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Article

Homologues of the Easily Ionized Compound $Mo_2(hpp)_4$ Containing Smaller Bicyclic Guanidinates

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Two bicyclic guanidinate ligands consisting of 5,5-membered (tbo) and 5,6-membered (tbn) rings have been used for the preparation of dimolybdenum compounds, such as $Mo_2(tbo)_4$ and $Mo_2(tbo)_4Cl$, and species containing $Mo_2(tbn)_4^{n+}$ with $n = 0–2$. The compounds with quadruply bonded Mo_2^{4+} species are strong reducing agents and have potentials of about –1 V (vs Ag/AgCl) for the $Mo_2^{5+/4+}$ process. The structure of the THF solvate of $Mo_2(tbo)_4$ shows the longest Mo–Mo bond distance, 2.1453(4) Å, for a quadruply bonded species, and this is due to a large divergent angle induced by the geometry of the ligand. This distance increases to 2.2305(8) Å upon oxidation by CH_2Cl_2 to $Mo_2(tbo)_4Cl$. For the 5,6-membered-ring ligand tbn, even though the divergent angle is large compared to formamidinate ligands, it is not as large as that in tbo, and the Mo–Mo distance in $Mo_2(tbn)_4$, 2.082(1) Å, is in the normal range for paddlewheel Mo_2^{4+} compounds. This distance increases to 2.2233(8) Å upon oxidation by O_2 in CH_2Cl_2, which forms $Mo_2(tbn)_4Cl_2 \cdot CH_2Cl_2$.

Introduction

The hpp ligand, **I** (hpp = anion of the guanidine-type compound 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine), has now been widely used to make paddlewheel compounds of the type $M_2(hpp)_4L_2$, where the axial ligands, L, may or may not be present.[1] The hpp ligand has two principal advantages: (1) It has exceptional stability under harsh reaction conditions[2] owing to its bicyclic structure. (2) It has the ability to stabilize the M_2^{n+} unit in very high oxidation states, such as in Re_2^{7+}[3] and Os_2^{7+}.[4] Closely related to this second property is the fact that when the M_2 unit in an $M_2(hpp)_4$ molecule is in a low oxidation state, as in an M_2^{4+} species, the molecule has a very low ionization potential. This is exemplified in the extreme degree by the $W_2(hpp)_4$ molecule,[5] which has an onset ionization potential (3.51 eV) even lower than that of the Cs atom (3.89 eV).[6] Even for the Mo analogue, which has a higher ionization potential (4.01 eV) than the W complex, this potential is lower than that of Fr and Rb atoms.[5a] The ease of removal of electrons is also reflected in the redox potentials in solution. When the oxidation potentials are compared to those for the tetracarboxylates and tetraformamidinates, there is a lowering of more than 1.5 V for each of the two systems.[7,5b] Even the second oxidation, i.e., the process from Mo_2^{5+} to Mo_2^{6+}, which is not known for the formamidinates and carboxylates, becomes so easily accessible that it is negative (−0.44 V vs Ag/AgCl), and chemical oxidation is so highly favored that simple dissolution of $Mo_2(hpp)_4$ in chlorinated solvents such as CH_2Cl_2 immediately produces $Mo_2(hpp)_4Cl$.[7] Short contact of these solutions with atmospheric O_2 generates $Mo_2(hpp)_4Cl_2$.[8]

The reason for the extraordinary ability of these bicyclic guanidinate derivatives to stabilize higher oxidation potentials

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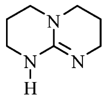
has been linked to the strong interaction of the ligand π orbitals and the electrons in the δ orbital of the quadruply bonded M_2^{4+} units.[5a,9] The strong destabilization[5a] of the dimetal δ orbitals favors oxidation of such species. For this reason, compounds of this type are potentially useful as reducing agents. This is of importance because there are rather few choices for strong organic-soluble chemical reducing agents that are available to synthetic chemists.[10]

It is worth noting that in comparison with other N analogues of carbonic acids and carboxylic acids (ureas, amidines, amides, and so on) the coordination chemistry of guanidines has been generally slow to develop although guanidines $[(R_2N)_2C{=}NR]$, guanidinates(1−) $\{[(RN)_2C{=}NR]^-\}$, and the dianionic guanidinates are capable of coordinating in a variety of ways to metal ions throughout the periodic table.[11] Only recently has much attention been focused on their coordination chemistry, but even this has been mostly on single-metal species.[12] It should also be noted that noncyclic guanidinates such as $(NPh)_2CNPh$ (triphenylguanidinate) are far less efficient at stabilizing high oxidation states in dimetal units.[13]

Because of the exceptional properties of hpp, especially as a bridging ligand in M_2 paddlewheel complexes, we considered it worthwhile to examine whether the effect that the hpp ligand imparts to dimetal units is general to other bicyclic guanidinate anions with rings of other sizes. We decided to begin with the anions of 1,4,6-triazabicyclo[3.3.0]-oct-4-ene (tbo, **II**) and 1,4,6-triazabicyclo[3.4.0]non-4-ene (tbn, **III**). Neither one is commercially available, and the literature concerning their preparation is sparse[14] and mainly limited to procedures described in a patent.[15]

We report here slightly modified procedures for preparing Htbo, Htbn,[16] and the new dimolybdenum complexes $Mo_2(tbo)_4$ (**1**), $Mo_2(tbo)_4Cl$ (**2**), $Mo_2(tbn)_4$ (**3**), $[Mo_2(tbn)_4]PF_6$ (**4**), and $Mo_2(tbn)_4Cl_2$ (**5**).



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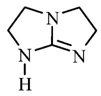

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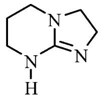

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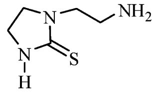

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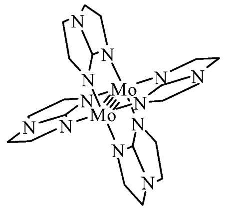

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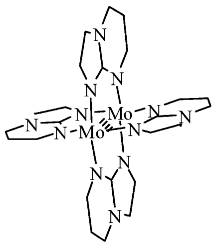

3

Experimental Section

General Procedures. All procedures were performed under a N_2 atmosphere unless otherwise noted, and all glassware was oven-dried prior to use. Unless otherwise noted, compounds were purchased from Aldrich. Diethylenetriamine, carbon disulfide, *p*-toluenesulfonic acid monohydrate, and (2-aminoethyl)-1,3-propanediamine were used as received. Hexanes and *p*-xylene were dried over 3-Å molecular sieves prior to use for organic synthesis. The solvents THF, CH_2Cl_2, benzene, and hexanes were purified using a Contour Glass solvent system. Lead(II) acetate, purchased from Strem, was also used as received. Evolution of H_2S in the syntheses of compound 1-(2-aminoethyl)-2-imidazolidinethione (**IV**), Htbo, and Htbn was monitored by passing the reaction exhaust through test strips of filter paper wetted with aqueous lead(II) acetate. Solutions of Bu^nLi (1.6 M in hexanes), purchased from Acros, were stored at −20 °C until used. The quadruply bonded compound $Mo_2(O_2CCF_3)_4$ was prepared according to a published procedure.[17]

Physical Measurements. Infrared (IR) spectra were recorded using a Perkin-Elmer 16PC Fourier transform IR (FT-IR) spectrometer or a Bruker Tensor 27 spectrometer. UV−vis spectra were recorded on a Shimadzu UV-2501 PC spectrometer. ^1H NMR spectra were recorded on a Unity Plus 300 NMR spectrometer, using the residual protonated solvent peaks to reference chemical shifts (δ, ppm). Cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) were recorded using a CH Instruments electrochemical analyzer with a 2-mm Pt disk working electrode, a Ag/AgCl reference electrode, and a Pt wire auxiliary electrode. Potentials are reported versus Ag/AgCl. The magnetic susceptibility was measured using a Johnson Matthey Mark II magnetic susceptibility balance. Elemental analysis was performed by Robertson Microlit Laboratories, Inc., Madison, NJ, on crystalline samples that had been placed under vacuum with the intention of removing the solvent. Mass spectroscopy (MS) data (electrospray ionization, ESI) were recorded at the Laboratory for Biological Mass Spectroscopy at Texas A&M University, using an MDS Qstar Pulsar with a spray voltage of 5 kV.

Syntheses. Preparation of 1,4,6-Triazabicyclo[3.3.0]oct-4-ene (Htbo). This compound was prepared following a procedure for the synthesis of bicyclic guanidines published in the patent literature.[15] Carbon disulfide (7.60 g, 100 mmol) was added, under N_2, to a solution of diethylenetriamine (10.3 g, 100 mmol) in 150 mL of *p*-xylene. A white precipitate immediately formed. The mixture was heated to boiling, and the solid dissolved. The solution was refluxed until evolution of H_2S ceased (ca. 10 days), and then the solvent was removed under vacuum, leaving a yellow-white

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solid. This solid was purified by sublimation, resulting in colorless crystals suitable for X-ray diffraction. Yield: 6.87 g (62.0 mmol, 62%). IR (KBr, cm^{-1}): 3310 (m), 3158 (m), 3111 (s), 3048 (s), 2955 (s), 2835 (s), 2372 (m), 2291 (w), 1750 (s), 1596 (s), 1545 (m), 1479 (s), 1447 (s), 1421 (s), 1341 (m), 1298 (s), 1268 (s), 1241 (s), 1202 (s), 1177 (m), 1117 (m), 1092 (s), 1059 (m), 990 (s), 933 (m), 897 (w), 875 (m), 815 (m), 771 (m), 726 (s), 708 (s), 672 (m), 623 (m), 454 (w). ^{1}H NMR ($CDCl_3$, ppm): 4.51 (br s, 1H (NH)), 3.08 (t, 4H, 2(CH_2)), 3.14 (t, 4H, 2(CH_2)). MS (ESI$^+$). Calcd for $(M + H)^+$: 112 amu. Found: 112 amu. The melting point (158−159 °C) is in good agreement with literature values of 158.5−159.5 °C.[14b]

Preparation of 1-(2-Aminoethyl)-2-imidazolidinethione (IV). When a reaction mixture similar to that used for the preparation of Htbo was refluxed for only 24 h (not 10 days) and the solvent was removed under vacuum, a colorless solid formed. Upon sublimation, colorless crystals suitable for X-ray diffraction were obtained. Yield: 11.2 g (77 mmol, 77%). IR (KBr, cm^{-1}): 3413 (w), 3327 (s), 3264 (s), 3090 (s), 3018 (s), 2939 (s), 2865 (s), 2803 (s), 2767 (s), 2677 (s), 2374 (m), 1655 (m), 1597 (s), 1524 (s), 1500 (s), 1475 (s), 1457 (s), 1445 (s), 1415 (s), 1361 (s), 1316 (s), 1281 (s), 1258 (s), 1214 (s), 1161 (s), 1094 (s), 1024 (s), 994 (s), 969 (s), 947 (s), 880 (s), 836 (s), 733 (m), 641 (s), 525 (s), 483 (m). ^{1}H NMR ($CDCl_3$, ppm): 6.17 (br s, 1H (NH)), 3.80−3.58 (mult., 6H (CH_2)), 2.95 (t, 2H (CH_2)), 1.21 (br s, 2H (NH_2)). MS (ESI$^+$). Calcd for $(M + H)^+$: 146 amu. Found: 146 amu. The melting point (110.0−110.5 °C) is as reported.[14a]

Preparation of 1,4,6-Triazabicyclo[3.4.0]non-4-ene (Htbn). This compound[14c] was synthesized similarly to Htbo[15] using a mixture of carbon disulfide (12.8 mL, 16.2 g, 213 mmol), *N*-(2-aminoethyl)-1,3-propanediamine (25.0 g, 210 mmol) in 150 mL of *p*-xylene. After heating to reflux under N_2 for 10 days until evolution of H_2S had ceased, removal of the solvent under vacuum left a yellow-white solid. The solid was purified by sublimation, resulting in colorless crystals suitable for X-ray diffraction. Yield: 22.7 g (182 mmol, 85%). IR (KBr, cm^{-1}): 3278 (m), 3172 (m), 3127 (m), 3052 (m), 2930 (s), 2843 (s), 1650 (s), 1501 (s), 1477 (s), 1438 (s), 1372 (m), 1320 (s), 1268 (s), 1198 (m), 1175 (m), 1147 (s), 1101 (m), 1032 (m), 974 (m), 941 (m), 842 (m), 754 (m), 722 (m), 692 (m), 543 (w), 471 (m). ^{1}H NMR ($CDCl_3$, ppm): 3.43 (td, 2H (CH_2)), 3.29−3.23 (mult, 4H (CH_2)), 3.10 (t, 2H (CH_2)), 1.92 (p, 2H (CH_2)). MS (ESI$^+$). Calcd for $(M + H)^+$: 126 amu. Found: 126 amu.

Preparation of $[H_2tbn](HCO_3)$. Crystals of $[H_2tbn](HCO_3)$, suitable for X-ray diffraction, were prepared in essentially quantitative yield by the slow evaporation in air of a solution of Htbn in 90% (v/v) ethanol/water.

Preparation of $Mo_2(tbo)_4$ (1). A Schlenk flask was charged with Htbo (0.689 g, 6.21 mmol) and THF (20 mL). To the resulting suspension was added BuLi (3.90 mL, 6.24 mmol), and the mixture was stirred for 30 min. A brilliant yellow solution of $Mo_2(O_2CCF_3)_4$ (1.00 g, 1.55 mmol) in THF (20 mL) was then added, and the mixture was stirred for 1 h. The solution rapidly darkened, and a reddish-orange precipitate of **1** was observed. The mixture was filtered, and the solid was washed with 20 mL of THF. Orange block crystals of **1**·THF were prepared by placing a saturated THF solution in a freezer at −20 °C for 1 week. Reddish plate-shaped crystals of **1** (without an interstitial solvent) were grown by layering a saturated benzene solution of **1** with hexanes. Yield: 0.778 g (1.23 mmol, 79%). IR (KBr, cm^{-1}): 3367 (w), 2956 (s), 2835 (s), 1686 (s), 1655 (m), 1625 (s), 1496 (s), 1464 (s), 1431 (s), 1339 (w), 1288 (m), 1270 (m), 1228 (m), 1198 (s), 1143 (m), 1108 (m), 1078 (s), 1023 (s), 933 (w), 914 (w), 851 (w), 804 (m), 785 (m), 729 (w), 670 (w), 521 (w), 485 (m). ^{1}H NMR (C_6D_6, ppm): 3.38 (t, 16H, 8(CH_2)), 2.45 (t, 16H, 8(CH_2)). UV−vis (THF): λ_{max}, nm (ϵ_M, L/mol·cm): 486.5 (1800), 355.0 (4400). MS (ESI$^+$). Calcd for $(M + H)^+$: 633 amu. Found: 633 amu.

Preparation of $Mo_2(tbo)_4Cl$ (2). Dichloromethane (20 mL) was added to a Schlenk flask containing red $Mo_2(tbo)_4$ (0.100 g, 0.158 mmol) at room temperature, and the resulting brown suspension was stirred for 1 h. A mixture of isomeric hexanes (60 mL) was added, and the suspension was filtered. The solid was washed with hexanes (20 mL) and briefly dried under vacuum. Crystals were prepared by layering a saturated CH_2Cl_2 solution of **2** with hexanes. The diffusion was complete after 2 weeks, at which time the crystals were collected. Yield: 0.085 g (0.127 mmol, 80%). IR (KBr, cm^{-1}): 3358 (m), 2963 (s), 2861 (m), 1654 (s), 1560 (m), 1543 (m), 1508 (s), 1474 (m), 1440 (m), 1342 (w), 1262 (s), 1199 (s), 1089 (s), 1021 (s), 924 (m), 864 (m), 800 (s), 720 (m), 623 (w), 516 (w), 475 (w). UV−vis (CH_2Cl_2): λ_{max}, nm (ϵ_M, L/mol·cm): 587 (sh), 497 (sh), 376 (sh), 348 (4000). $\mu_B = 1.68\ \mu_B$; $g = 1.94$. Elem anal. Calcd for $Mo_2(tbo)_4Cl\cdot 0.25CH_2Cl_2$: C, 35.28; H, 4.76, N, 24.39. Found: C, 35.30; H, 4.96; N, 24.58.

Preparation of $Mo_2(tbn)_4$ (3). A Schlenk flask was charged with Htbn (1.00 g, 8.00 mmol) and THF (10 mL). To the resulting solution was added BuLi (1.6 M, 5.00 mL, 8.00 mmol), and the solution was stirred for 10 min. This pale-yellow solution was then layered onto a brilliant-yellow solution of $Mo_2(O_2CCF_3)_4$ (1.29 g, 2.00 mmol) in THF (10 mL), forming a dark interface. The flask was shaken once and left standing overnight. The next day a yellow-orange microcrystalline precipitate was observed. The mixture was filtered, and the solid was washed with THF (10 mL). Yield: 0.991 g (1.44 mmol, 72%). Crystals, as yellow-orange plates suitable for X-ray diffraction, were grown by diffusion of hexanes into a saturated THF solution of **3** over the course of 2 weeks. The crystals were collected, washed with hexanes, and dried under vacuum. IR (KBr, cm^{-1}): 3405 (w), 2921 (s), 2816 (s), 1686 (m), 1655 (m), 1624 (m), 1575 (s), 1496 (s), 1468 (s), 1438 (s), 1375 (m), 1319 (m), 1270 (s), 1246 (m), 1198 (s), 1167 (s), 1119 (m), 1098 (m), 1058 (m), 983 (w), 938 (w), 899 (w), 803 (w), 776 (w), 710 (w), 655 (w), 553 (w), 523 (w), 431 (w). ^{1}H NMR (C_6D_6, ppm): 3.86 (m, 8H), 3.65 (m, 8H), 3.19 (m, 8H), 2.88 (m, 8H), 1.92 (m, 8H). UV−vis (THF): λ_{max}, nm (ϵ_M, L/mol·cm): 455.5 (1100), 351.0 (8900), 318.0 (12 000), 277.5 (16 000), 258.0 (23 000). MS (ESI$^+$). Calcd for $(M + H)^+$: 689 amu. Found: 689 amu.

Preparation of $[Mo_2(tbn)_4]PF_6$ (4). A deep-blue solution of $(Cp_2Fe)PF_6$ (0.050 g, 0.15 mmol) in 20 mL of MeCN was added to an orange solution of **3** (0.100 g, 0.150 mmol) in THF (20 mL). The resulting orange-brown solution was stirred for 30 min, and the solvent was removed under vacuum. The residue was then washed with 40 mL of isomeric hexanes to remove Cp_2Fe. The remaining solid was dried under vacuum and collected. Yield: 0.101 g (85%). IR (KBr, cm^{-1}): 3158 (m), 2963 (s), 1675 (s), 1619 (s), 1559 (s), 1483 (m), 1439 (m), 1372 (m), 1323 (m), 1262 (s), 1204 (m), 1099 (s), 1022 (s), 842 (s), 556 (m), 478 (w). $\mu_B = 1.70\ \mu_B$; $g = 1.95$. MS (ESI$^+$): Calcd: 688 amu. Found: 688 amu. UV−vis (CH_2Cl_2): λ_{max}, nm (ϵ_M, L/mol·cm): 486 (900), 380 (sh), 324 (sh). Elem anal. Calcd for **4**: C, 34.57; H, 4.84; N, 20.17. Found: C, 34.22; H, 4.53; N, 19.98.

Preparation of $Mo_2(tbn)_4Cl_2$ (5). A dichloromethane solution (20 mL) of **3** (0.100 g, 0.145 mmol) was briefly exposed to air (60 s). The flask was then evacuated and back-filled with N_2 three times, and the solution was layered with hexanes. Brown block crystals of **5**·$2CH_2Cl_2$ were harvested after 2 weeks. Yield: 0.087 g (79%). Crystals of **5** (without interstitial molecules) were prepared by vapor diffusion of ether into a CH_2Cl_2 solution. Crystals of **5**·$3CHCl_3$

Table 1. Crystallographic Parameters for **1**·THF, **1**−**3**, **5**, **5**·2CH_2Cl_2, and **5**·3$CHCl_3$

compd	**1**·THF	**1**	**2**	**3**	**5**	**5**·2CH_2Cl_2	**5**·3$CHCl_3$
empirical formula	$C_{24}H_{40}Mo_2N_{12}O$	$C_{20}H_{32}Mo_2N_{12}$	$C_{20}H_{32}ClMo_2N_{12}$	$C_{24}H_{40}Mo_2N_{12}$	$C_{24}H_{40}Cl_2Mo_2N_{12}$	$C_{26}H_{44}Cl_6Mo_2N_{12}$	$C_{27}H_{43}Cl_{11}$ Mo_2N_{12}
fw	704.56	632.46	667.91	688.56	759.46	929.31	1117.56
space group	$P2_1/n$	$P\bar{1}$	$I2/a$	$P\bar{1}$	$I4/m$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.604(2)	7.324(1)	15.636(5)	8.088(2)	9.592(4)	8.494(2)	9.602(2)
b (Å)	24.081(5)	8.334(2)	8.318(3)	8.858(2)	9.592(4)	10.113(2)	10.036(2)
c (Å)	11.473(2)	10.641(2)	19.924(6)	11.076(3)	15.48(1)	11.014(3)	13.051(2)
α (deg)	90	105.957(3)	90	74.167(4)	90	99.517(4)	102.568(3)
β (deg)	109.097(3)	105.308(3)	102.311(5)	70.104(4)	90	106.371(4)	97.518(3)
γ (deg)	90	98.391(3)	90	72.188(4)	90	92.737(4)	116.077(3)
V (Å^3)	2768.6(9)	585.4(2)	2532(1)	697.7(3)	1424(1)	890.8(4)	1065.1(3)
Z	4	1	4	1	2	1	1
d_{calcd} (g/cm^3)	1.690	1.794	1.752	1.639	1.772	1.732	1.742
μ (mm^{-1})	0.949	1.108	1.132	0.937	1.109	1.193	1.317
T (K)	213(2)	213(2)	213(2)	213(2)	110(2)	213(2)	213(2)
R1^a [$I > 2\sigma(I)$]	0.0271	0.0306	0.0320	0.0377	0.0619	0.0404	0.0652
wR2^b [$I > 2\sigma(I)$]	0.0653	0.0687	0.0800	0.0956	0.1502	0.0929	0.1821
R1^a (all data)	0.0375	0.0365	0.0418	0.0423	0.0844	0.0537	0.0789
wR2^b (all data)	0.0715	0.0709	0.0862	0.0981	0.1595	0.1004	0.1937

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

were prepared by vapor diffusion of hexanes into a $CHCl_3$ solution. IR (KBr, cm^{-1}): 3853 (w), 3743 (m), 3435 (w), 2932 (m), 2854 (s), 2370 (w), 1689 (s), 1621 (s), 1551 (s), 1446 (s), 1370 (s), 1322 (m), 1277 (s), 1203 (s), 1119 (s), 1049 (m), 940 (m), 800 (s), 727 (m), 430 (w). ^{1}H NMR ($CDCl_3$, ppm): 4.16 (m, 2H), 3.93 (m, 2H), 3.78 (m, 2H), 3.57 (m, 2H), 2.03 (m, 2H). UV−vis (CH_2Cl_2): λ_{max}, nm (ϵ_M, L/mol·cm): 523 (sh), 411 (28 000), 335 (18 000). Elem anal. Calcd for **5**·0.5CH_2Cl_2: C, 36.70; H, 5.15; N, 20.96. Found: C, 36.33; H, 5.44; N, 20.75.

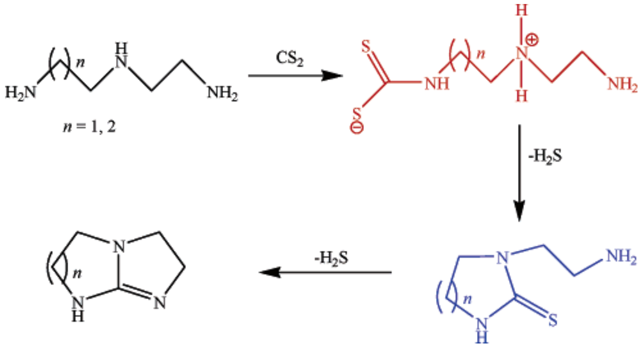
X-ray Structure Determinations. Single crystals of **IV**, Htbo, Htbn, **1**, **1**·THF, **2**, **3**, **5**, **5**·2CH_2Cl_2, **5**·3$CHCl_3$, and [H_2tbn](HCO_3) were placed in a cryoloop using a small amount of silicone grease. Data for **IV** were collected at 213 K on a Nonius FAST area detector. For the others, data were collected at 213 K [except for Htbn (193 K) and **5** (110 K)] on a Bruker SMART area detector using the *SMART* and *SAINT* programs.[18,19] The crystal structures were solved via direct methods and refined using *SHELXL-97*.[20] H atoms were placed at calculated positions. Non-H atoms were refined with anisotropic displacement parameters. Cell parameters and refinement results for organic compounds are summarized in Table S1 in the Supporting Information, while those for inorganic compounds are found in Table 1.

Results and Discussion

Ligand Syntheses. The preparations of the ligands Htbo and Htbn were accomplished by reaction of the appropriate triamine (Scheme 1) with carbon disulfide in a 1:1 ratio in *p*-xylene as the solvent, using a slight modification of a reported synthesis for bicyclic guanidines found in a patent.[15] This method has been used to prepare the commercially available Hhpp and is the most direct synthetic route available for bicyclic guanidines. It should be noted, however, that all three compounds have been prepared by alternative multistep routes.[14]

The initial reaction of polyamines with 1 equiv of carbon disulfide has been reported to produce a dithiocarbamate zwitterion.[21] This reactive intermediate, which we have not isolated, then forms the rings of the ligands in a stepwise fashion, as evidenced by the intermediates (**IV** for Htbo), which can be isolated by stopping the reaction before evolution of H_2S is complete. The synthesis of Htbn also shows a similar monocyclic intermediate, as evidenced by a peak at 160 amu in the MS spectrum [ESI$^+$, (M + H)$^+$]. The reaction pathway to produce the bicyclic guanidines Htbo and Htbn by reaction of a triamine with carbon disulfide is summarized in Scheme 1, where the presumed intermediate is at the top right in red and the isolable intermediate (**IV** for Htbo, n = 1) is at the bottom right in blue.

Scheme 1



The ligand precursors, Htbo and Htbn, are readily purified by sublimation as shown by the clean ^{1}H NMR spectra. Both compounds also show the appropriate parent ion peak in their MS spectra. The melting points are also in agreement with previously prepared samples for which their purity had been established by elemental analysis.[14a,b] These compounds readily absorb atmospheric water and CO_2, forming the corresponding bicarbonate salts, e.g., [H_2tbn](HCO_3). It is notable that Htbn reacts so quickly with air that crystals rapidly disintegrate and form a solution upon exposure to the normal laboratory atmosphere.

Syntheses and Reactivity of Dimolybdenum Compounds. The quadruply bonded, paddlewheel species, $Mo_2(tbo)_4$ and $Mo_2(tbn)_4$, were prepared similarly to $Mo_2(hpp)_4$[7] by reacting $Mo_2(O_2CCF_3)_4$ with the Li salt of

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

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

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

[21] Li, C.; Mella, S. L.; Sartorelli, A. C. *J. Med. Chem.* **1981**, *24*, 1089.

Table 2. Selected Bond Distances (Å) for Htbo, Htbn, and $[H_2tbn](HCO_3$

compound	C(3)−N(1)	C(3)−N(2)	C3−N(3)
Htbo	1.346(2)	1.297(2)	1.391(2)
Htbn	1.290(3)	1.347(3)	1.383(3)
$[H_2tbn](HCO_3)$	1.335(3)	1.315(3)	1.336(3)

the ligand precursor in THF. In this way, $Mo_2(tbo)_4$ and $Mo_2(tbn)_4$ were isolated in good yields as red and orange powders, respectively. Crystalline samples were prepared by layering dilute THF or benzene solutions with hexanes or placing THF solutions in a freezer at −20 °C.

These Mo_2^{4+} compounds are readily transformed to singly oxidized Mo_2^{5+} species upon dissolution in Cl-containing solvents such as CH_2Cl_2. Crystals of the tbo compound **2** were isolated by layering the dichloromethane solution with hexanes. Oxidation may also be accomplished by the addition of a stoichiometric amount of a mild oxidant in less reactive solvents. In this way, reaction of **3** and $(Cp_2Fe)PF_6$ produces **4** when a mixture of MeCN and THF is used as solvent. The doubly oxidized compound containing the Mo_2^{6+} species, **5**, was readily obtained by briefly exposing to air (60 s)[22] a dichloromethane solution of **3**. The solution was then purged of air and layered with hexanes to produce brown acicular crystals. Various attempts to isolate a $Mo_2(tbn)_4^{2+}$ analogue with tbo have been unsuccessful (vide infra).

All compounds are volatile under high vacuum, as shown by the presence of the appropriate parent ion peaks in the MS spectra. Elemental analysis provided satisfactory results for all of the oxidized species,[23] but for the highly reactive Mo_2^{4+} species, such an analysis is problematic because of their extreme sensitivity to both O_2 and water. Immediately upon exposure to air, the solids darken and form a thick paste. Such behavior is similar to that of $Mo_2(hpp)_4$. For the latter, thermogravimetric analysis showed that upon exposure to air there is a mass gain of approximately 20% within 90 s. Therefore, even a small exposure to air can cause considerable error in the elemental analysis.

Structural Characterization. Organic Compounds. Crystals of **IV**, Htbo, and Htbn were produced by sublimation. Because the ligand precursor Htbn is so hygroscopic, the crystal was suspended in silicone oil, mounted in a cryoloop, and placed on the diffractometer with a N_2 stream set at 193 K in order to freeze the oil. Slow evaporation of an ethanol solution of Htbn exposed to air produced crystals of $[H_2tbn](HCO_3)$ suitable for X-ray studies.

Displacement ellipsoid plots of these four compounds are shown in Figures S1−S3 in the Supporting Information. For **IV**, all of the C−C distances and angles are typical for the C atoms found in their respective environments. The C−N and C−S bond distances lie between that expected for a single or double bond. The N−C−S angles are 125° and 126°, and the N−C−N angle is 109°; the sum is 360°, suggesting sp^2 hybridization at the C atom in the NC(N)S unit.

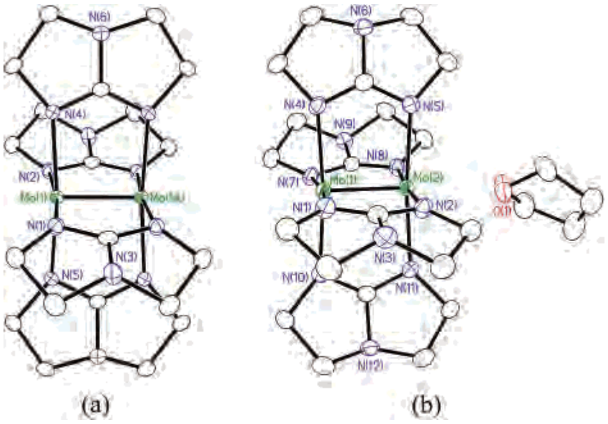

Figure 1. Structures of two crystallographic forms of **1**. (a) Unsolvated compound **1**. Mo(1)−Mo(1A) = 2.1321(7) Å, Mo−N(av) = 2.160(6) Å, Mo−Mo−N(av) = 93.2(2)°. (b) Compound **1**·THF. Mo(1)−Mo(2) = 2.1453(4) Å, Mo−N(av) = 2.165(5) Å, Mo(2)−O(1) = 2.588(2) Å, Mo(1)−Mo(2)−O(1) = 175.66(5)°, Mo−Mo−N(av) = 92.9(2)°. Displacement ellipsoids are drawn at the 50% probability level.

For Htbo and Htbn, selected bond distances are given in Table 2 and their structures are shown in Figure S2 in the Supporting Information. Again, the C−C bond distances are typical for single bonds, and all of the C−N distances fall between the expected values for single and double bonds, indicating the delocalized nature of the guanidine core. The environment around the C in the NC(N)N unit [C(3)] is essentially planar, suggesting sp^2 hybridization.

The structure of $[H_2tbn](HCO_3)$ is shown in Figure S3 in the Supporting Information, and selected bond distances and angles are shown in Table 2. The three C−N bond lengths are nearly identical, as in an ideal guanidinium cation. Each $[H_2tbn]^+$ cation is H-bonded to a bicarbonate anion, as shown by an N−O distance of 2.80 Å, which is shorter than the sum of van der Waals radii by 14%.[24]

Structures of Dimolybdenum Compounds. The two crystalline forms of the Mo_2^{4+} tbo compounds, **1** and **1**·THF, are shown in Figure 1. Selected interatomic distances and angles are provided in the caption. For **1**, the Mo−Mo distance is long [2.1321(7) Å], but it is even longer in the solvate **1**·THF [2.1453(4) Å]. This distance is the longest metal−metal distance recorded for a Mo_2^{4+} unit embraced by four ligands in a paddlewheel arrangement (i.e., Mo_2L_4 complexes, where L is a bridging ligand).[25] These distances contrast with the short Mo−Mo distance in $Mo_2(hpp)_4$ [2.067(1) Å],[12a] being longer by 0.065 Å for **1** and 0.078 Å for **1**·THF. Such a drastic increase is attributable to the large divergent bite angle (ca. 23°) of the ligand.

As shown in Figure 2a, the tbo ligand in **1** is puckered into a boat conformation. If regular geometries are assumed (i.e., regular pentagons with 108° angles) for the bicyclic

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[22] Care must be taken not to expose the solution to air for an extended period of time because the compound is hygroscopic and decomposes in the presence of water.

[23] For elemental analyses, the crystalline samples were briefly placed under vacuum with the intention of removing interstitial molecules. However, in some cases, not all were removed. For example, the analysis of **4** shows that 0.5 CH_2Cl_2 molecules remained and **2** analyzed as **2**·$0.25CH_2Cl_2$.

[24] Cotton, F. A.; Wilkinson, G.; Gaus, P. L. *Basic Inorganic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1995; p 278.

[25] Cotton, F. A.; Daniels, L. M.; Hillard, E. A.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 2466.

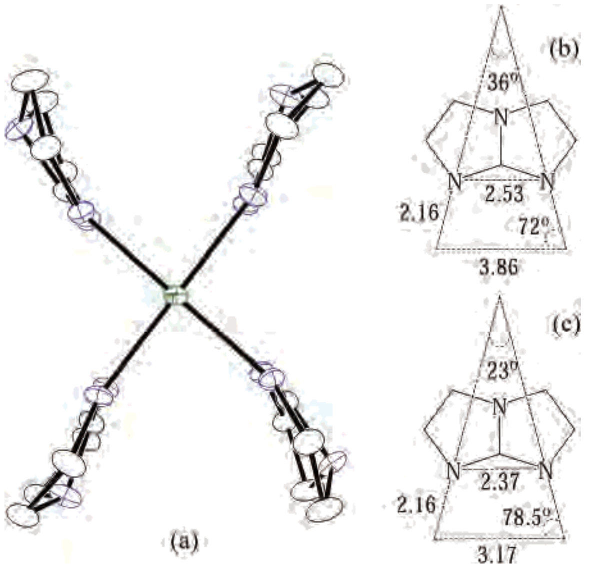

Figure 2. (a) View of **1** along the Mo−Mo axis, showing the boat conformation adopted by the tbo ligand. (b) Estimation of the Mo−Mo distance based on purely geometric considerations using an average Mo−N distance of 2.16 Å. (c) Estimation of the Mo−Mo distance based on the geometric values from in the crystal structure. All distances are in angstroms.

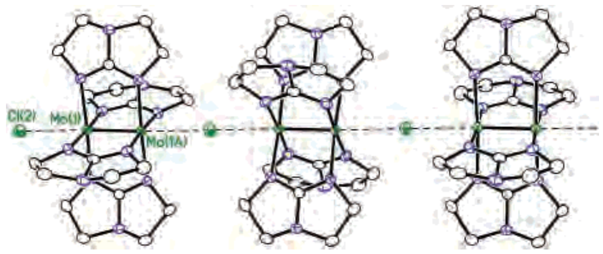

Figure 3. Structure of **2** showing how the Cl anions are between the cations. Ellipsoids are drawn at the 50% probability level. Mo(1)−Mo(1A) = 2.2305(8) Å, Mo−N(av) = 2.121(8) Å, Mo(1)−Cl(2) = 2.7947(9) Å, Mo(1A)−Mo(1)−Cl(2) = 177.64(3)°, Mo−Mo−N(av) = 91.7(2)°.

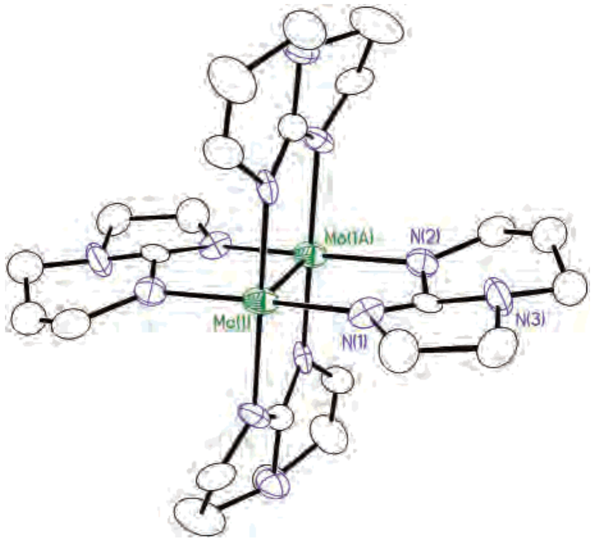

Figure 4. View of one of the orientations in the disordered crystal of **3**. Ellipsoids are drawn at the 50% probability level. H atoms are removed for clarity. Mo(1)−Mo(1A) = 2.082(1) Å, Mo−N(1)(av) = 2.14(3) Å, Mo−N(2)(av) = 2.18(3) Å, Mo−Mo−N(1)(av) = 92.6(1)°, Mo−Mo−N(2)(av) = 93.6(1)°.

ligand, a rough estimate of the Mo−Mo distance can be obtained (3.86 Å) when an average Mo−N distance of 2.16 Å is used, as in Figure 2b. One may expect an enhanced estimate if values from the crystal structure for the bicyclic anion are used, as shown in Figure 2c. In this manner, the angle of divergence decreases from 36° to 23° and the expected Mo−Mo distance is reduced from 3.86 to 3.17 Å. However, this value is still far greater than the distance found in a quadruply bonded dimolybdenum unit, or a dimolybdenum unit in any known oxidation state.[25] Despite such an unfavorable situation, the paddlewheel compound with four such bridging ligands forms, attesting to the high stability of the dimetal bond. Interaction of the N orbitals with the dimolybdenum unit is probably increased by the puckering of the ligand into a boat conformation, and this may contribute to elongation of the Mo−Mo bond.

The structure of **2** is shown in Figure 3, with selected bond distances and angles given in the caption. Again, the Mo−Mo distance of 2.2305(8) Å is exceptionally long for a bond order of 3.5 in a dimolybdenum paddlewheel species. The resulting increase in the Mo−Mo distance (0.099 Å) relative to $Mo_2(tbo)_4$ is about twice that found between $Mo_2(hpp)_4Cl$ and $Mo_2(hpp)_4$ (0.049 Å) and similar to the increase when two electrons are removed from $Mo_2(hpp)_4$ to form $Mo_2(hpp)_4Cl_2$ (0.107 Å).[8,26] The chloride groups are located between symmetry-related paddlewheel units, and the Mo−Cl distance [2.7947(9) Å] is long.

The structure of **3** is shown in Figure 4, where selected interatomic distances and angles are given in the caption. The Mo−Mo distance [2.082(1) Å] is typical[25] of dimolybdenum units but longer than that in $Mo_2(hpp)_4$ by 0.015 Å. Such an elongation is again attributable to the ligand bite angle, which, by purely geometric considerations, is divergent by 18° but not as divergent as that in tbo (36°). Because of the asymmetry of the tbn ligand, the structure shows disorder in all positions except for the dimolybdenum unit, making estimations of the bite angle in the crystal structure unreliable.

Because the bicyclic system of 7-azaindole (azin, **V**) is structurally similar to that of tbn, it is useful to contrast the structure of **3** to that of the azin analogue. Two solvates, $Mo_2(azin)_4{\cdot}2THF$ and $Mo_2(azin)_4{\cdot}2acetone$, have been structurally characterized and have Mo−Mo distances of 2.1239(9) and 2.135(1) Å, respectively.[27] These distances are considerably longer than that for **3** and longer than the average of those of Mo_2^{4+} paddlewheel compounds.[25] The grounds for the long distances in the azin compounds have been discussed in terms of ligand geometry, ligand basicity, and incorporation of interstitial solvent molecules.[27] The much shorter Mo−Mo distance in the tbn compound relative to that in the azin analogue indicates primarily that the bicyclic guanidinate ligands interact much more strongly with the dimetal unit than the azin anion. This may also be due to a little flexibility on the part of the saturated bicyclic system.

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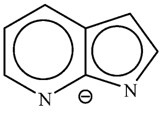
(26) Cotton, F. A.; Timmons, D. J. *Polyhedron* **1998**, *17*, 179.

(27) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Zhou, H. C. *Inorg. Chim. Acta* **2000**, *300−302,* 319.



V

We were unable to crystallize the Mo_2^{5+} tbn compounds, but the structures of three Mo_2^{6+} species having the formula $Mo_2(tbn)_4Cl_2 \cdot n$Solvent were determined (nSolvent = nothing, $2CH_2Cl_2$, and $3CHCl_3$). Figure 5 shows the structure of **5** in **5**·$2CH_2Cl_2$. Selected bond distances and angles for **5**, as well as for the solvated forms, **5**·$2CH_2Cl_2$ and **5**·$3CHCl_3$, are provided in Table 3. The paddlewheel structure in **5**·$2CH_2Cl_2$ and **5**·$3CHCl_3$ is well-ordered, with the ligands arranged around the dimetal unit in a centrosymmetric fashion. The unsolvated form, **5**, crystallized in the body-centered tetragonal space group $I4/m$ with two molecules in the unit cell. The molecule resides on a site of $4/m$ symmetry, resulting in disorder of the ligand set. The difficulties associated with the proper solution and refinement of such systems have been discussed previously.[8] The Mo−Mo distances [average 2.229(3) Å] are increased by ca. 0.15 Å from the distance in $Mo_2(tbn)_4$. This increase is greater than that of 0.108 Å found between $Mo_2(hpp)_4$ and $Mo_2(hpp)_4Cl_2$.[8,26] The Mo−Cl distances (ca. 2.77−2.80 Å) are long, and the Mo−Cl bond appears to be weak.[28]

Electrochemistry. The DPVs of $Mo_2(tbo)_4$ and $Mo_2(tbn)_4$, measured using THF solutions of approximately 1 mM concentration, are depicted in Figure 6. The two peaks observed at −1.01 and −0.56 V for $Mo_2(tbn)_4$ are related to the following successive one-electron processes:

$$\mathrm{Mo_2}^{6+} \overset{+e^-}{\rightleftharpoons} \mathrm{Mo_2}^{5+}$$

$$\mathrm{Mo_2}^{5+} \overset{+e^-}{\rightleftharpoons} \mathrm{Mo_2}^{4+}$$

For $Mo_2(tbo)_4$, the peak at −0.99 V corresponds to a reversible one-electron-transfer process ($Mo_2^{5+/4+}$). The second peak at −0.19 V has a current ratio of less than 1 in the CV (i_{pa}/i_{pc}), and this ratio varies with the scan rate, suggesting that the electron-transfer process is irreversible. Such irreversibility is the most likely the reason we have been unable to isolate any $Mo_2(tbo)_4^{2+}$ species. Also, this is consistent with a smaller interaction between the tbo anion with the δ electrons of the Mo_2 unit than with the hpp anions, which leads to a smaller destabilization of such electrons than in the hpp case. However, the first redox potential for the $Mo_2^{5+/4+}$ process (−0.99 V) is significantly more favorable than that for other dimolybdenum paddlewheel compounds with all N donors such as formamidinates (range of about 0.24−0.79 V)[29] and even for noncyclic guanidinate derivatives such as $Mo_2[(NPh)_2CNPh]_4$, in which the corresponding process occurs at a potential of −0.05 V.[13]

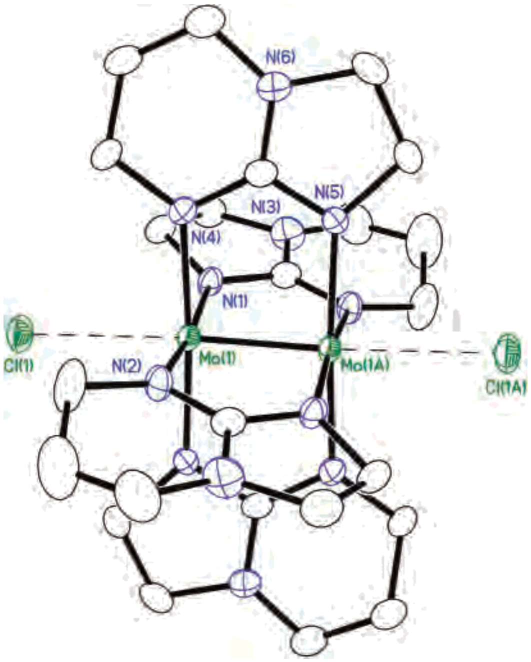


Figure 5. Structure of $Mo_2(tbn)_4Cl_2$ in **5**·$2CH_2Cl_2$. Displacement ellipsoids are drawn at the 50% probability level. H atoms are removed for clarity.

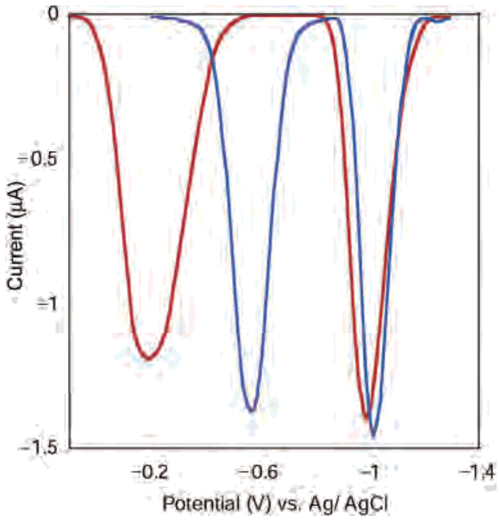


Figure 6. DPVs of $Mo_2(tbo)_4$ (red) and $Mo_2(tbn)_4$ (blue). For each compound, the redox wave at ca. −1 V corresponds to the $Mo_2^{5+/4+}$ process. The others are for the $Mo_2^{6+/5+}$ process.

Table 3. Selected Bond Distances (Å) and Angles (deg) in Three Crystalline Forms of Complex **5**

	5	**5**·CH_2Cl_2	**5**·$3CHCl_3$
Mo−Mo	2.240(3)	2.2233(8)	2.224(1)
Mo−Cl	2.771(4)	2.771(1)	2.806(2)
Mo−N(1)	2.123(8)	2.082[4]	2.073[8]
Mo−N(2)	2.098(9)	2.119[4]	2.121[8]
Mo−Mo−Cl	180	173.22(4)	177.5(5)
Mo−Mo−N(1)	88.3(6)	89.6[1]	90.9[8]
Mo−Mo−N(2)	94.3(6)	93.1[1]	92.1[8]

All of the potentials are listed in Table 4, which also shows the potential versus ferrocene for $Mo_2(hpp)_4$. All three compounds have very large negative $E_{1/2}^{(1)}$ potentials.

The negative potentials observed for $Mo_2(tbn)_4$ and $Mo_2(tbo)_4$ are consistent with the observation that simple dissolution in CH_2Cl_2 leads to the formation of Mo_2^{5+} species

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(28) One has to be careful, however, in judging the ability of relatively long M−Cl distances in paddlewheel compounds having M_2 units because even long M−C distances can have a noticeable effect on the M−M distance, as shown in $W_2(hpp)_4Cl_2$. See ref 5b.

(29) Lin, C.; Protasiewicz, J. D.; Smith, E. T.; Ren, T. *Inorg. Chem.* **1996**, *35*, 6422.

Table 4. Comparison of the Redox Potentials[a] for $Mo_2(hpp)_4$, $Mo_2(tbo)_4$, and $Mo_2(tbn)_4$

	$E^{(1)}_{1/2}$ (Mo_2^{5+}/Mo_2^{4+})		$E^{(2)}_{1/2}$ (Mo_2^{6+}/Mo_2^{5+})		
	Ag/AgCl	Fc/Fc$^+$	Ag/AgCl	Fc/Fc$^+$	ref
$Mo_2(hpp)_4$[b]	−1.27	−1.79	−0.44	−0.97	7
$Mo_2(tbo)_4$[c]	−0.99	−1.65	−0.19	−0.85	this work
$Mo_2(tbn)_4$[c]	−1.01	−1.68	−0.56	−1.23	this work

[a] Under the experimental conditions, the Fc/Fc$^+$ couple was measured at 0.66 V. [b] Bu_4NBF_4·3toluene. [c] THF/Bu_4NBF_4 (0.1 M).

(the reduction potential of CH_2Cl_2 has previously been measured at −1.638 V vs ferrocene).[7,30] $E^{(2)}_{1/2}$ for **3** is also consistent with oxidation to the Mo_2^{6+} state easily accomplished by O_2 and mild oxidizing agents. The processes that take place at ca. −1 V for both $Mo_2(tbo)_4$ and $Mo_2(tbn)_4$ are consistent with these compounds being strong reducing agents.

The $\Delta E_{1/2}$ values defined as $E^{(2)}_{1/2} - E^{(1)}_{1/2}$ for both compounds allow for the calculation of the comproportionation constant, K_C, for the process below[31] using the relationship of Richardson and Taube, $K_C = \exp(\Delta E_{1/2}/25.69)$.

$$Mo_2^{6+} + Mo_2^{4+} \rightleftharpoons Mo_2^{5+}$$

$\Delta E_{1/2}$ for the $Mo_2(tbn)_4$ system is 451 mV, and K_C is 3.48×10^{13}. For the $Mo_2(tbo)_4$ system, $\Delta E_{1/2}$ is 801 mV and K_C is 1.51×10^{31}; the latter is only an approximation because of the irreversibility of the oxidation process leading to the $Mo_2(tbo)_4^{2+}$ species. As with the $Mo_2(hpp)_4$ system ($K_C = 9.56 \times 10^{13}$), the large values are not due to instability of the Mo_2^{6+} species [although this may play a greater role for $Mo_2(tbo)_4^{2+}$] but to the greater oxidizability of the Mo_2^{4+} species toward even very mild oxidizing agents such as CH_2Cl_2.[7]

It should be noted that structural effects in $Mo_2(tbo)_4$ and $Mo_2(tbn)_4$ species that influence the ability of the guanidinate ligands to interact with the electrons in the δ orbitals of the Mo_2 unit have important consequences in the electrochemical behavior of such compounds. Nevertheless, the two compounds have potentials that make them strong reducing agents.

Magnetic Behavior. While both $Mo_2(tbo)_4$ and $Mo_2(tbn)_4$ are only sparingly soluble in common NMR solvents, their ^1H NMR spectra were observed in dilute C_6D_6 solutions by collecting many transients. In **1**, there is only one symmetrical species in solution, but overlapping peaks in the spectrum of $Mo_2(tbn)_4$ suggest the presence of isomers. All of the signals are in the normal regions and of normal sharpness, consistent with both compounds being diamagnetic, as expected for a $\sigma^2\pi^4\delta^2$ configuration.

Magnetic measurements taken on a Gouy balance show that both of the singly oxidized species, **2** and **4**, have an unpaired electron. The g values, 1.94 for **2** and 1.95 for **4**, are essentially the same as that found for $Mo_2(hpp)_4Cl$[7] and are less than 2.00 owing to spin−orbit coupling associated with the Mo atoms.

The ^1H NMR spectrum of $Mo_2(tbn)_4Cl_2$ reveals that this compound is diamagnetic, as expected for the triply bonded Mo_2^{6+} core. As in the parent compound **3**, there is a complex pattern of signals, which suggests the presence of isomers in the bulk sample, even though crystals of **5**·$2CH_2Cl_2$ and **5**·$3CHCl_3$ analyzed by X-ray diffraction show a well-ordered structure of the cis isomer.

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Supporting Information Available: X-ray crystallographic files in CIF format for **IV**, Htbo, Htbn, **1**, **1**·THF, **2**, **3**, **5**, **5**·$2CH_2Cl_2$, **5**·$3CHCl_3$, and $[H_2tbn](HCO_3)$ and a table of cell parameters and refinement results for organic compounds **IV**, Htbo, Htbn, and $[H_2tbn](HCO_3)$ as well as displacement ellipsoid plots for these organic species (Figures S1−S3) and ^1H NMR spectra for Htbo, **1**, Htbn, **3**, and **5** (Figures S4−S8) in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) The redox potentials are also consistent with the ionization energies for **1** and **3** that were determined while this manuscript was under review. The energies (eV) for $Mo_2(tbo)_4$ are a band maximum of 4.82 and a band onset of 4.4. For $Mo_2(tbn)_4$, the energies are a band maximum of 4.50 and a band onset of 4.2 eV. See: Cotton, F. A.; Durivage, J. C.; Gruhn, N. E.; Lichtenberger, D. L.; Murillo, C. A.; Van Dorn, L. O.; Wilkinson, C. C. *J. Phys. Chem. B* **2006**, ASAP.

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