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Dalton Transactions

ARTICLE

Redox activity and π bonding in a tripodal seven-coordinate molybdenum(VI) tris(amidophenolate)

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A tris(aminophenol), tris(2-(3',5'-di-*tert*-butyl-2'-hydroxyphenyl)amino-4-methylphenyl)amine, MeClampH$_6$, is prepared in three steps from tri-*p*-tolylamine. The ligand reacts with dioxomolybdenum(VI) bis(acetylacetonate) to form an oxo-free heptadentate complex, (MeClamp)Mo, with a capped octahedral geometry. The molybdenum is formally in the +6 oxidation state, with significant π donation of the amidophenolates, as judged by intraligand bond distances. Two ligand-based oxidations and one metal-centered reduction are observed by cyclic voltammetry. Analysis of the optical spectrum of the compound gives an estimate of the energetic stabilization of the ligand π orbitals by bonding to the molybdenum of approximately 0.9 eV, corresponding to about 40 kcal mol^{-1} per π bond.

Introduction

Tripodal ligands contain a central donor atom, typically nitrogen or phosphorus, attached to three arms that contain additional donor atoms. These strongly chelating ligands are capable of stabilizing unusual geometries such as trigonal monopyramids,[1] but are also often observed in trigonal bipyramidal or octahedral geometries. They have been used to protect metal centers against hydrolysis,[2] to maintain mononuclearity throughout complex catalytic cycles,[3] to promote metal-metal bond formation in homo- and heterobimetallic complexes,[4] and to control the nature of the second coordination sphere.[5]

We were interested in combining the high stability of the tripodal framework with the redox activity of amidophenolate ligands. Amidophenolates have attracted attention for their ability to engage in ligand-centered redox activity, forming monoanionic iminosemiquinonate or neutral iminoquinones when bonded to transition or main group metals. Such ligands have been used as electron reservoirs to enable oxidative addition[6] or reductive elimination[7] reactions of early transition metals.

We have previously studied molybdenum complexes of the 2,2'-biphenyl-bridged bis(amidophenoxide) ligand ^{t}BuClip^{4-} (^{t}BuClipH$_4$ = 4,4'-di-*tert*-butyl-*N*,*N*'-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-2,2'-diaminobiphenyl) containing ancillary terminal oxo, bridging nitrido, and alkoxide ligands.[8] These compounds do undergo ligand-centered oxidation reactions. More significantly, the high-lying ligand orbital responsible for the redox-activity is also capable of strong π donation to molybdenum(VI). This has important structural consequences, for example determining the isomers favored in oxo[9,10] and nitrido complexes. The π donor ability also appears to have

chemical consequences, for example allowing the replacement of all oxo ligands in oxomolybdenum(VI) reagents.[11,12]

Here we describe the preparation of a novel tripodal ligand, tris(2-(3',5'-di-*tert*-butyl-2'-hydroxyphenyl)amino-4-methylphenyl)amine, MeClampH$_6$, in which the three arms emanating from the central triarylamine donor are *o*-aminophenols. The fully deprotonated MeClamp^{6-} forms a very stable seven-coordinate tris(amidophenolate) complex with molybdenum(VI) which undergoes ligand-centered oxidations. Furthermore, the spectroscopy of the complex can be used to make a rare semiquantitative estimate of the stabilization of the complex due specifically to π bonding.

Experimental

General Procedures

Unless otherwise noted, all procedures were carried out on the benchtop without precautions to exclude air or moisture. NMR spectra were measured on Varian VXR-300 spectrometer or Bruker Avance DPX 400 spectrometers. Chemical shifts for ^{1}H and ^{13}C{^{1}H} spectra are reported in ppm downfield of TMS, with spectra referenced using the known chemical shifts of the solvent residuals. Infrared spectra were recorded by ATR on a Jasco 6300 FT-IR spectrometer. UV-Visible spectra were recorded in 1-cm quartz cells on a Beckman DU-7500 or a ThermoFisher Evolution Array diode array spectrophotometer. ESI mass spectra were obtained using a Bruker micrOTOF-II mass spectrometer, and peaks reported are the mass number of the most intense peak of isotope envelopes. Elemental analyses were performed by Robertson Microlit Labs (Ledgewood, NJ) or M-H-W Laboratories (Phoenix, AZ).

Syntheses

Tris(2-nitro-4-methylphenyl)amine, N(C₆H₃-2-NO₂-4-CH₃)₃. This compound is prepared by a variation of a previous procedure[13] that avoids chromatography and produces the desired material in high yield. Into a 250 mL Erlenmeyer flask is weighed tri-*p*-tolylamine (TCI, 1.85 g, 6.44 mmol). Acetic anhydride (75 mL) is added and the mixture stirred until most of the solid dissolves. To the stirred mixture is added $Cu(NO_3)_2 \cdot 2.5\ H_2O$ (3.00 g, 12.9 mmol, 2.00 equiv) and the flask is sealed with parafilm. The solution is initially blue and then turns a brownish green with a green precipitate. After stirring 2 h, the mixture is poured into 300 mL H_2O and stirred overnight. The brownish-orange solid is isolated by suction filtration on a glass frit, washed thoroughly with 2 × 30 mL H_2O and 3 × 20 mL CH_3OH, and air-dried 1 h to yield 2.20 g tris(2-nitro-4-methylphenyl)amine as a yellow powder (82%). ^{1}H NMR (CDCl₃): δ 2.37 (s, 9H, C*H*₃), 7.05 (d, 8Hz, 3H, Ar*H*-6), 7.29 (dd, 8, 1.5 Hz, 3H, Ar*H*-5), 7.61 (d, 1.5 Hz, 3H, Ar*H*-3). ^{13}C{^{1}H} NMR (CDCl₃): δ 20.88 (*C*H₃), 126.49, 128.20, 134.77, 136.33, 136.80, 143.62. IR (cm⁻¹): 3066 (w), 2922 (w), 1614 (w), 1564 (w), 1526 (vs, ν_as, NO₂), 1499 (s), 1453 (w), 1403 (w), 1385 (w), 1346 (vs, ν_sym, NO₂), 1281 (s), 1250 (s), 1218 (w), 1189 (w), 1154 (m), 1092 (w), 1038 (w), 919 (w), 889 (w), 829 (m), 801 (m), 763 (w), 706 (w), 601 (w). ESI-MS: 445.1107 (M+Na, calcd 445.1124). Anal. Calcd for C₂₁H₁₈N₄O₆: C, 59.71; H, 4.30; N, 13.26. Found: C, 59.78; H, 4.49; N, 13.11.

Tris(2-amino-4-methylphenyl)amine, N(C₆H₃-2-NH₂-4-CH₃)₃. In a 50 mL round-bottom flask, 158.0 mg tris(2-nitro-4-methylphenyl)amine (0.374 mmol) is dissolved in 4 mL THF. 15 mL methanol is added and upon stirring, a precipitate forms. To the stirred slurry is added 344.6 mg CuCl (3.48 mmol, 9.3 equiv) in a single portion, followed by 430.4 mg KBH₄ (7.98 mmol, 21.3 equiv) in small portions over 5 min. After vigorous gas evolution, the solution turns brown, but becomes colourless with a coarse black precipitate about 6 min after complete borohydride addition. After stirring 25 min, the mixture is suction filtered and the precipitate washed with 20 mL ethyl acetate. The filtrate is stripped down on the rotary evaporator and partitioned between 30 mL each of ethyl acetate and water. After removing the water layer, the EtOAc layer is washed with dilute aqueous sodium dithionite followed by brine and dried over MgSO₄. After removing the EtOAc on the rotary evaporator, the residue is slurried in 5 mL CH_3OH and isolated by suction filtration. Washing the solid with 5 mL CH_3OH and air-drying 20 min furnishes 78.3 mg triamine as a grey-white solid (62%). ^{1}H NMR (CDCl₃): δ 2.24 (s, 9H, C*H*₃), 3.64 (br s, 6H, N*H*₂), 6.50 (sl br dd, 8, 2.5 Hz, 3H, Ar*H*-5), 6.53 (s, 3H, Ar*H*-3), 6.79 (d, 8 Hz, 3H, Ar*H*-6). ^{13}C{^{1}H} NMR (CDCl₃): δ 21.28 (*C*H₃), 117.21, 119.74, 125.40, 130.55, 135.27, 141.09. IR (cm⁻¹): 3455 (m, ν_NH), 3368 (m, ν_NH), 2952 (w), 2916 (w), 2859 (w), 1736 (w), 1611 (m), 1574 (w), 1506 (s), 1455 (w), 1427 (w), 1304 (m), 1234 (s), 1195 (w), 1172 (w), 1137 (w), 951 (w), 865 (w), 850 (w), 808 (m), 739 (w), 596 (w). ESI-MS: 333.2119 (M+H, calcd 333.2080). Anal. Calcd for

C₂₁H₂₄N₄: C, 75.87; H, 7.28; N, 16.85. Found: C, 76.19; H, 7.04; N, 17.00.

Tris(2-(3',5'-di-*tert*-butyl-2'-hydroxyphenyl)amino-4-methylphenyl)amine, MeClampH₆. In a 50 mL round-bottom flask, 403.7 mg tris(2-amino-4-methylphenyl)amine (1.21 mmol) and 809.9 mg 3,5-di-*tert*-butylcatechol (Aldrich, 3.64 mmol, 3.0 equiv) are added to 20 mL hexanes and 200 μL glacial acetic acid. The flask is sealed with parafilm and the mixture is stirred for 2 d. The dark brown slurry is filtered on a glass frit and the solid washed thoroughly with 6 × 6 mL CH_3OH to remove colored impurities. The solid is air-dried 1 h to yield 829.2 mg MeClampH₆ (72%). ^{1}H NMR (CDCl₃): δ 1.09 (s, 27H, *t*Bu), 1.36 (s, 27H, *t*Bu), 2.20 (s, 9H, C*H*₃), 5.38 (br s, 3H, N*H*), 6.02 (s, 3H, O*H*), 6.40 (d, 1.5 Hz, 3H, Ar*H*-3), 6.49 (d, 2 Hz, 3H, Ar*H*-4'), 6.67 (dd, 8, 1.5 Hz, 3H, Ar*H*-5), 6.98 (d, 8 Hz, 3H, Ar*H*-6), 7.10 (d, 2 Hz, 3H, Ar*H*-6'). ^{13}C{^{1}H} NMR (CDCl₃): δ 21.56 (Ar*C*H₃), 29.76, 31.62 (C(*C*H₃)₃), 34.41, 35.13 (*C*(CH₃)₃), 116.81, 121.26, 121.42, 121.91, 124.91, 128.09, 131.42, 135.63, 136.44, 140.87, 142.45, 149.09. IR (cm⁻¹): 3456 (w, ν_OH), 3374 (w, ν_NH), 2952 (m), 2868 (w), 1608 (w), 1577 (w), 1510 (w), 1485 (m), 1460 (w), 1420 (m), 1391 (w), 1362 (m), 1336 (w), 1309 (m), 1254 (w), 1213 (m), 1196 (m), 1161 (w), 1121 (w), 1023 (w), 978 (w), 880 (w), 818 (w), 798 (m), 739 (w), 712 (w), 660 (m), 624 (m), 595 (w). ESI-MS: 941.6319 (M⁺-3H, calcd 941.6309). Anal. Calcd for C₆₃H₈₄N₄O₃: C, 80.04; H, 8.96; N, 5.93. Found: C, 79.81; H, 8.72; N, 5.82.

κ⁷-[Tris(2-(3',5'-di-*tert*-butyl-2'-oxyphenyl)amido-4-methylphenyl)amine]molybdenum(VI), (MeClamp)Mo. In the drybox, 0.1131 g MeClampH₆ (0.1196 mmol) and 0.0595 g MoO₂(acac)₂ (0.184 mmol, 1.5 equiv) are dissolved in 4 mL CH_2Cl_2 and allowed to stand 36 h at room temperature. During this time the solution changes from dark brown to deep purple. In the air, the solvent is removed on the rotary evaporator and the black residue is slurried with 5 mL acetonitrile and vacuum filtered through a glass frit. The solid is washed with 5 mL CH_3CN and air-dried 15 min to yield 46.1 mg (MeClamp)Mo (37%). ^{1}H NMR (CDCl₃, with added trace of Cp*₂Fe): δ 1.22 (s, 27H, *t*Bu), 1.31 (s, 27H, *t*Bu), 2.29 (s, 9H, C*H*₃), 6.56 (sl br dd, 8, 2 Hz, 3H, Ar*H*-5), 6.81 (d, 8 Hz, 3H, Ar*H*-6), 6.88 (d, 2 Hz, 3H, Ar*H*-4'), 7.23 (s, 3H, Ar*H*-3), 7.29 (d, 2 Hz, 3H, Ar*H*-6'). ^{13}C{^{1}H} NMR (CD₂Cl₂, with added trace of Cp*₂Fe): δ 22.08 (Ar*C*H₃), 30.29, 32.01 (C(*C*H₃)₃), 35.15, 35.53 (*C*(CH₃)₃), 107.51, 119.09, 119.36, 122.33, 123.35, 128.86, 138.06, 140.08, 142.50, 143.63, 144.35, 147.34. IR (cm⁻¹): 2952 (s), 2903 (m), 2867 (m), 1588 (m), 1490 (s), 1457 (m), 1421 (m), 1409 (m), 1388 (w), 1360 (m), 1343 (w), 1305 (s), 1281 (w), 1260 (m), 1232 (m), 1201 (m), 1171 (m), 1000 (m), 945 (m). ESI-MS: 1036.4996 (M+H, calcd 1036.3099). UV-Vis (CH₂Cl₂): λ_max = 295 nm (sh, ε = 19500 L mol⁻¹ cm⁻¹), 356 (12000), 513 (sh, 8500), 563 (10700), 985 nm (6900). Anal. Calcd for C₆₃H₇₈MoN₄O₃: C, 73.09; H, 7.59; N, 5.41. Found: C, 70.19; H, 7.38; N, 5.10.

Electrochemistry

Cyclic voltammograms were performed at a scan rate of 120 mV s^{-1} using a BAS Epsilon potentiostat, with glassy carbon working and counter electrodes and a silver/silver chloride pseudo-reference electrode. The electrodes were connected to the potentiostat through electrical conduits in the drybox wall. The sample of (MeClamp)Mo was 1 mM in CH_2Cl_2, with 0.1 M Bu_4NPF_6 as the electrolyte. Potentials were referenced to ferrocene/ferrocenium at 0 V,[14] with the reference potential established by spiking the test solution with a small amount of ferrocene.

DFT Calculations

Geometry optimizations and orbital calculations were performed using the crystal structure of (MeClamp)Mo as a starting structure, and with all *tert*-butyl groups and methyl groups replaced with hydrogens. Calculations used the hybrid B3LYP method, with an SDD basis set for molybdenum and a 6-31G* basis set for all other atoms, using the Gaussian09 suite of programs.[15] The optimized geometries were confirmed as minima by calculation of vibrational frequencies. Plots of calculated Kohn-Sham orbitals were generated using Gaussview (v. 5.0.8) with an isovalue of 0.04.

X-ray crystallography

Crystals of (MeClamp)Mo•CH_3CN were grown by slow evaporation of acetonitrile solutions while crystals of (MeClamp)Mo•3 C_6H_6 were grown by layering a concentrated 10:1 dichloromethane:hexane solution with benzene. Crystals were placed in inert oil before being transferred to the cold N_2 stream of a Bruker Apex II CCD diffractometer. Data were reduced, correcting for absorption, using the program SADABS. The structures were solved using direct methods. All nonhydrogen atoms not apparent from the initial solutions were found on difference Fourier maps, and all heavy atoms were refined anisotropically. In the acetonitrile solvate, two *tert*-butyl groups (those attached to C28 and C68) were refined in two alternate orientations, with opposing methyl groups constrained to have the same thermal parameters. The minor components refined to 12.6(5)% and 12.4(5)% occupancy, respectively. Hydrogen atoms on the metal complex in the benzene solvate were located on difference maps and refined isotropically, while all other hydrogen atoms were placed in calculated positions, with thermal parameters for the hydrogens tied to the isotropic thermal parameters of the atoms to which they are bonded (1.5 × for methyl, 1.2 × for others). Calculations used SHELXTL (Bruker AXS),[16] with scattering factors and anomalous dispersion terms taken from the literature.[17] Further details about the structures are in Table 1.
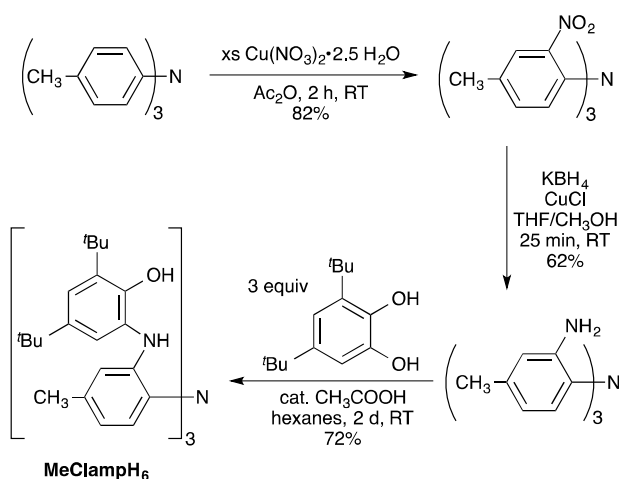
Scheme 1. Synthesis of MeClampH$_6$.

Results and Discussion

Synthesis of the tris(aminophenol) MeClampH$_6$

Chelating bis(aminophenol) ligands have been prepared previously with aromatic (1,2-benzenediyl[18] or 2,2-biphenyldiyl[8,19,20]) or aliphatic[21] linkers bridging the two nitrogen atoms. A chelating tris(aminophenol) ligand had not been previously prepared, but we anticipated that one would be able to bind to a single metal in a hexa- or heptadentate fashion based on six- and seven-coordinate molybdenum bis(amidophenolate)-catecholates[11] and on numerous examples of octahedral tris(iminosemiquinonates).[22]

The tris(aminophenol) ligand designated MeClampH$_6$ is prepared in three steps from commercially available tri-*p*-tolylamine (Scheme 1), with the three aminophenols attached to the *ortho* positions of the tritolylamine. Tris(2-aminophenyl)amine has been prepared previously[23] and has been successfully elaborated into tripodal ligands.[24] The use of the methyl substituent *para* to the central nitrogen in the present synthesis allows one to avoid the cumbersome nucleophilic aromatic substitution used to assemble the unsubstituted compound. Furthermore, *para*-substitution of triarylamines is known to greatly increase the stability of their radical cations,[25] which may be important if the ligand or its complexes are to be investigated under oxidative conditions.

Tri-*p*-tolylamine is readily nitrated with excess copper(II) nitrate in acetic anhydride to furnish the trinitro compound $N(C_6H_3\text{-}2\text{-}NO_2\text{-}4\text{-}CH_3)_3$. This nitration was previously described by Fry and coworkers to give the compound as a mixture that required chromatographic separation from products of partial nitration.[13] We find that use of a modest excess of copper nitrate (2 mol/mol triarylamine) suffices to drive the reaction to completion, and the desired product can be isolated by filtration of the reaction mixture in good yield and high purity. Reduction of the nitro groups to the triamine is accomplished using $KBH_4/CuCl$,[26] a method that has previously been employed for the reduction of *o*-nitro-*N*-arylanilines.[27]

Hydrogenation over 10% Pd/C is also successful, but the reaction is slower and yields are lower. Condensation of the triamine proceeds smoothly in the presence of catalytic acetic acid to afford the desired tris(aminophenol), MeClampH$_6$, in good yield after filtration and washing with methanol. Triethylamine has been more commonly used as a catalyst in this condensation reaction,[8,20,28] but is ineffective here.

Synthesis and structure of (MeClamp)Mo

Commercially available oxomolybdenum(VI) bis(acetylacetonate), MoO$_2$(acac)$_2$, has been used as a convenient starting material for the preparation of catecholate and amidophenolate complexes containing zero,[11,12] one[10,29] or two[8] remaining oxo groups. The hexaprotic ligand MeClampH$_6$ reacts with MoO$_2$(acac)$_2$ over the course of 36 h to produce oxo-free, air-stable, dark purple (MeClamp)Mo (eq 1),

$$+ \; MoO_2(acac)_2 \xrightarrow[-2\;H_2O]{-2\;Hacac} \qquad (1)$$

MeClampH$_6$ → **(MeClamp)Mo**

which can be isolated by precipitation from acetonitrile. Production of free Hacac is observed *in situ* by ^{1}H NMR spectroscopy. Loss of both oxo ligands is suggested by the mass spectrum (which shows a parent ion at *m/z* = 1036) and the lack of an oxo stretch in the IR spectrum. ^{1}H NMR spectra of the as-prepared material are appreciably broadened, as we[30] and others[31] have sometimes observed in complexes with easily oxidized ligands, where a minute amount of the radical cation can rapidly undergo electron transfer with the neutral compound and broaden the entire spectrum. Addition of a trace of decamethylferrocene reduces any adventitiously oxidized material, and results in sharp ^{1}H and ^{13}C{^{1}H} NMR spectra with peaks corresponding to a symmetrical ligand at normal, diamagnetic chemical shifts.

Fig. 1. Thermal ellipsoid plot (50% ellipsoids) of the metal complex in (MeClamp)Mo•3 C$_6$H$_6$. Hydrogen atoms are omitted for clarity.

Table 1. Crystal data for (MeClamp)Mo•CH$_3$CN and (MeClamp)Mo•3 C$_6$H$_6$

	(MeClamp)Mo•CH$_3$CN	(MeClamp)Mo•3 C$_6$H$_6$
Molecular formula	C$_{65}$H$_{81}$MoN$_5$O$_3$	C$_{81}$H$_{96}$MoN$_4$O$_3$
Formula weight	1076.29	1269.56
T/K	120(2)	120(2)
Crystal system	Monoclinic	Rhombohedral
Space group	*P*2$_1$/*c*	*R*$\bar{3}$
λ/Å	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Total data collected	194202	48841
No. of indep reflns.	24403	5931
R_{int}	0.1778	0.0255
Obsd refls [*I* > 2σ(*I*)]	13890	5380
a/Å	20.1764(12)	17.2078(5)
b/Å	46.334(3)	17.2078(5)
c/Å	12.7362(7)	17.2078(5)
α/°	90	60.5230(10)
β/°	94.734(4)	60.5230(10)
γ/°	90	60.5230(10)
V/Å^3	11866.0(12)	3645.56(18)
Z	8	2
μ/mm^{-1}	0.269	0.229
Crystal size/mm	0.35 × 0.14 × 0.04	0.58 × 0.35 × 0.21
No. refined params	1361	372
*R*1, *wR*2 [*I* > 2σ(*I*)]	*R*1 = 0.0574, *wR*2 = 0.1137	*R*1 = 0.0308, *wR*2 = 0.0826
*R*1, *wR*2 [all data]	*R*1 = 0.1305, *wR*2 = 0.1400	*R*1 = 0.0360, *wR*2 = 0.0874
Goodness of fit	0.986	0.969

Table 2. Selected bond distances (Å), metrical oxidation states and angles (°) in (MeClamp)Mo (X-ray), (Clamp)Mo (DFT) and (Clamp)Mo$^+$ (DFT).

	X-ray (MeClamp)Mo • 3 C$_6$H$_6$	X-ray^a (MeClamp)Mo • CH$_3$CN	DFT^b (Clamp)Mo	DFT^b (Clamp)Mo$^+$
Mo–O1	2.0077(9)	1.994(16)	2.016	2.032
Mo–N1	2.0726(11)	2.066(17)	2.102	2.111
Mo–N10	2.2940(19)	2.273(15)	2.340	2.344
C11–O1	1.3300(16)	1.334(6)	1.324	1.312
C12–N1	1.3778(17)	1.381(10)	1.379	1.362
C11–C12	1.4120(18)	1.408(8)	1.424	1.438
C12–C13	1.4076(19)	1.397(9)	1.410	1.419
C13–C14	1.3815(19)	1.384(7)	1.391	1.381
C14–C15	1.413(2)	1.405(7)	1.407	1.419
C15–C16	1.388(2)	1.384(6)	1.389	1.383
C16–C11	1.4168(18)	1.404(8)	1.403	1.408
MOS	−1.47(5)	−1.58(6)	−1.47(7)	−1.20(6)
O1–Mo–O1A	83.42(4)	83(3)	84.0	85.4
O1–Mo–N1	74.49(4)	74.6(6)	74.5	74.4
O1–Mo–N1A	157.17(4)	157(2)	157.8	158.8
O1–Mo–N1B	88.32(4)	88(2)	87.9	86.5
O1–Mo–N10	129.80(3)	130(3)	129.4	128.5
N1–Mo–N1A	109.95(3)	110(5)	109.8	110.1
N1–Mo–N10	71.01(3)	71.2(7)	70.9	71.1
C21–N10–Mo	106.00(9)	106.5(12)	105.4	105.4
C21–N10–C21A	112.71(8)	112.3(14)	113.2	113.3
C12–N1–Mo	118.26(9)	118(2)	117.5	117.8
C22–N1–Mo	116.69(9)	117.0(8)	116.0	115.6
C12–N1–C22	124.61(11)	124.8(13)	125.9	126.3
C11–O1–Mo	119.86(8)	119.8(13)	119.7	119.5

^{a}Values represent averages over chemically equivalent examples in the two crystallographically unique molecules of (MeClamp)Mo; esd's include the variation among the observations as well as the statistical uncertainty of the fit. ^{b}Structure optimization (B3LYP; SDD basis for Mo, 6-31G* for all others) performed on compound with all ^{t}Bu and CH$_3$ groups replaced with H.

The solid-state structure of (MeClamp)Mo was determined by X-ray crystallographic analysis of the complex as both a benzene and an acetonitrile solvate (Table 1). The molecular structure of the complex is essentially identical in both crystals (Fig. 1, Table 2), and is seven-coordinate, adopting a C_3-symmetric, capped octahedral structure with the triarylamine nitrogen supplying the capping ligand. This is very similar to the structure adopted by $(3,5-^tBu_2Cat)_3Mo(py)$,[32] and the Mo–NAr_3 distance of 2.28 Å (Table 2) is close to the Mo–py distance of 2.274(2) Å in the tris(catecholate) structure. Heptadentate coordination of anionic tripodal ligands is well known for lanthanides[33] and main group elements,[34] but is uncommon for transition metals.[35]

The intraligand bond distances in amidophenoxides and related catecholates have been used extensively to gauge the degree of oxidation of the ligand.[36] Given the diamagnetism of the compound, a formal oxidation state of +6 for molybdenum with fully reduced amidophenoxide ligands seems chemically secure. Analysis of the bond distances using established correlations[37] gives an apparent metrical oxidation state (MOS) of −1.52(9), averaged between the values in the two crystal structures (Table 2). Such noninteger values of the MOS do not generally map onto formal oxidation states (which would require a Mo oxidation state of 4.5 in this case), and instead are most sensibly interpreted in terms of π bonding,[37,38] with the decrease in electron density in the amidophenolate HOMO due to π donation to the Mo center causing bond distance changes akin to those caused by outright oxidation of the amidophenoxide. The MOS values observed for (MeClamp)Mo are typical of other molybdenum(VI) amidophenoxides.[8,11]

Outer-sphere redox chemistry of (MeClamp)Mo

Inner-sphere oxygen atom donors such as amine-*N*-oxides do not react with (MeClamp)Mo, in contrast to their behavior toward Mo(VI) catecholate complexes.[10,32] Presumably this is because the heptadentate chelation blocks access to the molybdenum. This multidentate chelation stabilizes the metal as it undergoes outer-sphere redox chemistry, leading to the observation of three reversible waves in the cyclic voltammogram of (MeClamp)Mo (Fig. 2). The two waves at −0.17 and +0.55 V vs. Fc⁺/Fc are attributed to amidophenolate-centered oxidations, and the reduction at −1.40 V is Mo-centered. (Free tri-*p*-tolylamine oxidizes at +0.33 V,[39] but coordination of the amine to molybdenum will make this oxidation much more difficult.)

The monocation [(MeClamp)Mo]⁺ is generated in solution by treatment with chemical oxidants such as ferrocenium hexafluorophosphate. Titration of (MeClamp)Mo with [Cp₂Fe]PF₆ generates a new optical spectrum with clean isosbestic points and requires 1.0 equiv of oxidant for complete reaction (Fig. 3). EPR spectroscopy of solutions of *in situ* generated [(MeClamp)Mo]⁺ at room temperature shows a strong signal with no discernible hyperfine coupling at g = 2.016, consistent with a ligand-centered radical. Simiar EPR
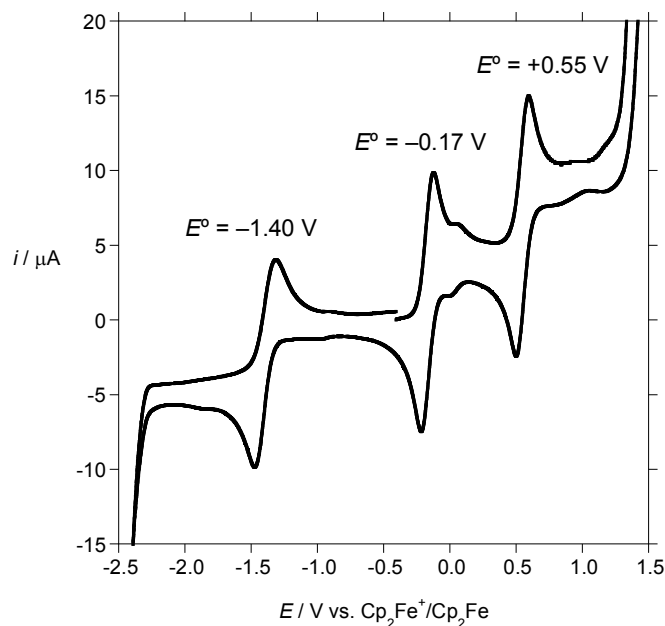
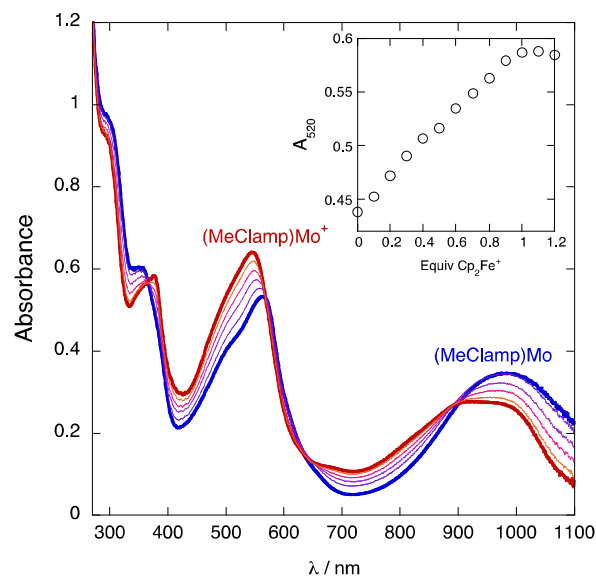Fig. 2. Cyclic voltammogram of (MeClamp)Mo in CH_2Cl_2 (0.1 M Bu_4NPF_6, 120 mV s⁻¹).

Fig. 3. UV-Vis-NIR titration of (MeClamp)Mo (5×10^{-5} M, CH_2Cl_2) with $[Cp_2Fe]PF_6$. Scans are shown every 0.2 equiv Cp_2Fe^+ from 0 to 1.0 equiv. Inset: Absorbance at 520 nm as a function of added $[Cp_2Fe]PF_6$.

behavior is observed in oxidized ruthenium and osmium tris(amidophenolate) complexes.[22f,h]

π Bonding in (MeClamp)Mo

The intraligand bond lengths in (MeClamp)Mo show evidence of significant amidophenolate-to-metal π donation. Density functional theory calculations on (Clamp)Mo (with the *tert*-butyl and methyl groups replaced by hydrogen) support the presence of strong π bonding. Calculations converge on a C_3-symmetric minimum-energy structure whose geometry is

strikingly similar to experimental observations (with the exception of a slight overestimate of the metal-nitrogen distances by theory, Table 2). In particular, DFT captures the intraligand distances faithfully, giving an MOS value of -1.47(7), in excellent agreement with experiment.

The three ligand-centered redox-active orbitals split into an E set and an A combination in C_3 symmetry (Fig. 4). Of these, the E orbitals interact strongly with the Mo $d\pi$ orbitals and form a bonding and an antibonding combination. The A symmetry ligand-centered combination has little overlap with the metal d_{z^2} orbital (its only symmetry match among the d orbitals) and is essentially nonbonding. This analysis is essentially the same as in other threefold symmetric metal complexes with three (σ + 2π) ligands; familiar examples include $(\eta^5\text{-}C_5H_5)_3ZrX$,[40] $(RCCR)_3W(L)$,[41] and $(RN)_3WL$.[42]

There is thus a formal π bond order of 2 in (MeClamp)Mo, delocalized over the three amidophenolate ligands. This is in good agreement with the structural data. For comparison, in the oxobis(amidophenolate) complex (^{t}BuClip)MoO(3,5-lut), one amidophenolate must compete with the oxo ligand for π bonding to the molybdenum and has a π bond order of zero (MOS = $-2.00(9)$), while the other amidophenolate donates into a strictly nonbonding $d\pi$ orbital and has a π bond order of one (MOS = $-1.34(12)$). The amidophenolates in (MeClamp)Mo, with a π bond order of 2/3, have MOS values ($-1.52(9)$) two-thirds of the way between these two values.

According to the MO analysis, oxidation of (MeClamp)Mo should cause loss of an electron from the A-symmetry, π nonbonding orbital and would give a delocalized but ligand-centered radical. This is consistent with the relatively facile oxidation of (MeClamp)Mo (E^o = -0.17 V vs. ferrocene/ferrocenium) and with the EPR spectrum of the cation. It is also supported by DFT calculations on the cation, which show only small changes in bond distances and angles (Table 2); the MOS becomes more positive overall by 0.81, suggesting that the degree of π bonding has not changed substantially. The small changes in geometry and delocalization of charge suggest a small reorganization energy for the (MeClamp)Mo/(MeClamp)Mo$^+$ redox couple, predicting rapid degenerate electron transfer, consistent with the experimental observation that even traces of the cation strongly broaden the NMR spectra of the neutral species.

If the π bonding is strong enough, one would predict that the dication would lose the second electron from the A orbital to form a delocalized singlet bis(iminosemiquinone) species. The second oxidation (at $+0.55$ V) is at a low enough potential to suggest that this is plausible; in (^{t}BuClip)MoO(py), the π-nonbonding amidophenolate is oxidized at $+0.06$ V, but the π-bonded amidophenolate is not oxidized below $+1.1$ V.[8] Unfortunately, we have been unable to generate stable solutions of (MeClamp)Mo^{2+}, so no experimental data are available to address its bonding.

The π bonding of the neutral (MeClamp)Mo can be addressed through an analysis of its optical spectrum. In their seminal study of the optical spectra of iron(III)[43] and vanadium(IV)[44] tris(catecholates), Solomon and Raymond
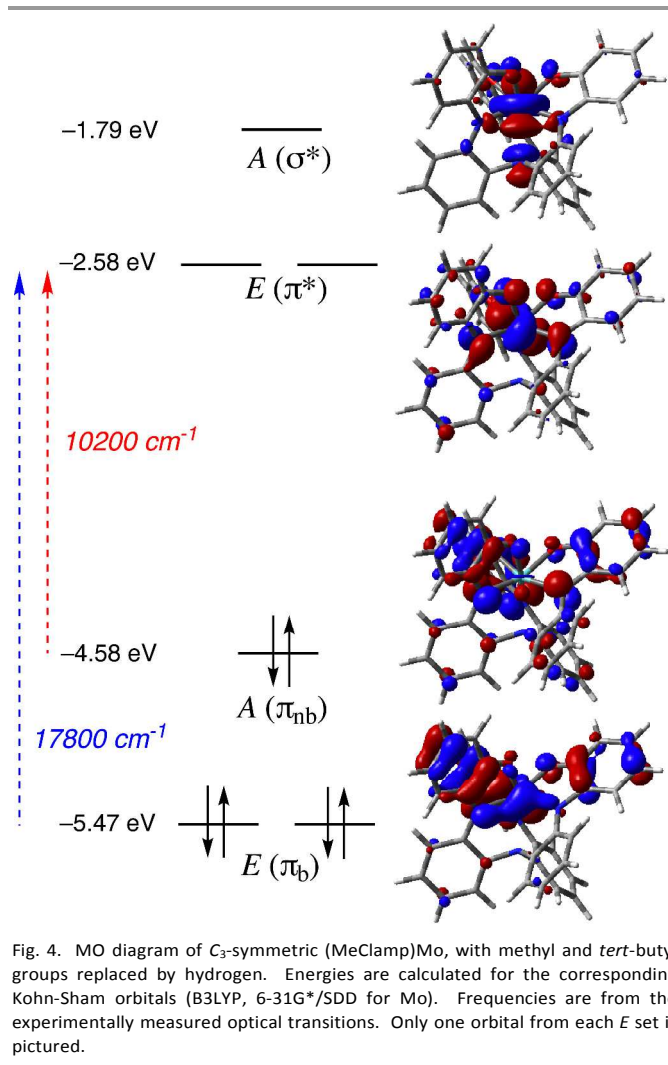

Fig. 4. MO diagram of C_3-symmetric (MeClamp)Mo, with methyl and *tert*-butyl groups replaced by hydrogen. Energies are calculated for the corresponding Kohn-Sham orbitals (B3LYP, 6-31G*/SDD for Mo). Frequencies are from the experimentally measured optical transitions. Only one orbital from each E set is pictured.

noted that the difference in energy in the two lowest-energy charge-transfer bands, the a_2 (Cat π_{nb}) $\rightarrow$ e ($d\pi^*$) and e (Cat π_b) $\rightarrow$ e ($d\pi^*$), corresponded to the difference in energy of the catecholate orbitals caused by metal-ligand π bonding (a value they called γ). The bonding picture in (MeClamp)Mo is similar to that of a metal tris(catecholate), with the exception that d_{z^2}, which is strictly nonbonding in the octahedral D_3-symmetric tris(catecholate), is substantially raised in energy in (Clamp)Mo due to its strong σ^* interaction with the central triarylamine. The two lowest-energy transitions observed in the optical spectrum of (MeClamp)Mo are at 10200 and 17800 cm^{-1}, and TDDFT calculations support their assignment as being due to the a (π_{nb}) $\rightarrow$ e (π^*) and e (π_b) $\rightarrow$ e (π^*) transitions, respectively, with calculated transitions at 11400 and 18100 cm^{-1}, respectively. Thus, for (MeClamp)Mo, $\gamma = 7600$ cm^{-1} (0.94 eV), which is in excellent agreement with the difference in the calculated energies of the respective Kohn-Sham orbitals (0.89 eV). Unsurprisingly, the π bonding in this Mo(VI) tris(amidophenoxide) is substantially stronger than that seen in Fe(III) ($\gamma = 3600$ cm^{-1})[43] or V(IV) ($\gamma = 3900$ cm^{-1})[44] tris(catecholate) complexes. The difference likely originates from greater basicity of amidophenolates relative to

catecholates, the higher oxidation state of molybdenum, and the fact that Mo is a second-row transition metal.

Equating γ to the stabilization afforded to the ligand by π bonding to the metal neglects any effects caused by different electron-electron repulsion terms in the excited states. In $[Fe(Cat)_3]^{3-}$, this neglect was justified by the fact that the donor orbitals were ligand-localized and the acceptor orbital metal-localized.[43] That assumption should still be roughly true in (MeClamp)Mo, though the increased covalency and orbital mixing in this compound does make this approximation less exact. With this caveat in mind, one can translate the one-electron energy $\gamma = 7600$ cm^{-1} to an estimate that each of the (two-electron) π bonds formed by the amidophenolates contributes roughly 40 kcal mol^{-1} to the overall stability of the molecule. Such quantitative experimental estimates of the π component of bonding are extremely rare, especially for strongly π bonding ligands; they are only possible in this case due to the presence of analogous ligand nonbonding orbitals to serve as a sort of internal standard. Computationally, dissecting interactions into σ and π components is more tractable, and has been carried out by methods such as energy decomposition analysis, which allows one to partition bonding stabilization into σ and π components (when these are of different irreducible representations).[45] Such an analysis, when applied to MoOCl$_4$, furnishes an estimate of 36 kcal mol^{-1} of stabilization energy for each Mo–O π bond.[46] Since this value is derived from combination of singlet MoCl$_4$ with an O atom in the $(p\sigma)^0(p\pi)^4$ configuration, it represents a donor-acceptor interaction that should be analogous to the experimental estimate obtained here for amidophenoxides,[47] though quantitative comparison of values obtained by such different methods is problematic. Nevertheless, based on the data obtained here, the amidophenoxide ligand is clearly a strong π donor. This is undoubtedly an important factor in the amidophenolate's unusual ability to replace all the oxo groups in molybdenum(VI) compounds.[8,11,12]

Conclusions

A C_3-symmetric tris(aminophenol) ligand with the amino groups bonded to the *ortho* positions of a triarylamine, MeClampH$_6$, is prepared in three steps from tri-*p*-tolylamine. It is metalated by MoO$_2$(acac)$_2$ to form oxo-free (MeClamp)Mo, in which the ligand is heptadentate, binding through all three amidophenolates and through the neutral amine nitrogen. Structural data and DFT calculations indicate that the compound is well described as molybdenum(VI) bound to fully reduced amidophenolates, with strong π donation to molybdenum from the *E* combination of amidophenolate orbitals. Analysis of the optical spectrum, using the essentially nonbonding *A* combination of amidophenolate orbitals as a benchmark, allows one to estimate the energetic stabilization of the ligand donor orbitals due to π bonding as about 0.9 eV, corresponding to roughly 40 kcal mol^{-1} for each π bond.

Acknowledgments

Notes and references

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Electronic Supplementary Information (ESI) available: Energy and Cartesian coordinates for calculated structures of (Clamp)Mo and (Clamp)Mo$^+$ and TDDFT calculations for (Clamp)Mo. Crystallographic data in CIF format have been deposited with the CCDC, deposition numbers 1023169-1023170. See DOI: 10.1039/b000000x/

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Redox activity and π bonding in a tripodal seven-coordinate molybdenum(VI) tris(amidophenolate)

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A tripodal seven-coordinate tris(amidophenolato)molybdenum(VI) complex shows strong ligand-to-metal π donation (40 kcal mol^{-1} per π bond) and undergoes facile ligand-centered oxidation.