1**.

Finally, the comparison of C−N bond lengths in guanidines, guanidinium hydrochlorides, and guanidine complexes (Lewis acid adducts) allows us to estimate the extent of electron density donation to a proton or a Lewis acid, respectively. The greater the donation, the more the imino nitrogen−carbon bond length should become equivalent to the peripheral C−NMe$_2$ bond lengths. In the dangling guanidine group of **6**, a short C−N$_{guanidine}$ bond [127.6(4) pm] and two long bonds to the peripheral C−NMe$_2$ groups [139.6(4) and 137.8(4) pm] are observed. The differences between these three guanidine C−N bond lengths become much smaller when the guanidine is coordinated to a Lewis acid (e.g. **2**), and become negligible upon protonation as a result of complete charge delocalization (Table 5).

Cyclic Voltammetric Measurements

In order to gain additional information about the synthesized compounds, cyclic voltammetry experiments were carried out. A reversible $Mn^{+3/+2}$ couple could be observed for **2** ($E_{1/2}$ = +0.47 V, $\Delta E_{1/2}$ = 0.11 V, i_a/i_c = 1), along with

Table 5. Bond angle sums [°] and selected guanidine C−N distances [pm] in the non-coordinated guanidine of **6**, the coordinated guanidine in **2**, and the protonated guanidine in bis(tetramethylguanidino)ethane hydrochloride

		[Mo(TMG$_3$tren)(CO)$_3$] (**6**)			
Σ° N(8)	–	Σ° N(9/10)	344.5/358.8	Σ° C(17)	359.9
C(17)−N(8)	127.6(4)	C(17)−N(9)	139.6(4)	C(17)−N(10)	137.8(4)
		[Mn^{II}(TMG$_3$tren)Cl]Cl (**2**)			
Σ° N(1)	359.4	Σ° N(2/3)	357.8/359.6	Σ° C(3)	359.9
C(3)−N(1)	131.9(2)	C(3)−N(2)	135.5(2)	C(3)−N(3)	136.9(2)
		TMG$_2$en·2HCl[11a]			
Σ° N(3)	358.1	Σ° N(1/2)	359.9/359.9	Σ° C(5)	360.0
C(5)−N(3)	133.6(2)	C(5)−N(1)	134.2(2)	C(5)−N(2)	133.8(2)

an additional wave ($E_{1/2}$ = +0.92 V, $\Delta E_{1/2}$ = 0.22 V, i_a/i_c = 4) for the couple $Mn^{+4/+3}$. The latter was irreversible, pointing to rapid decomposition of the oxidized species (Figure 7).

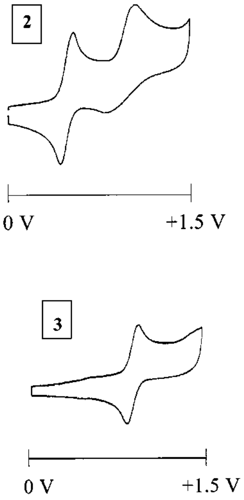

Figure 7. Cyclic voltammograms of **2** and **3** (CH_3CN/TBAP, 2 mm glassy carbon/SCE/Pt, v = 100 mV s^{-1}, 20 °C)

Complex **3** shows only a single wave in the anodic region at $E_{1/2}$ = +0.88 V ($\Delta E_{1/2}$ = 0.09 V, i_a/i_c = 1), corresponding to the reversible couple $Mn^{+3/+2}$. The Mn^{II} → Mn^{III} transition for compound **2** was found to occur at a lower oxidation potential than the corresponding step for **3** owing to the presence of the anionic chloro ligand, which facilitates the oxidation of **2**. The oxidation potential of Mn^{III} → Mn^{IV} does not lie within the window of 0 to 1.5 V.

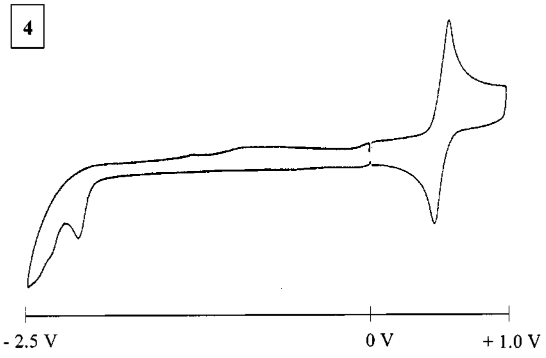

Figure 8. Cyclic voltammogram of **4** (CH_3CN/TBAP, 2 mm glassy carbon/SCE/Pt, v = 100 mV s^{-1}, 20 °C)

Complex **4** displays a potential of $E_{1/2}$ = +0.52 V ($\Delta E_{1/2}$ = 0.11 V) for the Fe^{II} → Fe^{III} electron transfer, i_a/i_c = 1 (Figure 8). The irreversible wave in the cathodic region (− 2.09 V) can only cautiously be assigned to an Fe^{II} → Fe^{I} reduction because of its low intensity and position near the border of the electrochemical window.

The values of the normal potentials can only be compared indirectly due to the different recording conditions (solvent, temperature) but can still be used to draw qualitative conclusions. All the complexes display lower oxidation potentials compared to the redox potentials of the aqua complexes Mn (II → III): +1.54 V; Fe (II → III): +0.77 V[40] as a result of the electron-donating TMG$_3$tren ligand. As expected, the monocationic complex **2** is more easily oxidized than the dicationic compound **3** (Table 6).

Table 6. Selected redox potentials

Metal complex	$E_{1/2}$[40] [V]
$[Mn(H_2O)_6]^{2+}$ (+3/+2)[a]	+1.54
[(**1**)Mn(NCMe)]$^{2+}$ (+3/+2)[b]	+0.88
[(**1**)Mn−Cl]$^{+}$ (+3/+2)[b]	+0.47
$[Fe(H_2O)_6]^{2+}$ (+3/+2)[a]	+0.77
[(**1**)Fe(NCMe)]$^{2+}$ (+3/+2)[b]	+0.52

[a] Recorded in H_2O. − [b] Recorded in MeCN.

Besides the inherent donor abilities of a given ligand, steric factors cannot be neglected with regard to the resulting oxidation potential and stability of the oxidized species.[41] This statement is related to the investigations of Ray[42] and Schrock,[43] who commented on the oxidation potentials of various transition metal complexes with tren-like amido ligands possessing varying degrees of steric strain. We believe that the instability of our oxidized complexes is due to the steric strain of the ligand periphery imposed by the reduced radius of the cation in its oxidized form.

Conclusions

Peralkyloligoguanidines are an unexplored class of multidentate nitrogen ligands within the large family of chelating N-donors typically containing amines, imines (Schiff bases), and azaaromatic building blocks. The novel tripod ligand TMG$_3$tren (**1**), a derivative of tren with three superbasic pentaalkylguanidine donor functions and a geometry constrained to coordinate metal ions preferably in a trigonal-bipyramidal mode, has been introduced. Due to its ability to delocalize positive charge over the three guanidinium moieties, **1** stabilizes cationic and even dicationic complexes, which are not so common for the corresponding parent compounds with tren ligands. However, increasing steric strain on the ligand periphery as a consequence of the decreased ionic radii of highly oxidized metal cations seems to limit the stability of such high-valent species. Initial evidence that larger cations are coordinated more favourably than smaller ones was provided by the bite angle and steric constraints of the tripodal ligand sphere of **1**. Our current interest is focused on the Lewis acid activation of small molecules other than acetonitrile and their transformations in the molecular pocket imposed by the guanidine ligand environment. Furthermore, we are extending our investigation of this class of ligands to other metals and other guanidine building blocks.

Experimental Section

Materials and Methods: All experiments were carried out in glassware that was assembled while hot and cooled under vacuum. Inert gas argon 4.8 was dried with granulated P_4O_{10}. Solvents were purified according to literature procedures and were also kept under an inert gas. Tris(2-aminoethyl)amine and the metal salts were used as purchased from Fluka. Triethylamine was freshly distilled and stored under argon prior to use. Substances sensitive to air and moisture were kept in a nitrogen-flushed glove-box (Braun, Type MB 150 BG-1). − Spectra were recorded with the following spectrometers: NMR: Bruker AM 400 (^{13}C: gated-decoupled). − IR: Bruker IFS 88 FT. − MS (EI, 70 eV): Varian MAT CH-7a. − Elemental analysis: Heraeus CHN-Rapid. − Melting points: Büchi MP B-540 apparatus (uncorrected values). − X-ray crystallography: Enraf−Nonius CAD4 and Siemens P4. − Magnetic susceptibility: Momentum apparatus, using the Evans method.[29]

Electrochemical Measurements: Cyclic voltammetry (CV) was performed with electrochemical equipment from AMEL (Milano) consisting of a Model 552 potentiostat, a Model 563 multipurpose unit, a Nicolet Model 3091 storage oscilloscope, and a Kipp & Zonen Model BD 90 x/y recorder. The electrochemical cell was operated under argon, with glassy carbon, platinum rod, and saturated calomel (SCE) serving as working, counter, and reference electrodes, respectively. For temperature control, the cell was immersed in a thermostatted cooling bath. CV curves were obtained at a scan rate of 100 mV s^{-1} working at 20 °C in MeCN/0.1 M nBu$_4$NClO$_4$.

Caution! Phosgene is a severe toxic agent that can cause pulmonary embolism and in cases of heavy exposure may be lethal. It should only be used in a well-ventilated fume hood. Perchlorate salts are potentially explosive and should be handled with care.

Chlorotetramethylformamidinium Chloride:[19] In a flask fitted with a reflux condenser cryostatted at −30 °C, phosgene was passed through a solution of tetramethylurea (50.00 g, 430 mmol) in toluene (200 mL) kept at 0 °C for 2 h. The phosgene inlet was then closed and the solution was allowed to warm to room temperature under stirring for a period of 24 h, with the reflux condenser being maintained at −30 °C. The precipitate formed was collected by filtration, washed three times with dry diethyl ether, and dried in vacuo. Yield ca. 95%.

1,1,1-Tris{2-[*N*^{2}-(1,1,3,3-tetramethylguanidino)]ethyl}amine (1): To a solution of tris(2-aminoethyl)amine (14.62 g, 100 mmol) and triethylamine (30.36 g, 41.6 mL, 300 mmol) in acetonitrile (50 mL), a solution of $[(Me_2N)_2CCl]Cl$ (51.32 g, 300 mmol) in acetonitrile (150 mL) was slowly added under cooling in an ice bath. After the exothermic reaction had occurred, the mixture was refluxed for 3 h, in the course of which a clear solution was produced. NaOH (12.00 g, 300 mmol) in water (30 mL) was subsequently added under vigorous stirring in order to deprotonate the Et$_3$NHCl. After evaporation of the solvents and excess NEt$_3$, TMG$_3$tren (**1**) was obtained by deprotonation of **1A** [tris(hydrochloride)] with 50% KOH (50 mL) and extracting the aqueous phase with MeCN (3 × 50 mL). The combined extracts were concentrated to dryness and the residue was taken up in warm hexane. The resulting solution was dried with MgSO$_4$, stirred with activated charcoal while still warm to eliminate impurities, and then filtered through Celite. Finally, removal of the solvent and drying of the residue in vacuo gave TMG$_3$tren (**1**) as a pale-yellow slowly crystallizing oil in 86% yield (38.03 g, 86 mmol). − M.p. 59−60 °C. − ^{1}H NMR (200.1 MHz, CDCl$_3$, 25 °C, CDCl$_3$): δ = 3.23 (m, 6 H, CH$_2$), 2.84−2.59 (m, 42 H, CH$_2$ + CH$_3$). − ^{13}C NMR (50.3 MHz, CDCl$_3$, 25 °C, CDCl$_3$): δ = 160.4 (CN$_3$), 58.2, 48.3 (CH$_2$), 39.6, 38.8 (CH$_3$). − IR (film): $\tilde{\nu}$ = 2880 s, 2839 sh, 1620 s [ν(C=N)], 1495 m, 1453 w, 1364 s, 1236 w, 1130 m, 1062 w, 989 w cm^{-1}. − UV/Vis (MeCN): λ_{max} (ε) = 216 nm (24000 mol^{-1} dm^3 cm^{-1}). − MS (70 eV, EI): m/z (%) = 439.0 (1) $[M - H]^+$, 312.0 (100) $[C_{15}H_{34}N_7]^+$, 210.0 (73) $[C_{11}H_{22}N_4]^+$, 142.0 (43) $[C_7H_{16}N_3]^+$, 128.0 (54) $[C_6H_{14}N_3]^+$, 85.0 (82) $[C_4H_9N_2]^+$, 72.0 (26) $[C_3H_8N_2]^+$, 58.0 (80) $[C_2H_6N_2]^+$. − $C_{21}H_{48}N_{10}$ (440.7): calcd. C 57.24, H 10.98, N 31.78; found C 56.87, H 10.83, N 31.45.

1,1,1-Tris{2-[*N*^{2}-(1,1,3,3-tetramethylguanidinium)]ethyl}amine Trichloride (1A; 1·3HCl): The hydrochloride salt could be obtained by treating the free oligoguanidine base (0.57 g, 1.13 mmol) dissolved in EtOH (10 mL) with the requisite amount of 1 M HCl (3.5 mL). Recrystallization from EtOH/Et$_2$O gave strongly hygroscopic, colorless crystals that analyzed as the trihydrate. Yield 0.51 g (0.84 mmol, 74%). Following our synthesis of **1**, the TMG$_3$tren tris(hydrochloride) **1A** could also be obtained without isolation of the free base. After deprotonation of Et$_3$NHCl with an equimolar amount of NaOH dissolved in the minimum volume of water and removing all volatiles in vacuo, the crude tris(hydrochloride) was redissolved in warm MeCN. The resulting solution was dried with MgSO$_4$, treated with activated charcoal, passed through Celite, and the solvent was evaporated. The residue was washed with dry diethyl ether and dried in vacuo to yield the tris(hydrochloride) **1A** as a colorless, strongly hygroscopic solid that analyzed as the trihydrate. − M.p. 153 °C (dec.). − ^{1}H NMR (200.1 MHz, CD$_3$CN, 25 °C, CD$_3$CN): δ = 8.91 (br. s, 3 H, NH), 3.76 (br., 12 H, CH$_2$), 2.92 (s, 36 H, CH$_3$), 2.55 (br., 6 H, H$_2$O). − ^{13}C NMR (50.3 MHz, CD$_3$CN, 25 °C, CD$_3$CN): δ = 161.3 (CN$_3$), 51.7 (CH$_2$), 39.5 (CH$_3$), 39.3 (CH$_2$). − IR (KBr): $\tilde{\nu}$ = 3431 s, 1627 s, 1584 s [ν(C=N)], 1457 m, 1406 s, 1311 w, 1233 w, 1176 w, 1136 w, 1067 w, 900 m, 668 br cm^{-1}. − UV/Vis (H$_2$O): λ_{max} (ε) = 213 nm (34000 mol^{-1} dm^3

cm^{-1}). − MS (70 eV, EI): *m*/*z* (%) = 440.0 (1) [M − 3 HCl]$^+$, 312.0 (95) [$C_{15}H_{34}N_7$]$^+$, 255.0 (28) [$C_{12}H_{27}N_6$]$^+$, 222.0 (17) [$C_{10}H_{18}N_6$]$^+$, 210.0 (67) [$C_{11}H_{22}N_4$]$^+$, 197.0 (28) [$C_{10}H_{21}N_4$]$^+$, 142.0 (91) [$C_7H_{16}N_3$]$^+$, 128.0 (94) [$C_6H_{14}N_3$]$^+$, 97.0 (45) [$C_6H_{11}N$]$^+$, 85.0 (94) [$C_4H_9N_2$]$^+$, 71.0 (64) [$C_3H_7N_2$]$^+$, 58.0 (95) [$C_2H_6N_2$]$^+$, 36.0 (100) [HCl]$^+$. − $C_{21}H_{51}Cl_3N_{10}\cdot 3H_2O$ (604.1): calcd. C 41.75, H 9.51, N 23.19; found C 41.69, H 9.86, N 22.83.

General Procedure for the Synthesis of the TMG$_3$tren Complexes: The metal salts were first dehydrated by the orthoester method.[25] Thus, the hydrated salts were stirred in dry EtOH containing twice the molar amount, with respect to the water present in the salt, of triethyl orthoformate at 60 °C for 1 h. Equimolar amounts of the dehydrated metal salt and **1** were separately dissolved in 5-mL portions of dry MeCN under argon. These solutions were then combined and the resulting mixture was stirred for 30 min. at 40−50 °C, filtered through Celite, and concentrated to a volume of ca. 3 mL. The complex was then precipitated by the addition of dry diethyl ether (10 mL), washed with absolute diethyl ether, and dried in vacuo. Single crystals suitable for X-ray analysis could be grown by slow diffusion of diethyl ether into the respective acetonitrile solutions.

Chloro{1,1,1-tris[*N*^{2}-(1,1,3,3-tetramethylguanidino)ethyl]amine}manganese(II) Chloride (2): The general procedure was followed using $MnCl_2$ (0.15 g, 1.12 mmol) and **1** (0.66 g, 1.15 mmol). Yield 0.59 g (1.04 mmol, 93%) as colorless crystals. − M.p. 230 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 2947 m, 2881 m, 1618 s, 1573 s [ν(C=N)], 1553 vs, 1427 m, 1395 m, 1342 w, 1164 sh, 1151 s, 1075 m, 891 m, 764 m cm^{-1}. − UV/Vis (MeCN): λ_{max} (ε) = 226 nm (49000 mol^{-1} dm^3 cm^{-1}). − MS (70 eV, EI): *m*/*z* = 312.0 (60) [$C_{15}H_{34}N_7$]$^+$, 210.0 (33) [$C_{11}H_{22}N_4$]$^+$, 142.0 (32) [$C_7H_{16}N_3$]$^+$, 128.0 (43) [$C_6H_{14}N_3$]$^+$, 85.0 (100) [$C_4H_9N_2$]$^+$, 71.0 (31) [$C_3H_7N_2$]$^+$, 58.0 (74) [$C_2H_6N_2$]$^+$, 28.0 (80) [CH_2N]$^+$. − μ_{eff} (Evans method, 5% [D$_6$]benzene in CD_3CN, 25 °C): μ_B/mol = 5.9±0.1. − CV (MeCN/TBAP, 2 mm GC/SCE/Pt, v = 100 mV s^{-1}, 20 °C): $E_{1/2}(+3/+2)$ = 0.47 V, $\Delta E_{1/2}(+3/+2)$ = 0.11 V, $I_{pa/pc}$ = 1; $E_{1/2}(+4/+3)$ = 0.92 V, $\Delta E_{1/2}(+4/+3)$ = 0.22 V, $I_{pa/pc}$ = 4. − $C_{21}H_{48}Cl_2MnN_{10}$ (566.5): calcd. C 44.52, H 8.54, N 24.72; found C 44.06, H 8.53, N 23.73.

Acetonitrile(1,1,1-tris{2-[*N*^{2}-(1,1,3,3-tetramethylguanidino)]-ethyl}amine)manganese(II) Diperchlorate (3): The general procedure was followed using $Mn(ClO_4)_2$ (0.47 g, 1.86 mmol) and **1** (0.84 g, 1.90 mmol). Yield 1.30 g (1.77 mmol, 95%) as colorless crystals. − IR (KBr): $\tilde{\nu}$ = 2893 m, 2275 w [ν(C≡N)], 1616 sh, 1565 vs, 1535 s [ν(C=N)], 1463 m, 1427 m, 1398 s, 1346 w, 1257 w, 1164 m, 1092 vs [ν(Cl=O)], 906 w, 892 w, 769 m, 624 s cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 128.0 (24) [$C_6H_{14}N_3$]$^+$, 85.0 (100) [$C_4H_9N_2$]$^+$, 71.0 (25) [$C_3H_7N_2$]$^+$, 44.0 (46) [C_2H_6N]$^+$. − μ_{eff} (Evans method, 5% [D$_6$]benzene in CD_3CN, 25 °C): μ_B/mol = 5.8±0.1. − CV (MeCN/TBAP, 2 mm GC/SCE/Pt, v = 100 mV s^{-1}, 20 °C): $E_{1/2}(+3/+2)$ = 0.88 V, $\Delta E_{1/2}(+3/+2)$ = 0.09 V, $I_{pa/pc}$ = 1. − $C_{23}H_{51}Cl_2MnN_{11}O_8$ (735.6): calcd. C 37.56, H 6.99, N 20.95; found C 37.42, H 6.95, N 20.62

Table 7. Crystal data and details of the structure refinement for **2**, **3**, and **4**

Complex	[Mn^{II}(TMG$_3$tren)Cl]Cl (**2**)	[Mn^{II}(TMG$_3$tren)NCMe](ClO_4)$_2$ (**3**)	[Fe^{II}(TMG$_3$tren)NCMe](ClO_4)$_2$ (**4**)
Empirical formula	$C_{21}H_{48}Cl_2MnN_{10}$	$C_{23}H_{51}Cl_2MnN_{11}O_8$	$C_{23}H_{51}Cl_2FeN_{11}O_8$
Molecular mass [g mol^{-1}]	607.59	735.59	736.50
Temperature [K]	223(2)	198(2)	198(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a [pm]	1174.6(3)	1619.1(1)	1614.4(1)
b [pm]	1227.4(2)	1333.6(1)	1329.3(1)
c [pm]	1298.1(2)	1651.1(1)	1641.7(1)
α [°]	92.451(9)	90	90
β [°]	96.182(10)	94.669(10)	94.460(10)
γ [°]	117.907(10)	90	90
Volume [Å^3]	1635.1(5)	3553.1(5)	3512.7(4)
Z	2	4	4
ρ [Mg m^{-3}]	1.234	1.375	1.393
μ [mm^{-1}]	0.598	0.580	0.640
F(000)	650	1556	1560
Crystal size [mm]	0.40 × 0.30 × 0.20	0.39 × 0.33 × 0.15	0.28 × 0.21 × 0.10
Diffractometer	Siemens P4	Enraf Nonius CAD4	Enraf Nonius CAD4
Scan technique	ω-scan	ω-scan	ω-scan
θ range for data collection [°]	1.89−27.71	2.48−24.99	3.06−24.98
Index ranges	$0 \le h \le 13$	$0 \le h \le 19$	$-19 \le h \le 0$
	$-14 \le k \le 14$	$0 \le k \le 15$	$-15 \le k \le 0$
	$-14 \le l \le 14$	$-19 \le l \le 19$	$-19 \le l \le 19$
Reflections collected	5996	6462	6379
Independent reflections	5720	6227	6150
R_{int}	0.0461	0.0169	0.0309
Observed reflections [$F \ge 4\sigma(F)$]	5230	5272	3741
Data/restraints/parameters	5720/0/366	6227/0/430	6150/0/430
Goodness of fit on F^2	1.033	1.106	1.032
$R1$ [$F_0 \ge 4\sigma(F)$][a]	0.0327	0.0487	0.0599
wR_2 (all data)[a]	0.0916	0.1655	0.1490
Transmission (min./max.)	0.8898/0.7959	0.9181/0.0855	0.9388/0.8412
Largest diff. peak and hole [eÅ^{-3}]	0.364/−0.316	0.532/−0.448	0.529/−0.364

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Acetonitrile(1,1,1-tris{2-[N^2-(1,1,3,3-tetramethylguanidino)]ethyl}amine)iron(II) Diperchlorate (4): The general procedure was followed using $Fe(ClO_4)_2$ (0.32 g, 1.26 mmol) and **1** (0.57 g, 1.30 mmol). Yield 0.83 g (1.13 mmol, 89%) as light-yellow crystals. − IR (KBr): $\tilde{\nu}$ = 2893 m, 2270 w [ν(C≡N)], 1614 sh, 1558 vs, 1533 sh [ν(C=N)], 1463 m, 1427 m, 1399 s, 1346 m, 1257 w, 1166 m, 1090 vs [ν(Cl=O)], 908 w, 894 m, 772 m, 623 s cm^{-1}. − μ_{eff} (Evans method, 5% [D_6]benzene in CD_3CN, 25 °C): μ_B/mol = 5.4±0.1. − CV (MeCN/TBAP, 2 mm GC/SCE/Pt, v = 100 mV s^{-1}, 20 °C): $E_{1/2}(+3/+2) = 0.52$ V, $\Delta E_{1/2}(+3/+2) = 0.11$ V, $I_{pa/pc} = 1$, $E_{1/2}(+2/+1) = -2.09$ V. − $C_{23}H_{51}Cl_2FeN_{11}O_8$ (736.5): calcd. C 37.51, H 6.98, N 20.92; found C 36.90, H 7.03, N 20.52.

Acetonitrile(1,1,1-tris{2-[N^2-(1,1,3,3-tetramethylguanidino)]ethyl}amine)zinc(II) Diperchlorate (5): The general procedure was followed using $Zn(ClO_4)_2$ (0.41 g, 1.54 mmol) and **1** (0.71 g, 1.60 mmol). Yield 0.96 g (1.29 mmol, 84%) as colorless crystals. − ^{1}H NMR (200.1 MHz, $CDCl_3$, 25 °C, $CDCl_3$): δ = 3.02−2.77 (br. m, 48 H, CH_3 + CH_2), 2.04 (s, 3 H, $NCCH_3$). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C, $CDCl_3$): δ = 165.9 (CN_3), 53.8 (CH_2), 46.6 (CH_2), 39.3 (CH_3). − IR (KBr): $\tilde{\nu}$ = 2948 w, 2894 w, 2251 w [ν(C≡N)], 1620 sh, 1571 s, 1555 s [ν(C=N)], 1463 w, 1427 m, 1398 s, 1348 w, 1250 w, 1165 m, 1146 m, 1096 vs [ν(Cl=O)], 894 w, 766 w, 625 m cm^{-1}. − MS (70 eV, EI): m/z (%) = 85.0 (100) $[C_4H_9N_2]^+$, 71.0 (33) $[C_3H_7N_2]^+$, 44.0 (60) $[C_2H_6N]^+$. − $C_{23}H_{51}Cl_2N_{11}O_8Zn$ (746.0): calcd. C 37.03, H 6.89, N 20.65; found C 36.88, H 7.09, N 20.53.

Tricarbonyl(*fac*-tris{2-[N^2-(1,1,3,3-tetramethylguanidino)]ethyl}amine)molybdenum(0) (6): The general procedure was followed using $[Mo(CH_3CN)_3(CO)_3]$ (0.42 g, 1.40 mmol) and **1** (0.88 g, 2.00 mmol). Yield 0.69 g (1.11 mmol, 79%) as a yellow powder. − ^{1}H NMR (300.1 MHz, CD_3CN, 25 °C, CD_3CN): δ = 3.50 (m, 2 H, CH_2), 3.16 (m, 6 H, CH_2), 2.70 (m, 40 H, CH_3 + CH_2). − ^{13}C NMR (75.5 MHz, CD_3CN, 25 °C, CD_3CN): δ = 232.7, 230.1 (CO), 166.5 (CN_3, coordinated TMG), 160.8 (CN_3, free TMG), 66.1, 57.2, 50.7, 46.2 (CH_2), 39.8, 39.3 (CH_3). − IR (KBr): $\tilde{\nu}$ = 2889 s, 1883 s, 1740 vs, 1730 sh [ν(C=O)], 1619 s, 1577 s, 1553 sh, 1515 s [ν(C=N)], 1455 m, 1424 w, 1390 s, 1236 m, 1142 m, 1060 w, 1026 w, 976 w, 895 w, 763 w cm^{-1}. − MS (70 eV, EI): m/z (%) = 621.0 (1) $[M]^+$, 594.0 (2) $[M - CO]^+$, 312.0 (98) $[C_{15}H_{34}N_7]^+$, 255.0 (17) $[C_{11}H_{25}N_7]^+$, 210.0 (52) $[C_{11}H_{22}N_4]^+$, 142.0 (60) $[C_7H_{16}N_3]^+$, 128.0 (64) $[C_6H_{14}N_3]^+$, 101.0 (40) $[C_5H_{13}N_2]^+$, 85.0 (96) $[C_4H_9N_2]^+$, 72.0 (53) $[C_3H_8N_2]^+$, 58.0 (100) $[C_2H_6N_2]^+$, 44.0 (37) $[C_2H_6N]^+$, 28.0 (72) $[CH_2N]^+$. − $C_{21}H_{48}MoN_{10}O_3$ (620.7): calcd. C 46.45, H 7.80, N 22.57; found C 45.89, H 8.07, N 22.29.

X-ray Structure Analysis: Crystal data and experimental conditions are listed in Tables 7 and 8. The molecular structures are illustrated as SCHAKAL[44] plots in Figures 1−6. Selected bond lengths and angles with standard deviations in parentheses are presented in Table 1. Intensity data were collected with graphite-monochromated Mo-K_α radiation (λ = 71.069 pm). The collected reflections were corrected for Lorentz and polarization effects. The structures

Table 8. Crystal data and details of the structure refinement for **5** and **6**

Complex	$[Zn^{II}(TMG_3tren)NCMe](ClO_4)_2$ (**5**)	$[Mo^0(TMG_3tren)(CO)_3]$ (**6**)
Empirical formula	$C_{23}H_{51}Cl_2N_{11}O_8Zn$	$C_{21}H_{48}MoN_{10}O_3$
Molecular mass [g mol^{-1}]	746.02	661.72
Temperature [K]	193(2)	223(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a [pm]	1618.2(10)	1006.0(2)
b [pm]	1320.4(9)	1259.5(2)
c [pm]	1634.3(6)	1529.3(2)
α [°]	90	66.470(12)
β [°]	94.63(4)	75.237(9)
γ [°]	90	76.840(15)
Volume [Å^3]	3481(3)	1700.3(5)
Z	4	2
ρ [Mg m^{-3}]	1.424	1.292
μ [mm^{-1}]	0.918	0.429
F(000)	1576	700
Crystal size [mm]	0.25 × 0.25 × 0.25	0.45 × 0.35 × 0.25
Diffractometer	Enraf Nonius CAD4	Siemens P4
Scan technique	ω-scan	ω-scan
θ range for data collection [°]	2.30−26.01	1.78−25.04
Index ranges	$-19 \leq h \leq 19$	$0 \leq h \leq 11$
	$-16 \leq k \leq 0$	$-13 \leq k \leq 13$
	$0 \leq l \leq 20$	$-14 \leq l \leq 14$
Reflections collected	7086	5789
Independent reflections	6834	5483
R_{int}	0.0194	0.0281
Observed reflections [$F \geq 4\sigma(F)$]	5251	4982
Data/restraints/parameters	6834/0/418	5483/0/403
Goodness of fit on F^2	1.038	1.010
$R1$ [$F_0 \geq 4\sigma(F)$][a]	0.0418	0.0334
wR_2 (all data)[a]	0.1192	0.0907
Transmission (min./max.)	0.8030/0.8030	0.9004/0.8305
Largest diff. peak and hole [eÅ^{-3}]	0.595/−0.537	0.722/−0.619

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

of **2**, **5**, and **6** were solved by direct methods and refined by full-matrix least-squares methods on F^2, while those of **3** and **4** were solved using SIR-92.[45] Hydrogen atom positions were calculated and isotropically refined except for those of H23A, B, C of **3** and **4**, which were found and then isotropically refined. An empirical absorption correction based on the ψ-scans of 9 reflections ($T_{\min} = 0.4508$, $T_{\max} = 0.5098$) was performed for **4**.[46]

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