Electronic Supporting Information

Increasing the solubility of strong reducing agents containing Mo_2^{4+} units and alkyl-substituted guanidinate ligands

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The following abbreviations are used in this section (when available, CCDC numbers are given in parentheses):

HTMhpp = 3,3,9,9-tetramethyl-1,5,7-triazabicyclo[4.4.0]dec-4-ene

HTEhpp = 3,3,9,9-tetraethyl-1,5,7-triazabicyclo[4.4.0]dec-4-ene (CCDC reference number 645823).

SI·HCl = *N,N*-bis(2,2-dimethyl-3-iminohydroxypropyl)amine hydrochloride (CCDC reference number 645817).

SI = *N,N*-bis(2,2-dimethyl-3-iminohydroxypropyl)amine (CCDC reference number 645818).

SII = *N,N*-bis(3-amino-2,2-dimethylpropyl)amine.

Cd(**SII**)$_2$(NO$_3$)$_2$·H$_2$O = (CCDC reference number 645819).

[H$_2$TMhpp][HCO$_3$] = (CCDC reference number 645820).

SIII·HCl·H$_2$O = *N,N*-bis(2,2-diethyl-3-iminohydroxypropyl)amine hydrochloride monohydrate (CCDC reference number 645821).

Cd(**SIV**)$_2$(NO$_3$)$_2$·EtOH = (CCDC reference number 645822).

SIV = *N,N*-bis(3-amino-2,2-diethyl-propyl)amine.

Syntheses of Bicyclic Guanidinate Ligand Precursors

Preparation of 3,3,9,9-tetramethyl-1,5,7-triazabicyclo[4.4.0]dec-4-ene (HTMhpp).

This procedure was modified from that in a patent[1] and is described in Scheme 2 of the main text. *N,N*-bis(3-amino-2,2-dimethylpropyl)amine (2.00 g, 10.7 mmol) was dissolved in a mixture of 150 mL of *p*-xylene and CS$_2$ (0.650 mL. 0.823 g, 10.8 mmol). To this mixture *p*-toluenesulfonic acid monohydrate (0.103 g, 0.541 mmol) was then added.

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[1] A. Hopfinger, M. Söderlund and S. Reni, *Finn. Pat.*, 82445, 1988.

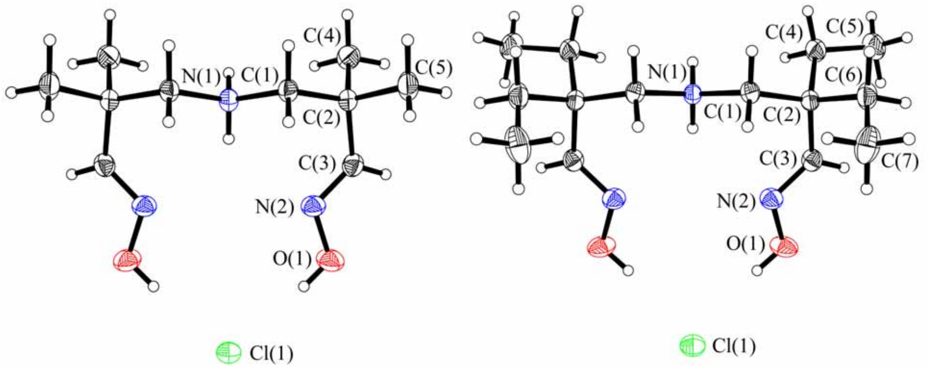
Initially a colorless precipitate formed. The solution was heated to reflux under nitrogen causing the precipitate to dissolve rapidly. The solution was refluxed until evolution of H_2S ceased (*ca* 3 days). While still hot, the solution was decanted away from any solid or oily residue present in the flask and the solution was then allowed to cool to room temperature under nitrogen. The solvent was then removed under vacuum and the resulting colorless microcrystalline powder was washed with acetonitrile (20 mL) and hexanes (5 mL). The solid was then placed in an oven at 100 °C for 1 h. Yield: 1.618 g (8.30 mmol, 78 %). IR (KBr, cm^{-1}): 3260 (w), 3188 (m), 3114 (m), 3064 (m), 3034 (m), 2950 (s), 2899 (s), 2858 (s), 1656 (s), 1572 (w), 1517 (s), 1478 (m), 1464 (m), 1442 (m), 1387 (m), 1360 (m), 1310 (m), 1297 (m), 1257 (s), 1212 (w), 1167 (s), 1113 (w), 1057 (m), 1023 (w), 1007 (w), 934 (w), 814 (w), 744 (w), 715 (w), 635 (w), 561 (w), 481 (w). ^1H NMR (C_6D_6, ppm): 5.49 (bs, 1H (NH)), 2.87 (s, 4H (CH_2)), 2.35 (s, 4H (CH_2)), 0.86 (s, 12 H (CH_3)). Mass Spectrum (ESI^+): Calcd. ($M+H^+$): 196 amu. Found 196 amu. Crystals of the bicarbonate salt, [H_2TMhpp](HCO_3), suitable for X-ray diffraction, were produced by slow evaporation in air of a solution of HTMhpp in 90% v/v EtOH/H_2O.

Preparation of 3,3,9,9-tetraethyl-1,5,7-triazabicyclo[4.4.0]dec-4-ene (HTEhpp). The procedure was similar to that used in the synthesis of HTMhpp. *N,N*-bis(3-amino-2,2-diethyl-propyl)amine (2.0 g, 8.2 mmol) was dissolved in a mixture of 150 mL of *p*-xylene and CS_2 (0.48 mL, 0.62 g, 8.2 mmol). To this solution the monohydrate of *p*-toluenesulfonic acid (0.078 g, 0.41 mmol) was then added. Initially a white precipitate formed but it rapidly dissolved as the solution was heated to reflux under nitrogen. Heating was continued until evolution of H_2S ceased. While still hot, the solution was decanted away from any solid or oily residue in the flask and then it was allowed to cool to room temperature under nitrogen. The solvent was removed under vacuum and the resulting colorless microcrystalline powder was washed with acetonitrile (20 mL) and hexanes (5 mL). The solid was then dried in an oven at 100 °C for 1 h. Yield: 0.89 g (3.6 mmol, 44%) IR (KBr, cm^{-1}): 3272 (w), 3197 (m), 3145 (m), 3071 (m), 3039 (m), 2965 (s), 2935 (s), 2861 (s), 2807 (s), 1650 (s), 1578 (w), 1520 (s), 1484 (m), 1461 (s), 1447 (s), 1375 (s), 1310 (m), 1292 (m), 1265 (m), 1232 (m), 1193 (w), 1153 (m), 1115 (w), 1069 (m), 1029 (w), 1005 (w), 941 (w), 914 (w), 804 (w), 770 (w), 736 (w), 711 (w), 679 (w), 651 (w), 566 (w), 528 (w). ^1H NMR (C_6D_6, ppm): 2.89 (s, 4H (CH_2)), 2.42 (s, 4H

($\mathrm{CH_2}$)), 1.35 – 1.16 (m, 8H ($-\mathrm{C}\mathit{H}_2\mathrm{CH}_3$)), 0.69 (t, 12H ($-\mathrm{CH_2C}\mathit{H}_3$)). Mass Spectrum (ESI$^+$): Calcd. (M+H$^+$): 251 amu. Found 251 amu. Colorless plate crystals, suitable for X-ray diffraction, were produced by slow evaporation of a *p*-xylene solution of HTEhpp under vacuum.

Structures of Ligand Precursors, Some Intermediates and Some Derivatives

(for intermediates, see Scheme 2 of the manuscript)



(a) (b)

Fig. S1 Structures of the salts (a) *N,N*-bis(2,2-dimethyl-3-iminohydroxypropyl)amine hydrochloride, **SI·HCl** and (b) *N,N*-bis(2,2-diethyl-3-iminohydroxypropyl)amine hydrochloride monohydrate, **SIII·HCl·H$_2$O**. Displacement ellipsoids are drawn at the 50% probability level. Interstitial solvent molecules are omitted for clarity.

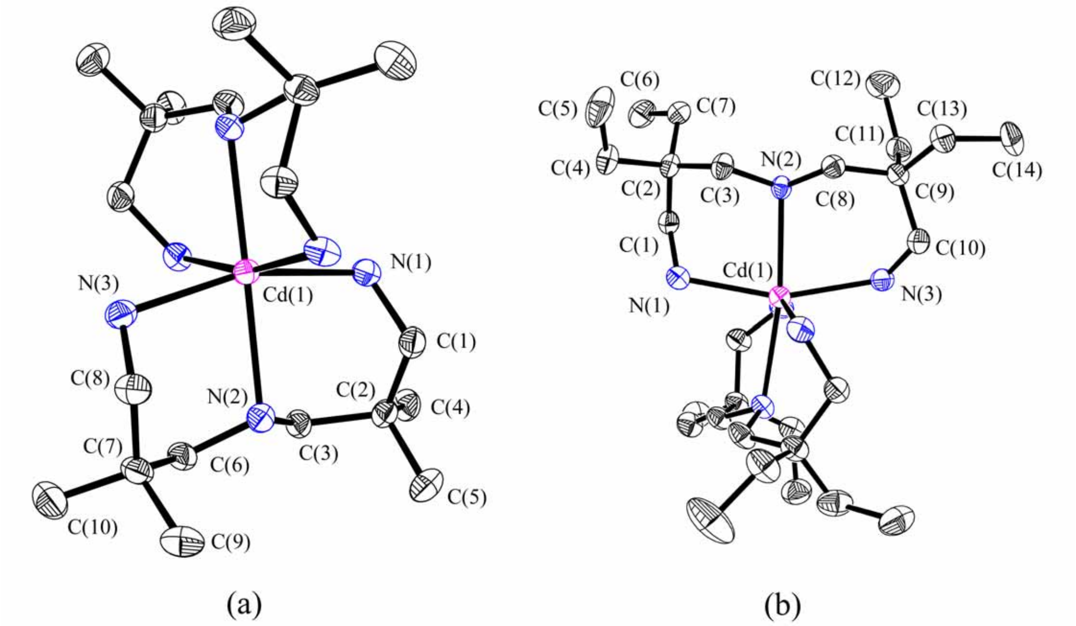


Fig. S2 Structure of (a) Cd(*N,N*-bis(3-amino-2,2-dimethylpropyl)amine)$_2$(NO$_3$)$_2$ Cd(**SII**)$_2$(NO$_3$)$_2$ and (b) Cd(*N,N*-bis(3-amino-2,2-diethyl-propyl)amine)$_2$(NO$_3$)$_2$·EtOH, Cd(**SIV**)$_2$(NO$_3$)$_2$·EtOH Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules and hydrogen atoms omitted for clarity.

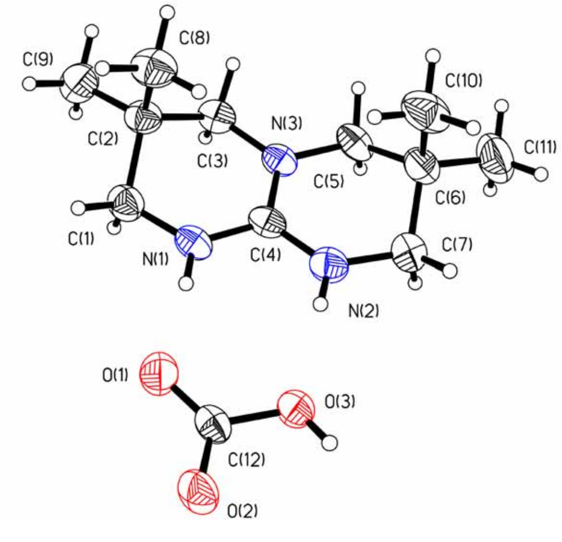


Fig. S3 The structure of the salt [H$_2$TMhpp](HCO$_3$). Ellipsoids are drawn at the 50% probability level. N(1)–C(4) = 1.334(2) Å, N(2)–C(4) = 1.335(2) Å, N(3)–C(4) = 1.333(2) Å. N(1)–C(4) –N(2) = 118.3(2)°, N(1)–C(4)–N(3) = 121.0(2)°, N(2)–C(4)–N(3) = 120.6(2)°.

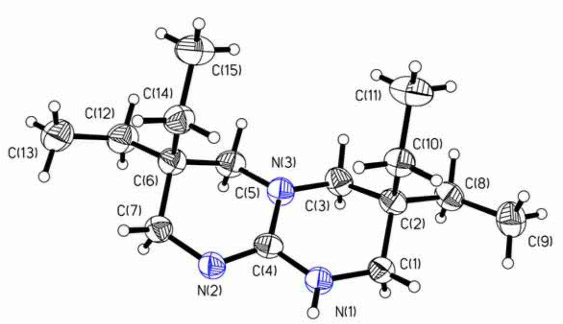


Fig. S4 The structure of HTEhpp. Ellipsoids are drawn at the 50% probability level. N(1)–C(4) = 1.355(2) Å, N(2)–C(4) = 1.299(2) Å, N(3)–C(4) = 1.382(2) Å. N(1)–C(4)–N(2) = 118.2(1)°, N(1)–C(4)–N(3) = 117.3(1)°, N(2)–C(4)–N(3) = 124.4(1)°.

X-ray Crystallography of Organic Derivatives. Single crystals of **SI**, **SI**·HCl, Cd(**SII**)$_2$(NO$_3$)$_2$·H$_2$O, [H$_2$TMhpp][HCO$_3$], **SIII**·HCl, Cd(**SIV**)$_2$(NO$_3$)$_2$·EtOH and HTEhpp were placed in a cryoloop with a minimum of silicone grease. Data were collected at 213 K on a Bruker SMART area detector using the programs SMART[2] and SAINT.[3] The crystal structures were solved via direct methods and refined using SHELXL-97.[4] Hydrogen atoms were placed at calculated positions. Non-hydrogen atoms were refined with anisotropic displacement parameters. Cell parameters and refinement results for organic compounds are summarized in Table S1.

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[2] *SMART Software for the CCD Detector System*, version 5.05; Bruker Analytical X-ray Systems, Inc.:, Madison, WI, 1998.

[3] *SAINT Data Reduction Software*, version 6.36A; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2002.

[4] Sheldrick, G. M. SHELXTL, version 6.12; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000.

Table S1 Crystallographic parameters for **SI**·HCl, **SI**, Cd(**SII**)$_2$(NO$_3$)$_2$·H$_2$O, [H$_2$TMhpp][HCO$_3$], **SIII**·HCl, Cd(**SIV**)$_2$(NO$_3$)$_2$·EtOH and HTEhpp

Compound	**SI**·HCl	**SI**	Cd(**SII**)$_2$(NO$_3$)$_2$·H$_2$O	[H$_2$TMhpp][HCO$_3$]	**SIII**·HCl	Cd(**SIV**)$_2$(NO$_3$)$_2$·EtOH	HTEhpp
Empirical formula	$C_{10}H_{22}ClN_3O_2$	$C_{10}H_{21}N_3O_2$	$C_{20}H_{52}CdN_8O_7$	$C_{12}H_{23}N_3O_3$	$C_{14}H_{32}ClN_3O_3$	$C_{30}H_{72}CdN_8O_7$	$C_{15}H_{29}N_3$
F W	251.76	215.30	629.10	257.33	325.88	769.36	251.41
Space group	*Cmca*	$P4_2/n$	*Cc*	$P2_1/c$	*Pnma*	$P\bar{1}$	$P\bar{1}$
a/Å	18.835(2)	19.424(2)	14.898(1)	13.853(3)	12.5762(9)	10.351(2)	5.833(2)
b/Å	8.1735(7)	19.424(2)	20.009(1)	15.973(4)	21.295(4)	12.056(3)	10.569(3)
c/Å	17.420(2)	6.843(1)	9.9762(7)	13.067(3)	6.6890(7)	16.131(4)	12.505(4)
α/°	90	90	90	90	90	78.651(5)	93.964(5)
β/°	90	90	97.611(1)	99.038(4)	90	77.981(6)	96.108(5)
γ/°	90	90	90	90	90	84.069(6)	97.355(5)
V/Å^3	2681.7(4)	2581.8(6)	2947.6(4)	2856(1)	1791.4(4)	1926.4(8)	757.5(4)
Z	8	8	4	8	4	2	2
d_{calc}/g cm^{-3}	1.247	1.108	1.418	1.197	1.208	1.326	1.102
μ/mm^{-1}	0.278	0.078	0.791	0.086	0.227	0.618	0.066
T/K	213(2)	213(2)	213(2)	213(2)	213(2)	213(2)	213(2)
$R1^a$	0.0380	0.0595	0.0148	0.0604	0.0406	0.0318	0.0495
$wR2^b$	0.0836	0.1561	0.0392	0.1218	0.1049	0.0885	0.1493

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$
[b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$

Table S2 Selected interatomic distances in **SI**, **SI**·HCl and **SIII**·HCl

Compound	N(1)–C(1)	N(2)–C(3)	N(2)–O(1)	O(1)–Cl(1)
SI	1.449[4]	1.261[4]	1.416[4]	–
SI·HCl	1.502(2)	1.261(2)	1.405(2)	3.054(1)
SIII·HCl	1.503(2)	1.258(2)	1.409(2)	3.098(1)

Table S3 Cd–N distances in $Cd(Amine)_2^{2+}$ complexes

Compound	Cd–N(1)	Cd–(N2)	Cd–N(3)	Ref
(3-aminopropyl)-1,3-propanediamine	2.351[5]	2.394[5]	2.385[4]	a
(2-aminoethyl)-1,3-propanediamine	2.339[6]	2.406[8]	2.375[4]	a
ethylenediamine	2.340(2)	2.431(2)	2.336(2)	a
SII	2.375[4]	2.456[3]	2.357[4]	this work
SIV	2.331[3]	2.490[3]	2.343[3]	this work

[a] Bartoszak-Adanska, E.; Bregier-Jarzebowska, R.; Lmozik, L. *Polyhedron*, 2002, **21**, 739.