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Molybdenum complexes of chiral C₂-symmetric picchxn-type ligands: Synthesis, characterization, and structural studies

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1. Introduction

Chiral C₂-symmetric ligands hold a special place in synthetic chemistry by virtue of their ability to create well-defined chiral environments around metal centers [1–3]. For octahedral complexes, tetradentate ligands are particularly desirable as they can render the two remaining coordination sites chemically equivalent. In recent years, the most-celebrated examples have been the salen-type ligands, which typically bond in a trans geometry and have been utilized in an impressive array of applications [4–6]. Other variations similarly built on chiral C₂-symmetric diamines but instead favoring a cis complexation geometry have also shown promise, particularly in instances where it is possible to isolate a stereoisomer with a cis-α configuration. Trans and cis-α configurations retain the ligand's C₂-symmetry, whereas cis-β configurations do not (Fig. 1) [7,8].

Picchxn (picchxn = trans-N,N-bis(pyridin-2-ylmethyl)-1,2-diaminocyclohexane), constructed using trans-1,2-diaminocyclohexane, is one such chiral C₂-symmetric tetradentate ligand that has garnered interest because of its ability to bond in a cis-α configuration. Picchxn-type ligands (N₄ ligands, trans-N,N-bis(heterocycl-2-ylmethyl)-1,2-diaminocyclohexanes) have been studied extensively on small 3d metals, with applications having been reported for Mn(II) [9–21], Fe(II) [19,22–32], Fe(III) [27], Fe(IV) [33–35], Co(III) [7,8,36–40], Cu(I) [41,42], Cu(II) [41,43], and Zn(II) [44,45] centers. The literature also includes reports of picchxn-type ligands on Cr(III) [8,46,47] as well as sparse Ru(II) [7,24,48–50], Rh(III) [51], Pd(II) [52], Ag(I) [43,53], and Cd(II) [54,55] examples, but the behaviors of these ligands on larger low-valent metal centers remains largely uninvestigated. Our interest in picchxn-type ligands stems from ongoing studies of low-valent π-basic molybdenum complexes with potential applications in dearomatization sequences [56–59]. We hypothesize that inclusion of a chiral C₂-symmetric tetradentate ligand in such a complex might allow for enantioselective dearomatizations. We anticipate that an...
effective dearomatizing molybdenum metal fragment based on a picchxn-type ligand would need to be a strong π base [57,60,61], so in addition to the parent ligand picchxn (1) and its N,N’-dimethyl variant picchxnMe2 (2), we also studied the more basic bis-imidazolyl analog Imchxn (3, Fig. 2). Owing to the possibility of complexation leading to a reactive NH group in 3 [51], we synthesized the corresponding novel N,N’-dimethyl variant ImchxnMe2 (4). A brief parallel investigation of a novel picchxn-type ligand incorporating the less-basic thiazolyl group (Thzchxn, 5) also provided insight. We describe herein syntheses, characterizations, and structural studies of Mo(0) and Mo(I) complexes formed from ligands 1–5.

2. Experimental

2.1. General methods

Molybdenum hexacarbonyl and potassium hexafluorophosphate were purchased from Strem Chemicals. Thiazole-2-carboxaldehyde was purchased from Ark Pharm Inc. All other reagents were purchased from Sigma–Aldrich. Solvents were purchased as anhydrous-grade as available and used without additional purification. Deuterated solvents were used as received from Cambridge Isotopes. Previously reported picchxn-type ligands were produced according to literature procedures [14,49,62–64], as described in Supplemental material. Reactions and electrochemical experiments were performed under a nitrogen atmosphere. NMR spectra were obtained on a 400 MHz Bruker Avance spectrometer. Chemical shifts are reported in ppm and are referred to tetramethylsilane (TMS) utilizing residual 1H or 13C signals of the deuterated solvents as internal standards, and coupling constants (J) are reported in hertz (Hz). Infrared spectra were recorded on a Perkin Elmer BX II, Spectrum 100, or Spectrum Two FT-IR spectrometer as concentrated solutions between NaCl plates. Peaks are reported in cm⁻¹, and solvents used in sample preparation are as indicated. Electrochemical experiments were performed using a Cypress Systems model CySy 2Ra potentiostat. Cyclic voltammetric data were taken at ambient temperature at 100 mV/s in a standard three-electrode cell from +1.5 to −1.5 V with a glassy-carbon working electrode, N,N-dimethylacetamide (DMA) solvent, and tetrabuty lammonium hexafluorophosphate (TBAH) electrolyte (~0.5 M).

All potentials are reported versus NHE (Normal Hydrogen Electrode) using cobaltocenium hexafluorophosphate (E1/2 = 0.78 V), ferrocene (E1/2 = 0.55 V), or decamethylferrocene (E1/2 = 0.04 V) as an internal standard. The peak-to-peak separation was less than 100 mV for all reversible couples. Elemental analyses (EA) were performed on a CE Instruments Flash EA 1112 Series Elemental Analyzer or obtained from Atlantic Microlabs, Inc. X-ray data was collected on a Bruker SMART APEX CCD, Bruker SMART APEX II, or Siemens R3 X-ray diffractometer. Measurements were taken at 100 K with graphite-monochromated Cu Kα radiation [65]. All collected data were corrected for Lorentz and polarization [66] effects as well as absorption using the crystallography program SADABS [67]. The structure was then solved through the use of direct methods. For all reflections, least-squares refinement on F2 was used. The SHELXTL software package was used for structure solution and refinement and the calculation of derived results [68]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by standard difference Fourier techniques and were refined with isotropic thermal parameters.

2.2. Novel picchxn-type ligands

2.2.1. Trans-N,N’-dimethyl-N,N’-bis(1-methylimidazol-2-ylmethyl)-1,2-diaminocyclohexane (ImchxnMe2, 4)

A solution of trans-N,N’-bis(1-methylimidazol-2-ylmethyl)-1,2-diaminocyclohexane (Imchxn, 3, 6.05 g, 20.0 mmol) in acetonitrile (73 mL) was stirred in a water bath held at 60 °C. Formaldehyde (37% by weight in water, 16.8 mL) was added, and sodium cyanoborohydride (3.73 g, 59.0 mmol) was dissolved in acetonitrile (16 mL). The sodium cyanoborohydride solution was added to the reaction mixture in portions over 1.5 h, and following each addition sufficient glacial acetic acid was added to achieve a pH of ~7. The reaction mixture was taken out of the water bath, cooled for 15 min, and evaporated to a volume of ~20 mL. Aqueous potassium hydroxide (2 M, 150 mL) was added and this strongly basic solution was extracted with methylene chloride (3 × 26 mL). The combined organic solution was washed with water (3 × 25 mL) and extracted with hydrochloric acid (1 M, 3 × 25 mL). The combined aqueous solution was washed with methylene chloride (3 × 25 mL) and made strongly basic with concentrated aqueous NaOH. It was extracted with methylene chloride (3 × 30 mL). The
combined organic extracts were dried over sodium sulfate (3 g) and potassium carbonate (3 g) for three days. The mixture was filtered, and the collected solid was rinsed with methylene chloride (25 mL, in portions). The combined filtrate was evaporated to give an orange oily liquid, which was further dried on a Schlenk line. A low-pressure distillation was performed using a Kugelrohr at 220 °C and 0.75 mmHg, giving a yellow-orange oil (4, 5.20 g, 82.4%).

1H NMR (CDCl₃, δ): 6.88 (d, J = 1.2, 2H, Im), 6.75 (d, J = 1.2, 2H, Im), 3.65 (s, 2H, NCH₂), 3.65 (s, 2H, NCH₂), 3.64 (s, 6H, ImCH₃), 2.59 (m, 2H, NCH₂), 1.59 (s, 6H, NCH₂), 1.87 (s, 2H, cyclohexyl), 1.71 (m, 2H, cyclohexyl), 1.12 (m, 4H, cyclohexyl). 13C NMR (CDCl₃, δ): 146.2 (Im 2), 126.8 (Im 4,5), 121.4 (Im 4,5), 62.0 (NCH₂), 59.9 (NCH₃, ImCH₃), 32.7 (NCH₃, ImCH₃), 25.6 (cyclohexyl), 24.5 (cyclohexyl). Anal. Calc. for C₁₁H₁₇N₅S₂: C, 54.48; H, 6.54; N, 18.16. Found: C, 54.20; H, 6.49; N, 17.86%.

2.3. (κ²-N,N'-Mo(CO)₃) complexes

2.3.1. (κ²-picHxnMo(CO)₃) (6)

A mixture of trans-N,N'-bis(pyridin-2-ylmethyl)-1,2-diaminocyclohexane (picHxn, 1, 5.06 g, 17.1 mmol), N,N-dimethylformamide (62.5 mL), and molybdenum hexacarbonyl (4.27 g, 16.2 mmol) was stirred under reflux for 1 h to give a brown solution. The heat source was removed, and after 2 h of stirring, the resulting solution was added in small portions to stirrer water (300 mL) to give a thick precipitate. The solid was collected by filtration, rinsed with water (4 × 20 mL) and diethyl ether (4 × 20 mL), and dried in vacuo to give an orange-yellow solid (6, 7.45 g, 96.6%). X-ray quality crystals were obtained by layering a methylene chloride solution of 6 with hexanes. 1H NMR (CD₂CN, δ, major diastereomer >20:1, based on integrations of resonances at 8.81, 8.57, and 8.54 ppm): 8.57 (d, J = 5.2, 1H, py 6), 8.54 (d, J = 4.8, 1H, py 6), 7.82 (td, J = 7.6, 1.2, 1H, py 4), 7.77 (td, J = 7.6, 2.0, 1H, py 4), 7.41 (d, J = 7.6, 1H, py 3) 7.34 (m, 3H, py 3, 2 × py 5), 4.41 (dd, J = 14.4, 2.0, 1H, NCH₂), 4.28 (m, 2H, NCH₂), 4.21 (dd, J = 15.6, 4.4, 1H, NCH₂), 3.99 (dd, J = 10.0, 3.6, 1H, NH), 2.99 (t, J = 10.0, 1H, NH), 2.67 (qd, J = 11.2, 4.0, 1H, cyclohexyl). 13C NMR (CD₂CN, δ, major diastereomer): 160.2 (py 2), 158.8 (py 2), 153.1 (py 6), 149.2 (py 6), 137.6 (py 4, 5), 124.8 (py 3, 5), 125.6 (py 3, 5), 118.4 (py 2), 112.7 (py 6), 56.5 (NCH₂), 56.7 (NCH₂), 56.5 (NCH₂), 53.1 (cyclohexyl), 50.3 (cyclohexyl), 24.9 (cyclohexyl). CO carbons not observed. IR (CH₂CN): 1898 (CO), 1766 (CO). CV: Epa = 0.09 V. Anal. Calc. for C₁₁H₁₇N₅Mo(CO)₃: C, 52.95; H, 5.08; N, 11.76. Found: C, 52.81; H, 5.10; N, 11.97. The structure of 6 was confirmed by single-crystal X-ray diffraction.

2.3.2. (κ²-picHxnMe₂)Mo(CO)₃ (7)

A mixture of molybdenum hexacarbonyl (0.503 g, 1.91 mmol), acetonitrile (10 mL), and trans-N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-1,2-diaminocyclohexane (picHxnMe₂, 2, 0.71 g, 2.2 mmol) was stirred under reflux for 4 h, during which time it became a deep orange-red solution. Diethyl ether (90 mL) was added, and a thick precipitate formed. The solid was collected by filtration, washed with small amounts of diethyl ether, and dried in vacuo to give a yellow solid (7, 0.709 g, 74%). 1H NMR (CD₃CN, δ, major diastereomer by 6:1, based on integrations of resonances at 8.88 and 8.71 ppm): 8.71 (d, J = 4.8, 1.6, 1H, py 6), 8.54 (d, J = 4.8, 1.6, 1H, py 4), 7.81 (td, J = 8.0, 1.6, 1H, py 4), 7.74 (td, J = 7.6, 1.6, 1H, py 4), 7.72 (m, 1H, py 3), 7.40 (d, J = 8.0, 1.6, 1H, py 3), 7.27 (m, 2H, 2 × py 5), 4.46 (d, J = 12.8, 1H, NCH₂), 4.41 (d, J = 12.4, 1H, NCH₂), 4.29 (d, J = 15.2, 1H, NCH₂), 4.12 (d, J = 15.6, 1H, NCH₂), 3.26 (td, J = 11.2, 3.2, 1H, CHN), 2.95 (s, 3H, CH₃), 2.22 (s, 3H, CH₃), 2.20 (td, J = 11.6, 4.0, 1H, CHN), 2.01 (d, J = 12.8, 1H, cyclohexyl), 1.65 (d, J = 12.4, 1H, cyclohexyl), 1.46 (m, 3H, 3 × cyclohexyl), 1.02 (tt, J = 12.4, 2.8, 1H, cyclohexyl). 0.90 (m, 2H, 2 × cyclohexyl); (minor diastereomer by 6:1, select resonances): 8.88 (d, J = 5.2, 1H, py 6), 8.47 (d, J = 4.0, 1H, py 6), 4.18 (d, J = 13.6, 1H, NCH₂), 3.79 (d, J = 14.0, 1H, NCH₂), 1.28 (qd, J = 12.8, 3.8, 1H, cyclohexyl). 13C NMR (CD₃CN, δ, major diastereomer):
A mixture of trans-\(N,N\)-bis(1-methylimidazol-2-ylmethyl)-1,2-diaminocyclohexane (ImchxnMe 2, 1.29 g, 5.00 mmol), molybdenum hexacarbonyl (1.203 g, 4.56 mmol), and \(N,N\)-dimethylformamide (12 mL) was stirred under reflux for 2 h, during which time it became a yellow solution. The solution was cooled to ambient temperature, and water (150 mL) was added. A thick precipitate was collected by filtration, rinsed with water and diethyl ether, and dried in vacuo to give a bright yellow solid (8, 2.03 g, 92.5%). X-ray-quality crystals were obtained by layering an acetone solution of 8 with diethyl ether. \(^1H\) NMR (CD\(_3\)CN, \(\delta\), major diastereomer by 7:1, based on integrations of resonances at 4.61 and 2.54 ppm): 6.97 (s, 1H, Im), 6.95 (s, 1H, Im), 6.86 (s, 1H, Im), 6.79 (d, J = 1.6, 1H, Im), 4.27 (dd, J = 14.6, 1H, NCH\(_2\)), 4.14 (d, J = 15.4, 1H, NCH\(_2\)), 3.83 (d, J = 15.4, 1H, NCH\(_2\)), 3.70 (d, J = 15.2, 1H, NCH\(_2\)), 3.79 (s, 3H, NCH\(_3\)), 3.60 (s, 3H, NCH\(_3\)), 2.88 (s, 3H, ImCH\(_3\)), 2.27 (s, 3H, ImCH\(_3\)), 2.97 (dd, brd, 1H, NCH), 1.96 (brd, 1H, cyclohexyl). \(^13\)C NMR (CD\(_3\)CN, \(\delta\), major diastereomer): 148.9 (Im 2), 144.5 (Im 2), 129.1 (Im 4.5), 128.0 (Im 4.5), 123.5 (Im 4.5), 122.6 (Im 4.5), 65.4 (NCH), 64.3 (NCH), 58.0 (NCH\(_2\)), 55.7 (NCH\(_2\)), 41.9 (NCH\(_2\)), 34.4 (ImCH\(_3\)), 34.1 (ImCH\(_3\)), 25.3 (cyclohexyl), 25.2 (cyclohexyl), 25.1 (cyclohexyl), 25.0 (cyclohexyl), CO carbons not observed. IR (CH\(_3\)CN): 1900 (CO), 1761 (CO). CV: \(E_{pa} = 0.21\) V. Anal. Calc. for C\(_{21}\)H\(_{30}\)MoN\(_{6}\)O\(_3\): C, 49.41; H, 5.28; N, 16.47. Found: C, 49.33; H, 5.73; N, 16.16%. The structure of 9 was confirmed by single-crystal X-ray diffraction.

A mixture of trans-\(N,N\)-bis(thiazol-2-ylmethyl)-1,2-diaminocyclohexane (Thzchxn, 0.327 g, 1.06 mmol), molybdenum hexacarbonyl (0.251 g, 0.951 mmol), and \(N,N\)-dimethylformamide (5 mL) was stirred under reflux for 2 h, during which time it turned dark orange. The resulting solution was cooled to ambient temperature, and water (40 mL) was added. A thick precipitate was collected by filtration, rinsed with water and diethyl ether, and dried in vacuo to give a bright yellow solid (10, 0.417 g, 89.9%). X-ray-quality crystals were obtained by layering an acetonitrile solution of 10 with diethyl ether. \(^1H\) NMR (CD\(_3\)CN, \(\delta\), major diastereomer by 7:1, based on integrations of resonances at 7.85, 7.79, and 7.77 ppm): 7.79 (d, J = 3.2, 1H, Thz), 7.78 (d, J = 3.2, 1H, Thz), 7.58 (d, J = 3.2, 1H, Thz), 7.50 (d, J = 3.2, 1H, Thz), 4.50 (m, 3H, 3 × NCH\(_2\)), 4.20 (m, 1H, NH), 4.14 (dd, J = 15.6, 4.8, 1H, NCH\(_2\)), 2.70 (qd, J = 12.0, 4.0, 1H, cyclohexyl), 2.66 (m, 1H, NH), 2.30 (d, J = 12.8, 1H, cyclohexyl), 2.22 (d, J = 11.6, 1H, cyclohexyl), 1.82 (qd, J = 10.0, 4.0, 1H, cyclohexyl), 1.71 (d, J = 13.6, 1H, cyclohexyl), 1.64 (d, J = 13.2, 1H, cyclohexyl), 1.29 (qd, J = 12.8, 3.6, 1H, cyclohexyl), 1.17 (qt, J = 13.2, 3.2, 1H, cyclohexyl), 1.05 (qt, J = 13.2, 3.6, 1H, cyclohexyl), 0.79 (qd, J = 10.8, 3.2, 1H, cyclohexyl); (minor diastereomer by 7:1, select resonances): 7.85 (d, J = 2.8, 1H, Thz), 7.82 (d, J = 3.2, 1H, Thz), 7.54 (d, J = 3.2, 1H, Thz), 2.90 (m, 1H, cyclohexyl). \(^13\)C NMR (CD\(_3\)CN, \(\delta\), major diastereomer): 170.3 (Thz 2), 168.3 (Thz 2), 144.7 (Thz 4.5), 142.7 (Thz 4.5), 121.8 (Thz 4.5), 120.5 (Thz 4.5), 65.9 (NCH), 64.2 (NCH), 53.1 (NCH), 53.1 (NCH\(_2\)), 31.8 (cyclohexyl), 30.7 (cyclohexyl), 25.4 (cyclohexyl), 24.9 (cyclohexyl), CO carbons not observed. IR (CH\(_3\)CN): 1901 (CO), 1766 (CO). CV: \(E_{pa} = 0.12\) V. Anal. Calc. for C\(_{14}\)H\(_{22}\)MoN\(_{6}\)O\(_2\): C, 48.10; H, 4.13; N, 11.47. Found: C, 41.70; H, 4.11; N, 11.79%. The structure of 10 was confirmed by single-crystal X-ray diffraction.

A mixture of potassium hexafluorophosphate (0.489 g, 2.66 mmol), sodium nitrite (0.225 g, 3.26 mmol), compound 6 (1.015 g, 2.13 mmol), and methanol (15 mL) was cooled in an ice-water bath for 5 min, and hydrochloric acid (12 M, 1.0 mL, 12 mmol) was added drop-wise over the course of six minutes. The initially yellow mixture became a dark brown solution, and bubbles were observed. After another ten minutes of stirring, aqueous potassium hydroxide (6 M, 1.17 mL, 10 mmol) was added to give a basic mixture. The mixture was heated under reflux for five minutes. It was removed from heat, cooled at ambient temperature for 30 min, and then cooled in an ice-water bath for 30 min. The resulting solid was collected by filtration, rinsed with water (3 × 3 mL) and diethyl ether (3 × 3 mL), and dried in vacuo to give dark brown crystals (11, 0.84 g, 66.5%). X-ray-quality crystals were obtained by layering an acetonitrile solution of 11 with diethyl ether. \(^1H\) NMR (CD\(_3\)CN, \(\delta\)): 8.94 (d, J = 5.2, 1H, py 6), 8.50 (d, J = 5.6, 1H, py 6), 8.05 (td, J = 7.6, 1.6, 1H, py 4), 7.82 (td,
were obtained by layering an acetonitrile solution of 12 to give a brown solid (purple solid (68)).

The structure of 11 was confirmed by single-crystal X-ray diffraction.

2.4.2. [(cis-2-picolinyl)Mo(0)(CO)]PF6 (12)
A mixture of potassium hexafluorophosphate (2.19 g, 11.9 mmol), compound 7 (1.008 g, 2.04 mmol), and acetic acid (glacial, 15 mL) was stirred for one minute, and a solution of sodium nitrite (0.223 g, 2.32 mmol) in water (2.5 mL) was added. The resulting mixture was stirred for one hour, during which time it became a bright yellow solution, and aqueous potassium hydroxide (2 M, 2.3 mL, 4.6 mmol) was added. The mixture changed to a brown solution, and after 5 min before hydrochloric acid (12 M, 0.3 mL, 3.6 mmol) was added. The resulting solution was heated under reflux for 40 min, left at ambient temperature for 10 min, and reduced to about half its initial volume using a rotary evaporator. Precipitate was collected in by filtration, rinsed with water (5 × 5 mL) and diethyl ether (5 × 10 mL), dried in vacuo for 40 h, and dissolved in acetonitrile (25 mL). The resulting brown solution was heated under reflux for one hour. Diethyl ether (500 mL) was added to the stirring solution, and a precipitate was collected by filtration, rinsed with diethyl ether (5 × 3 mL), and dried in vacuo to give a brown solid (12, 1.104 g, 88.40%). X-ray quality crystals were obtained by laying an acetonitrile solution of 12 with diethyl ether. 1H NMR (CD3CN, δ): 8.95 (d, J = 5.6, 1H, py 6), 8.83 (d, J = 5.6, 1H, py 6), 8.11 (td, J = 8.0, 1.6, 1H, py 4.5), 7.87 (td, J = 8.0, 1.4, 1H, py 4.5), 7.69 (d, J = 8.0, 1.0, py 3), 7.56 (t, J = 6.4, 1H, py 4.5), 7.53 (d, J = 7.6, 1H, py 3), 7.49 (t, J = 6.6, 1H, py 4.5), 4.57 (d, J = 16.0, 1H, NCH2), 4.39 (d, J = 15.2, 1H, NCH2), 4.30 (d, J = 15.6, 1H, NCH2), 4.13 (d, J = 15.6, 1H, NCH2), 2.47 (m, 2H, NCH2, cyclohexyl), 2.44 (s, 3H, CH3), 2.25 (s, 3H, CH3), 2.04 (d, J = 12.8, 1H, NCH2, cyclohexyl), 1.65 (m, 2H, cyclohexyl), 1.27 (m, 2H, cyclohexyl), 1.04 (m, 2H, cyclohexyl), 1 NCH or cyclohexyl buried under CHD2CN peak. 13C NMR (CD3CN, δ, 14B): 159.7 (NO), CV: Epa = 0.50 V. Anal. Calc. for C19H24F6MoN5O2P: C, 38.33; H, 4.06; N, 16.30. Found: C, 34.31; H, 4.60; N, 16.44%.

2.4.4. [(cis-2-LimxnMe2)Mo(NO)(CO)]PF6 (14), mixture of 4 diastereomers
A canary-yellow mixture of potassium hexafluoride (0.0982 g, 0.534 mmol), sodium nitrite (0.032 g, 0.46 mmol), compound 9 (0.195 g, 0.381 mmol), and methanol (6 mL) was stirred for 5 min before hydrochloric acid (12 M, 0.3 mL, 3.6 mmol) was added. The mixture changed to a brown solution, and after a minute aqueous potassium hydroxide (2 M, 2.0 mL) was added. The resulting solution was heated under reflux for 40 min, left at ambient temperature for 10 min, and reduced to about half its initial volume using a rotary evaporator. Precipitate was collected in by filtration, rinsed with water (3 × 5 mL) and diethyl ether (4 × 5 mL), and dried in vacuo to give a fluffy purple solid (14A, 14B, 14C, and 14D) in a ratio of ~6:5:trace:4 based on integrations of 1H resonances at 6.24, 6.04, 5.70, and 5.52 ppm (0.073 g; 28%). An X-ray-quality crystal 14A and 14B cocrystallized in a 2:3 ratio was obtained by laying with diethyl ether an acetonitrile solution of 14A:14B:14C:14D in an ~6:5:trace:4 ratio. An X-ray-quality crystal 14A and 14B cocrystallized in a 1:2 ratio was obtained by laying with diethyl ether an acetonitrile solution of 14A:14B:14D in an ~1:1:6:trace ratio. 1H NMR (CD3CN, δ, 14A, [(syn-cis-2-LimxnMe2)Mo(NO)(CO)]PF6 with NO and cyclohexyl amine trans, select resonances): 7.20 (d, J = 1.6, 1H, Im), 7.08 (d, J = 1.2, 1H, Im), 6.99 (d, J = 1.6, 1H, Im), 6.24 (d, J = 1.6, 1H, Im), 4.58 (d, J = 17.2, 1H, NCH2), 4.02 (d, J = 15.6, 1H, NCH2), 3.90 (d, J = 16.8, 1H, NCH2), 3.69 (s, 3H, ImCH3), 3.65 (s, 3H, ImCH3), 3.45 (d, J = 16.0, 1H, NCH2), 3.18 (s, 3H, NCH2), 2.60 (s, 3H, NCH2), 1.45 (qd, J = 12.0, 3.6, 1H, cyclohexyl); 14B, [(syn-cis-2-LimxnMe2)Mo(NO)(CO)]PF6 with NO and imidazolyl trans: 7.19 (d, J = 1.6, 1H, Im), 7.04 (d, J = 1.6, 1H, Im), 7.02 (d, J = 1.6, 1H, Im), 6.04 (d, J = 1.2, 1H, Im), 4.62 (d, J = 16.4, 1H, NCH2), 4.13 (d, J = 15.6, 1H, NCH2), 3.93 (d, J = 16.8, 1H, NCH2), 3.66 (s, 3H, ImCH3), 3.65 (s, 3H, ImCH3), 3.41 (d, J = 15.6, 1H, NCH2), 3.34 (td, J = 11.2, 3.6, 1H, NCH2), 3.15 (s, 3H, NCH2), 2.74 (s, 3H, NCH2), 2.21 (m, 1H, cyclohexyl), 2.10 (td, J = 11.6, 4.0, 1H, NCH2), 1.80 (m, 2H, cyclohexyl), 1.70 (m, 1H, cyclohexyl), 1.54 (qd, J = 12.0, 3.6, 1H, cyclohexyl), 1.26 (m, 2H, cyclohexyl), 1.08 (m, 1H, cyclohexyl); 14C, select resonances: 7.22 (buried, 1H, Im), 7.02 (d, J = 1.2, 1H, Im), 6.98 (buried, 1H, Im), 5.70 (d, J = 1.2, 1H, Im), 4.43, (d, J = 15.6, 1H, NCH2), 3.93 (d,
J = 16.0, 1H, NCH2), 3.03 (d, J = 15.2, 1H, NCH2), 2.98 (s, 3H, NCH3), 2.72 (s, 3H, NCH3); 1H, NCH2), 7.04 (d, J = 1.2, 1H, Im), 6.97 (dd, J = 1.2, 1H, Im), 5.52 (d, J = 15.6, 1H, NCH2), 4.01 (d, J = 15.6, 1H, NCH2), 3.87 (d, J = 14.8, 1H, NCH2), 3.70 (s, 3H, ImCH3), 3.60 (s, 3H, ImCH3), 2.88 (s, 3H, NCH3), 2.81 (s, 3H, NCH3). IR (CH3CN): 1622 (NO). CV (100 mV/s): 1247 (Im 4.5), 1247 (Im 4.5), 1247 (Im 4.5), 1247 (Im 4.5), 1247 (Im 4.5), 72.3 (NCH), 69.4 (NCH), 56.9 (NCH2), 53.7 (NCH2 and NCH3), 44.0 (NCH3), 35.0 (ImCH3), 34.9 (ImCH3), 26.1 (cyclohexyl), 26.2 (cyclohexyl), 25.1 (cyclohexyl), 24.4 (cyclohexyl). IR (CH3CN): 1877 (CO), 1586 (NO). CV: Epa = 0.34 V. Anal. Calc. for C19H30F6MoN7O2P: C, 36.26; H, 4.80; N, 10.48. Found: C, 36.2; H, 4.8; N, 10.4.

2.5. [(cis-κ4-N3)Mo(NO)Br]PF6 compounds

2.5.1. [(cis-κ4-pichxn)Mo(NO)PF6 (15)]

To compound 11 (2.990 g, 5.025 mmol) was added iodine (0.638 g, 2.51 mmol) dissolved in propionitrile (60 mL). The resulting yellow-brown solution was stirred at ambient temperature for 30 min and added to stirring diethyl ether (150 mL). Precipitate was collected by filtration, rinsed with diethyl ether (25 mL), a solution of bromine in acetonitrile (0.0850 M, 24 cm3), and dried in vacuo to give a bright yellow solid (15, 3.502 g, quantitative). IR (CH3CN): 1877 (CO), 1586 (NO). NO. CV: Epa = −0.10 V, ΔE = 0.08 V. Anal. Calc. for C19H30F6MoN7O2P: C, 36.2; H, 4.8; N, 10.4. Found: C, 36.2; H, 4.8; N, 10.4.

2.5.2. [(trans-κ4-pichxnMe2)Mo(NO)Br]PF6 (16)

To a solution of compound 12 (0.5101 g, 0.8188 mmol) in acetonitrile (25 mL), a solution of bromine in acetonitrile (0.0850 M, 4.70 mL, 0.400 mmol) was added, resulting in effervescence. After 5 min of stirring, this mixture was added to stirring diethyl ether (150 mL). Precipitate was collected by filtration, rinsed with diethyl ether (5 × 5 mL), and dried in vacuo to give a bright yellow solid (16, 0.5120 g, 92.6%). X-ray quality crystals were obtained by layering an acetonitrile solution of 16 with diethyl ether. IR (CH3CN): 1622 (NO). NO. CV (100 mV/s): Epa = −0.89 V, ΔE = 0.05 V. Anal. Calc. for C19H30F6MoN7O2P: C, 35.57, H, 4.18, N, 10.37. Found: C, 35.71, H, 4.28, N, 10.43. The structure of 16 was confirmed by single-crystal X-ray diffraction.

3. Results and discussion

3.1. Synthesis and characterization of fac-(κ3-κ4-N4)Mo(CO)3 complexes

Reported and novel picchxn-type (N4) ligands 1–5 are readily synthesized from trans-1,2-diaminocyclohexane via literature procedures or straightforward modifications thereof [14,49,62–64]. When necessary, purification is achieved through either low-pressure distillation or recrystallization of the corresponding tetrahydrochloride salt followed by liberation of the free base. Refluxing picchxn-type ligands with molybdenum hexacarbonyl gives corresponding fac-(κ3-κ4-N4)Mo(CO)3 complexes (6–10, Scheme 1), typically in moderate to high yield. These substitutions were performed in a range of solvents, including toluene, acetonitrile, and N,N-dimethylformamide. The lower yield of fac-(κ3-κ4-N4)Mo(NCMe2)Mo(CO)3 results mainly from use of a Soxhlet extraction to obtain analytically pure samples.

The 1H NMR spectra of fac-(κ3-κ4-N4)Mo(CO)3 complexes 6–10 show evidence of a minor isomer. Single-crystal X-ray structures were solved for 6, 8, 9, and 10 (Fig. 3). The structure of 6 shows the unbound pyridyl ring disordered between two sites but is consistent with those of 8 and 9 in showing a trans relationship for the substituents on the chelate ring formed from the cyclohexyl amine groups. The structure of 10 shows a syn relationship for the substituents on the chelate ring formed from the cyclohexyl amine groups. This difference stems from the inverse configuration (vs. that evident in the structures 6, 8, and 9) of the nitrogen bearing the uncomplexed heterocycle-2-ylmethyl group and suggests that the isomers observed in the 1H NMR spectra are most likely diastereomers differing in the configuration of this center. The unit cells of 6, 9, and 10 each show a single complex, whereas the unit cell of 8 includes two enantiomeric complexes. The unit cell of 9 includes a disordered m-xylene solvent molecule.

Consistent with similar molybdenum complexes bearing three fac amine groups and three carbonyls [58,59,70–73], fac-(κ3-κ4-N4) Mo(CO)3 complexes 6–10 display strong IR absorbances for symmetric and asymmetric CO stretching. Observed differences among CO stretching frequencies and oxidation potentials for non-methylated complexes 6, 8, and 10 (Table 1) are small but consistent with the relative basicities of pyridine, imidazole, and thiazole (which have protonated pKs values of 5.2, 7.0, and 2.5 respectively) [74]. Differences between CO stretching frequencies and oxidation potentials for non-methylated complexes 6 and 8 and their respective methylated analogs 7 and 9 are likewise small but in agreement with prior work suggesting that increased methylation decreases the σ-basicity of N-donor tetradentate ligands [75]. This effect was attributed to steric interactions weakening the Mo=N bonds, but interestingly, MoN bond lengths for the solved structure of (κ3-κ4-ImchxnMe2)Mo(CO)3 (9) do not show an obvious increase compared to those for the two complexes in the unit cell of (κ3-κ4-Imchxn)Mo(CO)3 (8). The observed CO lengths in 6, 8, 9, and 10 likewise show minimal variation.

With each of the three remaining κ-acidic carbonyl groups trans to a substantially σ-basic amine group, fac-(κ3-κ4-N4)Mo(CO)3 complexes 6–10 show a great deal of stability toward further intramolecular substitution of carbonyl groups, and attempts to produce (κ4-κ4-N4)Mo(CO)2 complexes under thermal (>200 °C reflux), microwave, and UV-irradiation conditions were uniformly unsuccessful. Examples of stable molybdenum complexes bearing four nitrogen donor groups and two carbonyls have been reported [76–78], but in all cases of the complexed nitrogen was part

Scheme 1. Reactions of picchxn-type (N4) ligands to give (κ3-κ4-N4)Mo(CO)3 complexes.
of a ligand with a substantial π-system such as 2,2′-bipyridyl or a conjugated imine, which likely allowed for a greater degree of π-backbonding from the electron-rich Mo(0) center.

3.2. Synthesis and characterization of [\(N_4\)Mo(NO)(CO)]\(_2\) compounds

Following from the structures of reported Mo(0) dearomatizing metal fragments [57,60,61], we were interested in substituting a linear NO\(^+\) group into the ligand set of fac-(\(\kappa^3\)-N4)Mo(CO)\(_3\)) complexes 6–9, recognizing that, as for similar Mo(0) complexes based on the hydridotris(1-pyrazolyl)borato (Tp) and tris(1-pyrazolyl)methane (Tpm) ligands [59,61], this change might subsequently allow a fourth amine group to substitute for an additional carbonyl group. Initial nitrosylation attempts using N-methyl-N-nitroso-p-toluene-sulfonamide (Diazald), as reported for [TpMo(CO)\(_3\)]\(^-\) [79], gave no reaction, possibly owing to the non-anionic nature of the complexes. The same outcome has been reported for the neutral TpmMo(CO)\(_3\) complex [57]. Nitrosylation was instead effected using NOCl(g) generated in situ from sodium nitrite and hydrochloric acid [80], as reported for other molybdenum complexes bearing three fac amine groups and three carbonyls [57–59,72,81,82]. When this reaction is performed at ambient temperature or 0°C in the presence of potassium hexafluorophosphate, fac-(\(\kappa^3\)-picchxn)Mo(CO)\(_3\) (6) initially yields a mixture showing CO stretches at 2023, 1933, and 1884 cm\(^{-1}\). Data for reported molybdenum complexes bearing three fac amine groups, two carbonyls, and one linear nitrosyl, such as [(dien)Mo(NO)(CO)]\(_2\)PF\(_6\) (dien = diethylenetriamine; \(\nu_{\text{CO}} = 2024\) and 1930 cm\(^{-1}\)) [57–59,82], strongly suggest that the first two peaks correspond to the CO stretches of one or more fac-(\(\kappa^3\)-picchxn)Mo

![Fig. 3. X-ray crystal structures (ORTEP, 50% probability ellipsoids) of (\(\kappa^3\)-picchxn)Mo(CO)\(_3\)](6), (\(\kappa^3\)-Imchxn)Mo(CO)\(_3\)](8), (\(\kappa^3\)-ImchxnMe\(_2\))Mo(CO)\(_3\)](9), and (\(\kappa^3\)-Thzchxn)Mo(CO)\(_3\)](10) [69].

### Table 1
IR, electrochemical, and crystal data for fac-(\(\kappa^3\)-N4)Mo(CO)\(_3\)] complexes (6–10).

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu_{\text{CO}}) (cm(^{-1}))</th>
<th>(E_{\text{pa}})^a</th>
<th>MoN (Å)</th>
<th>CO (Å)</th>
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<tr>
<td>((\kappa^3)-picchxn)Mo(CO)(_3)) (6)</td>
<td>1898, 1766</td>
<td>0.09</td>
<td>2.26, 2.30, 2.33</td>
<td>1.18, 1.18, 1.16</td>
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<td>((\kappa^3)-picchxnMe(_2))Mo(CO)(_3)) (7)</td>
<td>1900, 1767</td>
<td>0.21</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>((\kappa^3)-Imchxn)Mo(CO)(_3)) (8)</td>
<td>1896, 1756</td>
<td>0.00</td>
<td>2.27, 2.32, 2.33</td>
<td>1.18, 1.17, 1.16</td>
</tr>
<tr>
<td>((\kappa^3)-ImchxnMe(_2))Mo(CO)(_3)) (9)</td>
<td>1900, 1761</td>
<td>0.11</td>
<td>2.25, 2.33, 2.39</td>
<td>1.17, 1.20, 1.15</td>
</tr>
<tr>
<td>((\kappa^3)-Thzchxn)Mo(CO)(_3)) (10)</td>
<td>1901, 1766</td>
<td>0.12</td>
<td>2.27, 2.31, 2.35</td>
<td>1.17, 1.19, 1.19</td>
</tr>
</tbody>
</table>

^a Potential of anodic peak (V) vs. NHE.
(NO)(CO)₅PF₆ diastereomers, and data for molybdenum complexes bearing four amine groups and cis carbonyl and nitrosyl ligands, such as \( \text{Tp(Melm)}\text{Mo(NO)(CO)} \) (Melm = 1-methylimidazole, \( \nu_{\text{CO}} = 1865 \text{ cm}^{-1} \)) [59,61], strongly suggest that the latter peak corresponds to the CO stretch of one or more \([\text{cis-}\text{picchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) diastereomers. Moderate heating causes the 2023 cm\(^{-1} \) and 1933 cm\(^{-1} \) peak to recede and the 1883 cm\(^{-1} \) peak to grow, eventually giving samples of \([\text{cis-}\text{picchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (11, Scheme 2), which has been isolated in analytically pure form and fully characterized. \( ^1\text{H} \) NMR spectra of \([\text{cis-}\text{N}_2\text{Mo(NO)(CO)}\)] \( \text{PF}_6 \) compounds are distinctive in that the peaks appear in pairs, reflecting the \( \text{C}_2 \) symmetry of the \([\text{cis-}\text{N}_2\text{Mo}] \) fragment. However, prior to the complete formation of 11, \( ^1\text{H} \) NMR spectra of \([\text{fac-}\text{cis-}\text{picchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) nitrosylation products show a different compound that lacks such pairings but likewise corresponds to IR stretches at 1884 cm\(^{-1} \) \( (\nu_{\text{CO}}) \) and 1598 cm\(^{-1} \) \( (\nu_{\text{NO}}) \). These observations are taken as strong evidence that 6 initially undergoes a nitrosylation reaction to give one or more \([\text{fac-}\text{cis-}\text{picchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) diastereomers (Scheme 2). The kinetically favored intramolecular substitution product of \([\text{fac-}\text{cis-}\text{picchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) is one or more \([\text{cis-}\text{picchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) diastereomers, but under the conditions that promote this substitution \([\text{cis-}\text{picchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) diastereomers convert to the thermodynamically favored \([\text{cis-}\text{picchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (11) [83]. We have not been able to observe nitrosylation products that entirely lack 11, so direct formation of 11 from one or more \([\text{fac-}\text{cis-}\text{picchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) diastereomers is also a possibility.

Nitrosylation of \([\text{fac-}\text{cis-}\text{picchxn}Me_2]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (7) proceeds in a fashion similar to that of \([\text{cis-}\text{picchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (6), with IR peaks attributed to CO stretches of \([\text{fac-}\text{cis-}\text{picchxn}Me_2]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) diastereomers being observed at 2025 and 1937 cm\(^{-1} \) and \( ^1\text{H} \) NMR data indicating the formation of multiple \([\text{cis-}\text{picchxn}Me_2]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) diastereomers before equilibration to \([\text{cis-}\text{picchxn}Me_2]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (12) as the major product. Addition of aqueous sodium nitrite to a slurry of 7 in acetic acid was found to give cleaner samples of 12 than the usual procedure of adding concentrated hydrochloric acid dropwise to a suspension of the compound and sodium nitrite in methanol. Compound 12 has been isolated in analytically pure form and fully characterized, and crystal structures of both 11 and 12 have been solved (Fig. 4), indicating the cis-\( \alpha \) configuration and \( \it{A} \) helicity for both (\( \text{S,S} \)-picchxn) (in S,S-11) and (\( \text{S,S} \)-picchxnMe₂) (in S,S-12). They also show linear NO ligands in both 11 (Mo–N–O angle 174.9°) and 12 (Mo–N–O angle 176.3°), which has disordered NO and CO positions in the solved crystal. The formations of 11 and 12 from 6 and 7 are analogous to the production of \([\text{cis-}\text{a-PDP}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) and \([\text{fac-}\text{cis-}\text{picchxn}Me_2]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (8) and \([\text{fac-}\text{cis-}\text{picchxn}Me_2]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (7), showing CO stretches in the IR spectrum attributed to respective \([\text{cis-}\text{a-PDP}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (2023 and 1932 cm\(^{-1} \)) and \([\text{fac-}\text{cis-}\text{picchxnMe}_2]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (2024 and 1931 cm\(^{-1} \) ).

Nitrosylation sequences of \([\text{cis-}\text{Imchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (8) and \([\text{cis-}\text{ImchxnMe}_2]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (9) proceed initially in a fashion analogous to those of \([\text{cis-}\text{picchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (6) and \([\text{cis-}\text{picchxnMe}_2]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (7), showing CO stretches in the IR spectrum attributed to respective \([\text{fac-}\text{cis-}\text{Imchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (2023 and 1932 cm\(^{-1} \)) and \([\text{fac-}\text{cis-}\text{ImchxnMe}_2]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) (2024 and 1931 cm\(^{-1} \) ).

However, NMR monitoring experiments have given no evidence of either \([\text{cis-}\text{a-Imchxn}]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \) or \([\text{cis-}\text{a-ImchxnMe}_2]\text{Mo(NO)(CO)}\) \( \text{PF}_6 \), indicating that, unlike tetradeptate complexes of picchxn (1) and picchxnMe₂ (2), those of Imchxn (3) and ImchxnMe₂...
(4) have both a strong kinetic preference and a strong thermodynamic preference for cis-β configurations (Scheme 3). Analytically pure samples of [(cis-β-Imchxn)Mo(NO)(CO)]PF$_6$ (13) as predominantly one diastereomer (20:1) were isolated by allowing preparations to stir for several days at ambient temperature and then collecting precipitated compound from the methanolic mixture. Observing the reaction without isolation shows a 2:25:3:18 thermodynamic ratio of four diastereomers. Analytically pure samples of [(cis-β-ImchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (14) were isolated only in low yields as an approximately 6:5:trace:4 ratio of four diastereomers following a short reflux time. With additional heating in acetonitrile, the mixture equilibrates to a 7:7:2:3 ratio, from which a 1:16:0:trace ratio was isolated by selective precipitation in stirring diethyl ether.

The four observed diastereomers of 14 each show a single markedly shielded imidazolyl (Im) proton signal between 6.25 and 5.90 ppm. Layering with diethyl ether an acetoni- trile ring proton above the face of the other heterocycle ring, cis-ImchxnMe$_2$Mo(NO)(CO)]PF$_6$ (14B) gives the A configuration for the metal center. In addition, diastereomers 14A and 14B differ only in the respective locations of the CO and NO groups, in that 14A has the NO ligand opposite a cyclohexyl amine group and the CO ligand opposite a 1-methylimidazolyl group and 14B has these positions reversed.

With two N-heterocycle groups bonded to the metal center, [(cis-α-N$_4$)Mo(NO)(CO)]PF$_6$ compounds 11–14 show greater variations in IR stretching frequencies and oxidation potentials than were observed for fac-(κ$^2$-N$_4$)Mo(CO)$_3$ complexes 6–10 (Table 2). The greater basicities of the Imchxn (3) and ImchxnMe$_2$ (4) ligands as compared to those of the picchxn (1) and picchxnMe$_2$ (2) ligands result in more electron donation to the molybdenum center and

![Scheme 3. Reactions of (κ$^2$-Imchxn)Mo(CO)$_3$ (8) and (κ$^2$-ImchxnMe$_2$)Mo(CO)$_3$ (9) to give [(cis-β-Imchxn)Mo(NO)(CO)]PF$_6$ (13) and [(cis-β-ImchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (14).](image)

![Fig. 5. X-ray crystal structures (ORTEP, 50% probability ellipsoids) of [(d-R,R-cis-β-ImchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (1:20 14A:14B) and [(d-5,5-cis-picchxnMe$_2$)Mo(NO)Br]PF$_6$ (16) with PF$_6$ anions omitted.](image)

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{CO}$ (cm$^{-1}$)</th>
<th>$\nu_{NO}$ (cm$^{-1}$)</th>
<th>$E_{pa}$ $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(cis-α-picchxn)Mo(NO)(CO)]PF$_6$ (11)</td>
<td>1884</td>
<td>1598</td>
<td>0.45</td>
</tr>
<tr>
<td>[(cis-α-picchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (12)</td>
<td>1889</td>
<td>1602</td>
<td>0.56</td>
</tr>
<tr>
<td>[(cis-β-Imchxn)Mo(NO)(CO)]PF$_6$ (13)</td>
<td>1871</td>
<td>1579</td>
<td>0.30</td>
</tr>
<tr>
<td>[(cis-β-ImchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (14)</td>
<td>1877</td>
<td>1586</td>
<td>0.34</td>
</tr>
</tbody>
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$^a$ Potential of anodic peak (V) vs. NHE.
subsequent lower oxidation potentials and lower CO and NO stretching frequencies for \([\text{(cis}-\beta\text{-Imchxn})\text{Mo(NO)}\text{(CO)}]PF_6\) (13) and \([\text{(cis}-\beta\text{-ImchxnMe}_2\text{MO(NO)}\text{(CO)}]PF_6\) (14) as compared to those of \([\text{(cis}-\beta\text{-picchxn})\text{Mo(NO)}\text{(CO)}]PF_6\) (11) and \([\text{(cis}-\beta\text{-picchxnMe}_2\text{MO(NO)}\text{(CO)}]PF_6\) (12). As with \text{fac-(k}^3\text{-N}_4\text{Mo})(\text{CO})_3\text{ complexes 6–9, IR and electrochemical data for \([\text{(cis}-\beta\text{-N}_4\text{Mo(NO)}\text{(CO)}]PF_6\) compounds 11–14 indicate greater electron donation from non-methylated versions of picchxn-type ligands than from the respective methylated versions. The mixed occupancies in the CO and NO positions of solved 12 and 14 crystal structures prevent similar assessments of ligand properties based on CO and NO bond length data.

### 3.3. Synthesis and characterization of \([\text{N}_4\text{Mo(NO)}\text{X}]PF_6\) compounds

In previous work, substitution of the carbonyl ligand of Tp (MelM)Mo(NO)(CO) for a dihapto-bound aromatic was effected via a two-step oxidation–reduction sequence in which the complex was first reacted with elemental bromine to give the 17-electron Mo(I) complex Tp(MelM)Mo(NO)Br[61]. In order to assess the ability of \([\text{N}_4\text{Mo(NO)}\text{X}]PF_6\) fragments to form similar complexes with aromatic molecules, we first sought to remove the CO ligands from \([\text{N}_4\text{Mo(NO)}\text{X}]PF_6\) (11) and \([\text{N}_4\text{Mo(NO)}\text{X}]PF_6\) (12) with iodine proceed more slowly than that of 11, while evidence of \([\text{N}_4\text{Mo(NO)}\text{X}]PF_6\) formation was observed, in this instance bromine proved the more effective oxidant, giving \([\text{cis}-\beta\text{-picchxnMe}_2\text{Mo(NO)}\text{Br}]PF_6\) (16, Scheme 4, \(\nu_{\text{NO}} = 1619 \text{ cm}^{-1}\), \(E_{1/2} = 0.89 \text{ V}\)) in high yield. The structure of 16 was confirmed by a single-crystal X-ray structure (Fig. 5), which shows disorder in the respective occupancy of the NO and Br positions. IR and elemental analysis data suggest similar reactions of \([\text{(cis}-\beta\text{-Imchxn})\text{Mo(NO)}\text{(CO)}]PF_6\) (13) and \([\text{(cis}-\beta\text{-ImchxnMe}_2\text{Mo(NO)}\text{(CO)}]PF_6\) (14) samples likely produced \([\text{(cis}-\beta\text{-Imchxn})\text{Mo(NO)}]PF_6\) (\(\nu_{\text{NO}} = 1607 \text{ cm}^{-1}\)) and \([\text{(cis}-\beta\text{-ImchxnMe}_2\text{Mo(NO)}\text{Br}]PF_6\) (\(\nu_{\text{NO}} = 1616 \text{ cm}^{-1}\)) respectively, but owing to the tendency of Imchxn (3) and Imchxn (4) to give the undesired non-\(\text{C}^2\text{-symmetric} \text{cis}-\beta\) configuration, these compounds were not thoroughly characterized or extensively pursued.

### 3.4. Evaluations of \([\text{cis}-\beta\text{-N}_4\text{Mo(NO)}]PF_6\) fragments as potential dearamatizing \(\pi\)-bases

Attempts to form dihapto complexes with \(\pi\)-acids such as naphthalene, furan, and cyclohexene through chemical reductions of \([\text{(cis}-\beta\text{-picchxn})\text{Mo(NO)}]PF_6\) (15) and \([\text{(cis}-\beta\text{-picchxnMe}_2\text{Mo(NO)}\text{Br}]PF_6\) (16) were uniformly unsuccessful, with either no reaction or decomposition to multiple products being observed under various conditions (Scheme 5). Spectroscopic and electrochemical data for 15 (\(\nu_{\text{NO}} = 1622 \text{ cm}^{-1}\), \(E_{1/2} = -1.00 \text{ V}\)) and 16 (\(\nu_{\text{NO}} = 1619 \text{ cm}^{-1}\), \(E_{1/2} = -0.89 \text{ V}\)) suggest that the \([\text{cis}-\beta\text{-picchxn})\text{Mo(NO)}]PF_6\)" and \([\text{cis}-\beta\text{-picchxnMe}_2\text{Mo(NO)}]PF_6\) fragments are probably not sufficiently electron rich to effect dihapto coordination and subsequent activation of aromatic molecules. The least-electron-rich molybdenum fragment reported to do so (\([\text{Tp}(1\text{-methylimidazole})\text{Mo(NO)}]) has a corresponding Mo(I) \(\nu_{\text{NO}}\) of 1610 \text{ cm}^{-1} and \(E_{1/2}\) of \(-1.33 \text{ V}\) [61]. Under comparable reaction conditions, \(\text{Tp}([\text{PMem}_2\text{Mo(NO)}])\) (from \(\text{Tp}([\text{PMem}_2\text{Mo(NO)}]\text{Br})\) \(\nu_{\text{NO}} = 1617 \text{ cm}^{-1}\) and \(E_{1/2} = -1.19 \text{ V}\)) failed to give evidence of dihapto complex formation [61]. Electronic parameters have served as a useful guide in the development of \(\pi\)-basic dearamatization agents [56,57,60,61,85–88], but it should be noted that all molybdenum and tungsten (M) fragments that have thus far proven effective for this chemistry have had the common structure (Tp,l,M)NO, in which L is an amine, phosphine, or phosphate ligand. The possibility that other aspects of these systems are essential for dearamatization remains an open question.

### 3.5. Configurations and comparisons to other complexes with picchxn-type ligands

While it appears the current work will not directly serve our goal of producing novel \(\pi\)-basic molybdenum dearamatization agents, it demonstrates an interesting departure from the reported chemistry of picchxn-type ligands. Previous literature addressing picchxn-type ligands includes only a single tridentate (\(k^3\)) example, a dimethylamino-substituted variant on a 5-coordinate Fe(II) center [89]. In contrast, we find octahedral (\(k^3\)-N)_4Mo(CO)_3 complexes to be quite stable, consistent with reported molybdenum complexes bearing three fac amine groups and three carbonyls [58,59,70–73]. Unlike examples in which the amine groups are
identical, nitrosylation of \((\chi^3-N_2)\text{Mo(NO)}(CO)_3\) complexes is expected to give a complicated mixture of diastereomers, so while strong evidence of \([(\chi^3-N_2)\text{Mo(NO)}(CO)_2]\text{PF}_6\) compounds was observed, we did not attempt to isolate or fully characterize them.

Owing to the many stereogenic centers present, octahedral complexes bearing picchxn-type ligands complexed in a tetrahedral \((\chi^4\text{)}\) fashion could theoretically form a large range of diastereomers. In practice, however, only three such shapes are commonly observed. Steric interaction between the heterocycle groups is thought to generally prohibit the formation of trans diastereomers [Fig. 1], [84] though exceptions have been reported [25,90], and something akin to this ligand geometry, often with significant distortion, is observed on metals that favor square-planar complexes, such as Pd[II] [52]. Yamamoto proposes that only one cis-\(\text{–}\)picchxn configuration can form, with the trans-diaminocyclohexyl group's chiral centers limiting the configuration of the metal center such that the SS enantiomer of picchxn gives \(A\) helicity (as depicted in Scheme 2) and the RR enantiomer gives \(A\) helicity [47]. This configuration is favored by picchxn on Cr[III] [8,46,47] and Cd[II] [54,55], by picchxnMe on Co[III] [7,8,39], Mn[II] [10,12], Mn[III] [7,91], Mn[IV] [7,91] and Zn[II] centers [44], and by a 1-methylbenzimidazole-based version on Mn[II] [19]. On Fe[II], PicchxnMe2 can give the cis-\(\text{–}\) configuration under some reaction conditions [22,23]. Ru[II] does not show a strong preference, but cis-\(\text{–}\)picchxn and picchxnMe2 complexes have been isolated from diastereomeric mixtures [7,49]. In the current study of Mo[0] and Mo[II] complexes, the only tetradeinate configuration observed for picchxn (1) and picchxnMe2 (2) is the cis-\(\text{–}\) helicity as predicted by Yamamoto. When the two heterocycle groups of a picchxn-type ligand are cis to one another, one of two cis-\(\text{–}\)diastereomers is observed. In one of these, the heterocycle-2-ymlmethyl groups are anti on the central chelate ring and the SS \(N_4\) enantiomer gives \(A\) helicity (Fig. 6). This anti-cis-\(\text{–}\) configuration is favored by picchxn on Co[III] [7,36,37,40,92–94] and by a 2-pyridin-2-ylmethyl variant giving 2,2\(\text{–}\)symmetric cis-\(\text{–}\)picchxn [25,90]. cis-\(\text{–}\)picchxn and picchxnMe2 complexes have been isolated from diastereomeric mixtures [7,49]. In the current study of Mo[0] and Mo[III] complexes, the only tetradeinate configuration observed for picchxn (1) and picchxnMe2 (2) is the cis-\(\text{–}\) helicity as predicted by Yamamoto. When the two heterocycle groups of a picchxn-type ligand are cis to one another, one of two cis-\(\text{–}\)diastereomers is observed. In one of these, the heterocycle-2-ymlmethyl groups are anti on the central chelate ring and the SS \(N_4\) enantiomer gives \(A\) helicity (Fig. 6). This anti-cis-\(\text{–}\) configuration is favored by picchxn on Co[III] [7,36,37,40,92–94] and by a 2-pyridin-2-ylmethyl variant on Zn[II] [45]. On Fe[II], a picchxnMe2 derivative with 6-methylpyridyl groups can adopt the anti-cis-\(\text{–}\) configuration under some reaction conditions [23,27]. A Ru[II] complex with picchxn in this configuration can also be isolated from a mixture with the corresponding cis-\(\text{–}\)-picchxn diastereomer [7]. In the other cis-\(\text{–}\) diastereomer, the heterocycle-2-ymlmethyl groups are syn on the central chelate ring and the SS \(N_4\) enantiomer gives a \(A\) helicity (Fig. 6). This syn-cis-\(\text{–}\) configuration is favored by the picchxnMe2 derivative with 6-methylpyridyl groups on Fe[III] [27] and can also form on Fe[II] [23]. A Ru[II] complex with picchxnMe2 in this configuration can be isolated from a mixture with the corresponding cis-\(\text{–}\)-picchxnMe2 diastereomer [7,48,49], and in the current study it was the favored and solved configuration for \([(\text{cis-\(\text{–}\)}\text{–}\text{\text{-}Imchxn})\text{Mo(NO)}(\text{CO})_2]\text{PF}_6\) diastereomers [14A and 14B]. Because the cis-\(\text{–}\) configuration breaks the \(C_2\) symmetry of the \(N_4\) ligand, toggling the positions of the CO and NO\(\text{–}\) ligands accounts for four \([(\text{cis-\(\text{–}\)}N_2)\text{\text{-}Mo(NO)}(\text{CO})_2]\text{PF}_6\) diastereomers, consistent with \(^1\text{H NMR data for isolated \([(\text{cis-\(\text{–}\)}\text{\text{-}Imchxn})\text{\text{-}Mo(NO)}(\text{CO})_2]\text{PF}_6\) \((13) and \([(\text{cis-\(\text{–}\)}\text{\text{-}Imchxn})\text{\text{-}Mo(NO)}(\text{CO})_2]\text{PF}_6\) \((14) samples.}

Little precedent exists for complexes of picchxn-type ligands based on heterocycles other than pyridine. A more-substituted 1-methylimidazole variant was complexed to Rh[III] [51], but the product was not fully characterized, and a 1-methylbenzimidazole version gave the cis-\(\text{–}\) configuration on Mn[II] [19]. In addition to exploring novel picchxn variations, the current work represents a departure from earlier studies by virtue of the larger size of Mo (0) and Mo[II] compared to metal centers of previously reported complexes with picchxn-type ligands. Observed manifestations of the size difference are minor, however, with picchxn MoN bond lengths for \([(\text{cis-\(\text{–}\)}\text{picchxn})\text{\text{-}Mo(NO)}(\text{CO})_2]\text{PF}_6\) measuring 2.20, 2.27, 2.27, and 2.19 Å, only slightly longer than the CrN bonds of \([(\text{cis-\(\text{–}\)}\text{picchxn})\text{\text{-}Cr(NO)}(\text{CO})_2]\text{Cl}_2\) (2.12, 2.12, 2.11, and 2.06 Å) [46]. In this context, a greater size difference is observed between Mo(0) and Cd(II), with CdN bond lengths for \([(\text{cis-\(\text{–}\)}\text{picchxn})\text{\text{-}Cd(NO)}(\text{CO})_2]\text{PF}_6\) measuring 2.40, 2.44, 2.44, and 2.40 Å [54].

4. Conclusion

Picchxn-type \((N_4)\) ligands form \((\chi^3-N_2)\text{Mo(NO)}(CO)_3\), \((\chi^4-N_2)\text{Mo(NO)}(CO)_2\text{PF}_6\), and \((\chi^2-N_2)\text{Mo(NO)}X\text{PF}_6\) (X = Br, I) compounds analogous to other Mo(0) and Mo[II] examples. The \(\pi\)-basicity of \((\text{N}_4)\text{Mo(NO)}(\text{CO})_2\) fragments can be adjusted by varying the heterocycles of picchxn-type ligands, but unfortunately the more-electron-donating Imchxn and ImchxnMe$_2$ versions show a strong preference for non-C$_2$-symmetric cis-\(\text{–}\) configurations while picchxn and picchxnMe$_2$ form \([(\text{cis-\(\text{–}\)}N_2)\text{Mo(NO)}(\text{CO})_2]\text{PF}_6\) fragments that do not appear to be sufficiently electron-rich to serve as deaortanization agents. Ongoing studies in our lab are addressing both the corresponding tungsten examples and similar complexes bearing 2,2\(\text{–}\)-bispyrrolidine-based ligands, which may have a greater tendency to adopt the cis-\(\text{–}\) configuration [34,59].

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Appendix A. Supplementary material

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References
