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Molybdenum complexes of chiral C_2-symmetric picchxn-type ligands: Synthesis, characterization, and structural studies

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ABSTRACT

A series of molybdenum complexes based on chiral C_2-symmetric picchxn-type ligands (N_4 ligands, defined as *trans-N,N′*-bis(heterocycl-2-ylmethyl)-1,2-diaminocyclohexanes) has been synthesized and characterized. Reported and novel picchxn-type ligands form $(\kappa^3\text{-}N_4)Mo(CO)_3$, $[(\kappa^4\text{-}N_4)Mo(NO)(CO)]PF_6$, and $[(\kappa^4\text{-}N_4)Mo(NO)X]PF_6$ (X = Br, I) compounds. Multiple tridentate (κ^3) and tetradentate (κ^4) ligand configurations were observed, and the favored κ^4 configuration was found to vary with N_4 heterocycle identity. Heterocycle variation allowed for directed modification of the molybdenum electronic characteristics, but none of the studied $\{(\kappa^4\text{-}N_4)Mo(NO)\}^+$ fragments was found to be a suitable π-base for dearomatization chemistry. The crystal structures of eight molybdenum complexes with picchxn-type ligands were determined.

1. Introduction

Chiral C_2-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 C_2-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 C_2-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 C_2-symmetric tetradentate ligand that has garnered interest because of its ability to bond in a *cis-α* configuration. Picchxn-type ligands (N_4 ligands, *trans-N,N′*-bis(heterocycl-2-ylmethyl)-1,2-diaminocyclohexanes) have been studied extensively on small 3*d* 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 C_2-symmetric tetradentate ligand in such a complex might allow for enantioselective dearomatizations. We anticipate that an

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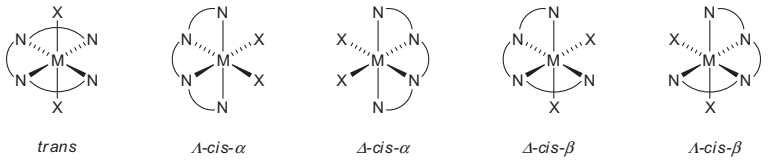


Fig. 1. Coordination geometries of chiral C_2-symmetric tetraamines on octahedral metal centers.

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 picchxnMe$_2$ (**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 ImchxnMe$_2$ (**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 referenced to tetramethylsilane (TMS) utilizing residual ^{1}H or ^{13}C 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 tetrabutylammonium 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 *F*2 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 (ImchxnMe$_2$, **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

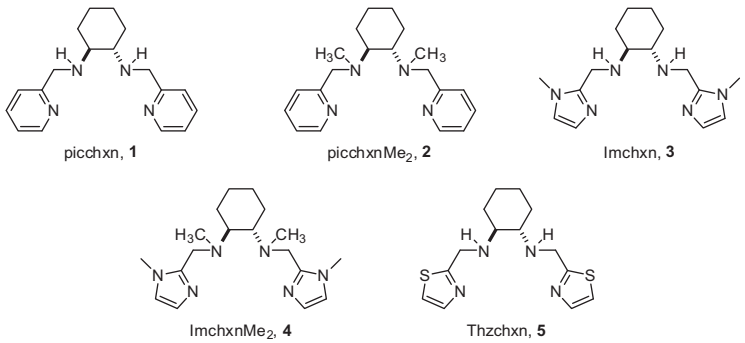


Fig. 2. Reported and novel picchxn-type (N_4) ligands studied.

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%). ^{1}H NMR (CD_3CN, δ): 6.88 (d, J = 1.2, 2H, Im), 6.75 (d, J = 1.2, 2H, Im), 3.65 (s, 2H, NCH_2), 3.65 (s, 2H, NCH_2), 3.64 (s, 6H, $ImCH_3$), 2.59 (m, 2H, NCH), 1.99 (s, 6H, NCH_3), 1.87 (m, 2H, cyclohexyl), 1.71 (m, 2H, cyclohexyl), 1.12 (m, 4H, cyclohexyl). ^{13}C NMR ($CDCl_3$, δ): 146.2 (Im 2), 126.8 (Im 4,5), 121.4 (Im 4,5), 62.0 (NCH), 50.9 (NCH_2), 35.4 (NCH_3, $ImCH_3$), 32.7 (NCH_3, $ImCH_3$), 25.6 (cyclohexyl), 24.5 (cyclohexyl). *Anal.* Calc. for $C_{16}H_{31}N_6 \cdot 1/4H_2O$: C, 64.54; H, 9.18; N, 25.09. Found: C, 64.48; H, 9.24; N, 25.12%.

2.2.2. Trans-N,N′-bis(thiazol-2-ylmethylene)-1,2-diaminocyclohexane

A solution of thiazole-2-carboxaldehyde (2.00 g, 17.7 mmol) in *N,N*-dimethylformamide (4.0 mL) was swirled as *trans-N,N′*-1,2-diaminocyclohexane (1.05 mL, 8.74 mmol) was added, which resulted in slight warming. After three days at ambient temperature, yellowish crystals were collected by filtration, rinsed with *N,N*-dimethylformamide (10 mL, in portions) and water (10 mL, in portions), and dried *in vacuo* (*trans-N,N′*-bis(thiazol-2-ylmethylene)-1,2-diaminocyclohexane, 1.91 g). After three days, a second crop of yellowish crystals was likewise collected from the initial filtrate (*trans-N,N′*-bis(thiazol-2-ylmethylene)-1,2-diaminocyclohexane, 0.33 g, 84.3% total yield). ^{1}H NMR ($CDCl_3$, δ): 8.36 (d, J = 0.8, 2H, imine), 7.81 (d, J = 3.2, 2H, Thz), 7.31 (dd, J = 3.2, 0.8, 2H, Thz), 3.48 (m, 2H, NCH), 1.84 (m, 4H, cyclohexyl), 1.79 (m, 2H, cyclohexyl), 1.47 (m, 2H, cyclohexyl). ^{13}C NMR ($CDCl_3$, δ): 167.1 (Thz 2), 154.7 (Thz 4,5), 143.8 (Thz 4,5), 121.3 (imine), 73.1 (NCH), 32.4 (cyclohexyl), 24.1 (cyclohexyl). *Anal.* Calc. for $C_{14}H_{16}N_4S$: C, 55.23; H, 5.30; N, 18.40. Found: C, 55.29; H, 5.55; N, 18.37%.

*2.2.3. Trans-N,N′-bis(thiazol-2-ylmethyl)-1,2-diaminocyclohexane (Thzchxn, **5**)*

To a mixture of sodium borohydride (0.21 g, 5.55 mmol) and ethanol (95%, 6.0 mL), *trans-N,N′*-bis(1-thiazol-2-ylmethylene)-1,2-diaminocyclohexane (0.637 g, 2.09 mmol) dissolved in ethanol (95%, 47 mL) was added. After stirring at ambient temperature for 18 h, the resulting solution was made strongly acidic by slow addition of hydrochloric acid (12 M, 1.5 mL) and reduced to dryness via rotary evaporation. The resulting solid was dissolved in water (6.5 mL) and washed with methylene chloride (3 × 10 mL). The aqueous layer was made strongly basic with aqueous sodium hydroxide (50% by weight), extracted with methylene chloride (3 × 20 mL), and dried over magnesium sulfate. The solution was filtered, reduced by rotary evaporation, and dried on a Schlenk line to give a viscous oil (crude **5**, 0.551 g). A sample of crude **5** (1.16 g) was dissolved in hydrochloric acid (1 M, 30 mL) and reduced to dryness by rotary evaporation. The resulting solid was dissolved in hot dry methanol (50 mL). Hot dry isopropanol (50 mL) was added, and the resulting solution was reduced to 50 mL by boiling. It was cooled slowly to room temperature and then in an ice bath. The resulting solid was collected by filtration, washed with cold isopropanol (3 × 5 mL), and dissolved in water (18 mL). This solution was made strongly basic with aqueous sodium hydroxide (50% by weight) and extracted with methylene chloride (3 × 55 mL). The combined organic extracts were dried over magnesium sulfate, filtered, reduced by rotary evaporation, and further dried on a Schlenk line to give a viscous oil (**5**, 1.01 g, 74.3% overall yield). ^{1}H NMR ($CDCl_3$, δ): 7.69 (d, J = 3.2, 2H, Thz), 7.24 (d, J = 3.2, 2H, Thz), 4.22 (d, J = 15.2, 2H, NCH_2), 4.09 (d, J = 15.2, 2H, NCH_2), 2.35 (m, 2H, cyclohexyl), 2.13 (d, J = 17.2, 2H, cyclohexyl), 2.0 (very broad, 2H, NH), 1.71 (m, 2H, cyclohexyl), 1.22 (m, 2H, cyclohexyl), 1.04 (m, 2H, cyclohexyl). ^{13}C NMR (CD_3CN, δ): 174.7 (Thz 2), 143.2 (Thz 4,5), 119.9 (Thz 4,5), 62.1 (NCH), 48.9 (NCH_2), 32.1 (cyclohexyl), 25.5 (cyclohexyl). *Anal.* Calc. for $C_{14}H_{20}N_4S_2$: C, 54.51; H, 6.54; N, 18.16. Found: C, 54.20; H, 6.49; N, 17.86%.

2.3. (κ^3-N_4)Mo(CO)$_3$ complexes

*2.3.1. (κ^3-picchxn)Mo(CO)$_3$ (**6**)*

A mixture of *trans-N,N′*-bis(pyridin-2-ylmethyl)-1,2-diaminocyclohexane (picchxn, **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 stirring water (500 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. ^{1}H NMR (CD_3CN, δ, major diastereomer by >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, NCH_2), 4.28 (m, 2H, NCH_2), 4.21 (dd, J = 15.6, 4.4, 1H, NCH_2), 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), 2.29 (t, J = 14.0, 2H, 2 × cyclohexyl), 1.70 (m, 2H, 2 × cyclohexyl), 1.61 (d, J = 13.6, 1H, cyclohexyl), 1.29 (qd, J = 12.4, 4.0, 1H, cyclohexyl), 1.16 (qt, J = 13.2, 3.2, 1H, cyclohexyl), 1.04 (qt, J = 13.2, 3.6, 1H, cyclohexyl), 0.66 (qd, J = 12.8, 3.6, 1H, cyclohexyl); (minor diastereomer by 15:1, select resonances) 8.81 (d, J = 5.2, 1H, py 6), 7.93 (bs, 1H, py 4,5), 3.84 (dd, J = 10.4, 3.2, 1H, NCH_2), 1.41 (qd, J = 11.2, 4.0, 1H, cyclohexyl). ^{13}C NMR (CD_3CN, δ, major diastereomer): 160.2 (py 2), 158.8 (py 2), 153.1 (py 6), 149.2 (py 6), 138.6 (py 4), 137.6 (py 4), 124.0 (py 3,5), 123.9 (py 3,5), 123.6 (py 3,5), 123.2 (py 3,5), 65.5 (NCH), 63.7 (NCH), 56.6 (NCH_2), 56.5 (NCH_2), 31.6 (cyclohexyl), 30.9 (cyclohexyl), 25.4 (cyclohexyl), 24.9 (cyclohexyl), CO carbons not observed. IR (CH_3CN): 1898 (CO), 1766 (CO). CV: E_{pa} = 0.09 V. *Anal.* Calc. for $C_{21}H_{24}MoN_4O_3$: 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. (κ^3-picchxnMe$_2$)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 (picchxnMe$_2$, **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%). ^{1}H NMR (CD_3CN, δ, major diastereomer by 6:1, based on integrations of resonances at 8.88 and 8.71 ppm): 8.71 (d, J = 4.8, 1H, py 6), 8.54 (dt, J = 4.8, 1.6, 1H, py 6), 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, 1H, py 3), 7.27 (m, 2H, 2 × py 5), 4.46 (d, J = 12.8, 1H, NCH_2), 4.41 (d, J = 12.4, 1H, NCH_2), 4.29 (d, J = 15.2, 1H, NCH_2), 4.12 (d, J = 15.6, 1H, NCH_2), 3.26 (td, J = 11.2, 3.2, 1H, CHN), 2.95 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 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, NCH_2), 3.79 (d, J = 14.0, 1H, NCH_2), 1.28 (qd, J = 12.8, 3.6, 1H, cyclohexyl). ^{13}C NMR (CD_3CN, δ, major diastereomer):

160.2 (py 2), 157.8 (py 2), 152.6 (py 6), 149.4 (py 6), 138.5 (py 4), 137.1 (py 4), 128.3 (py 3,5), 124.6 (py 3,5), 123.8 (py 3,5), 123.5 (py 3,5), 70.2 (NCH_2), 67.2 (NCH), 64.6 (NCH_2), 63.3 (NCH), 45.5 (CH_3), 40.7 (CH_3), 25.3 (cyclohexyl), 25.1 (cyclohexyl), 24.9 (cyclohexyl), 24.7 (cyclohexyl), CO carbons not observed. IR (CH_3CN): 1900 (CO), 1767 (CO). CV: E_{pa} = 0.21 V. *Anal.* Calc. for $C_{23}H_{28}MoN_4O_3$: C, 54.76; H, 5.59; N, 11.11. Found: C, 54.68; H, 5.70; N, 11.29%.

2.3.3. (κ^3-Imchxn)Mo(CO)$_3$ (**8**)

A mixture of *trans-N,N'*-bis(1-methylimidazol-2-ylmethyl)-1,2-diaminocyclohexane (Imchxn, **3**, 1.51 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 (2 × 30 mL) and diethyl ether (2 × 30 mL, 1 × 10 mL), and dried *in vacuo* to give a light yellow solid (**8**, 2.033 g, 92.5%). X-ray-quality crystals were obtained by layering an acetone solution of **8** with diethyl ether. ^{1}H NMR (CD_3CN, δ, 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 = 14.0, 8.4, 1H, NCH_2) 4.11 (dd, J = 11.0, 2.8, 1H, NCH_2), 4.06 (d, J = 15.0, 1H, NCH_2), 3.99 (dd, J = 9.2, 4.4, 1H, NH), 3.88 (dd, J = 15.0, 4.8, 1H, NCH_2), 3.66 (3H, s, CH_3), 3.59 (3H, s, CH_3), 2.67 (qd, J = 11.6, 4.0, 1H, cyclohexyl), 2.54 (br s, 1H, NH), 2.24 (t, J = 10.0, 2H, 2 × cyclohexyl), 1.75 (qd, J = 11.0, 4.0, 1H, cyclohexyl), 1.71 (d, J = 11.0, 1H, cyclohexyl), 1.63 (d, J = 11.0, 1H, cyclohexyl), 1.28 (qd, J = 12.0, 3.6, 1H, cyclohexyl), 1.15 (qt, J = 13.0, 3.6, 1H, cyclohexyl), 1.09 (qt, J = 12.0, 3.6, 1H, cyclohexyl), 0.72 (qd, J = 12.0, 3.6, 1H, cyclohexyl); (minor diastereomer by 7:1, select resonances): 7.03 (s, 1H, Im), 6.90 (s, 1H, Im), 4.61 (br s, 1H, NH). ^{13}C NMR (CD_3CN, δ, major diastereomer): 149.2 (Im 2), 146.7 (Im 2), 129.4 (Im 4,5), 127.02 (Im 4,5), 123.2 (Im 4,5), 122.1 (Im 4,5), 65.9 (NCH), 64.8 (NCH), 47.8 (NCH_2), 47.4 (NCH_2), 34.3 (CH_3), 32.9 (CH_3), 31.8 (cyclohexyl), 31.0 (cyclohexyl), 25.4 (cyclohexyl), 24.9 (cyclohexyl), CO carbons not observed. IR (CH_3CN): 1896 (CO), 1756 (CO). CV: E_{pa} = 0.0 V. *Anal.* Calc. for $C_{19}H_{26}MoN_6O_3$: C, 47.31; H, 5.43; N, 17.42. Found: C, 47.34; H, 5.57; N, 17.47%. The structure of **8** was confirmed by single-crystal X-ray diffraction.

2.3.4. (κ^3-ImchxnMe$_2$)Mo(CO)$_3$ (**9**)

A mixture of *trans-N,N'*-dimethyl-*N,N'*-bis(1-methylimidazol-2-ylmethyl)-1,2-diaminocyclohexane (ImchxnMe$_2$, **4**, 1.29 g, 3.91 mmol), molybdenum hexacarbonyl (0.946 g, 3.58 mmol), and *N,N*-dimethylformamide (25 mL) was stirred under reflux for 3 h, during which time it became first yellow and then dark brown. Water (65 mL) was added, and a yellow precipitate formed. The precipitate was collected by filtration, washed with diethyl ether (2 × 10 mL), and dried *in vacuo* to give a yellow solid (crude **9**, 1.12 g). The solid was extracted into hot toluene (75 mL) over 72 h using a soxhlet extraction apparatus. Diethyl ether (25 mL) was added, and solid was collected by filtration, washed with diethyl ether, and dried *in vacuo* to give a canary-yellow powder (**9**, 0.581 g, 33.7%). X-ray-quality crystals were obtained from a concentrated *m*-xylene solution of **9**. ^{1}H NMR (CD_3CN, δ, major diastereomer by 2.5:1, based on integrations of resonances at 6.94 and 6.84 ppm): 7.02 (d, J = 1.5, 1H, Im), 7.01 (d, J = 1.3, 1H, Im), 6.94 (d, J = 1.3, 1H, Im), 6.88 (d, J = 1.3, 1H, Im), 4.53 (d, J = 14.6, 1H, NCH_2), 4.35 (d, J = 14.9, 1H, NCH_2), 4.14 (d, J = 15.2, 1H, NCH_2), 3.72 (d, J = 15.2, 1H, NCH_2), 3.79 (s, 3H, $ImCH_3$), 3.60 (s, 3H, $ImCH_3$), 2.88 (s, 3H, NCH_3), 2.27 (s, 3H, NCH_3), 3.48 (ddd, J = 7.6, 7.6, 3.8, 1H, NCH), 2.24 (buried, 1H, NCH) 1.66 (m, 2H, cyclohexyl), 1.45 (m, 2H, cyclohexyl), 1.32 (m, 1H, cyclohexyl), 1.00 (m, 2H, cyclohexyl), 0.85 (m, 1H, cyclohexyl); (minor diastereomer by 2.5:1): 7.00 (s, 1H, Im), 6.99 (d, J = 1.3, 1H, Im), 6.89 (s, 1H, Im), 6.84 (s, 1H, Im), 4.27 (d, J = 15.2, 1H, NCH_2), 4.13 (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 (ddd, buried, 1H, NCH), 1.96 (buried, 1H, cyclohexyl). ^{13}C NMR (CD_3CN, δ, 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), 45.9 (NCH_3), 41.1 (NCH_3), 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_3CN): 1900 (CO), 1761 (CO). CV: E_{pa} = 0.11 V. *Anal.* Calc. for $C_{21}H_{30}MoN_6O_3$: C, 49.41; H, 5.92; N, 16.46. Found: C, 49.33; H, 5.73; N, 16.16%. The structure of **9** was confirmed by single-crystal X-ray diffraction.

2.3.5. (κ^3-Thzchxn)Mo(CO)$_3$ (**10**)

A mixture of *trans-N,N'*-bis(thiazol-2-ylmethyl)-1,2-diaminocyclohexane (Thzchxn, **5**, 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. ^{1}H NMR (CD_3CN, δ, major diasteromer 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), 7.77 (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_3CN, δ, 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_2), 53.1 (NCH_2), 31.8 (cyclohexyl), 30.7 (cyclohexyl), 25.4 (cyclohexyl), 24.9 (cyclohexyl), CO carbons not observed. IR (CH_3CN): 1901 (CO), 1766 (CO). CV: E_{pa} = 0.12 V. *Anal.* Calc. for $C_{17}H_{20}MoN_4O_3S_2$: C, 41.80; 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.

2.4. [(κ^4-N$_4$)Mo(NO)(CO)]PF_6 compounds

2.4.1. [(cis-α-picchxn)Mo(NO)(CO)]PF_6 (**11**)

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, 1.7 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**, 0.844 g, 66.5%). X-ray quality crystals were obtained by layering an acetonitrile solution of **11** with diethyl ether. ^{1}H NMR (CD_3CN, δ): 8.94 (d, J = 5.2, 1H, py 6), 8.90 (d, J = 5.6, 1H, py 6), 8.05 (td, J = 7.6, 1.6, 1H, py 4,5), 7.82 (td,

J = 8.0, 1.6, 1H, py 4,5), 7.65 (d, J = 7.6, 1H, py 3), 7.51 (t, J = 6.6, 1H, py 4,5), 7.47 (d, J = 7.6, 1H, py 3), 7.43 (t, J = 6.4, 1H, py 4,5), 4.56 (d, J = 16.4, 1H, NCH_2), 4.46 (dd, J = 16.0, 3.6, 1H, NCH_2), 4.37 (d, J = 15.6, 1H, NCH_2), 4.28 (dd, J = 16.0, 3.6, 1H, NCH_2), 4.22 (d, J = 7.2, 1H, NH), 3.77 (d, J = 6.0, 1H, NH), 2.26 (m, 2H, NCH), 1.64 (dd, J = 8.4, 2.4, 2H, cyclohexyl), 1.04 (m, 4H, cyclohexyl), 2 cyclohexyl buried under CHD_2CN peak. ^{13}C NMR (CD_3CN, δ): 159.9 (py 2), 157.6 (py 2,6), 157.0 (py 2,6), 150.9 (py 6), 140.9 (py 4), 137.8 (py 4), 125.3 (py 3,5), 125.2 (py 3,5), 124.6 (py 3,5), 124.4 (py 3,5), 63.4 (NCH), 62.7 (NCH), 55.0 (NCH_2), 54.0 (NCH_2), 29.0 (cyclohexyl), 28.9 (cyclohexyl), 23.5 (cyclohexyl) 23.4 (cyclohexyl), CO carbon not observed. IR (CH_3CN): 1884 (CO), 1598 (NO). CV: E_{pa} = 0.45 V. *Anal.* Calc. for $C_{19}H_{24}F_6MoN_5O_2P$: C, 38.33; H, 4.06; N, 11.76. Found: C, 38.51; H, 4.07; N, 11.46%. The structure of **11** was confirmed by single-crystal X-ray diffraction.

2.4.2. [(cis-α-picchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (**12**)

A mixture of potassium hexafluorophosphate (2.19 g, 11.9 mmol), compound **7** (1.008 g, 2.024 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, 160 mL) was added, giving a light brown mixture with a pH of 8. Solid was collected 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 layering an acetonitrile solution of **12** with diethyl ether. ^1H NMR (CD_3CN, 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, 1H, 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, NCH_2), 4.39 (d, J = 15.2, 1H, NCH_2), 4.30 (d, J 15.6, 1H, NCH_2), 4.13 (d, J = 15.6, 1H, NCH_2), 2.47 (m, 2H, NCH, cyclohexyl), 2.44 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.04 (d, J = 12.8, 1H, NCH, cyclohexyl), 1.65 (m, 2H, cyclohexyl), 1.27 (m, 2H, cyclohexyl), 1.04 (m, 2H, cyclohexyl), 1 NCH or cyclohexyl buried under CHD_2CN peak. ^{13}C NMR (CD_3CN, δ): 159.8 (py 2), 157.1 (py 2), 156.7 (py 6), 150.5 (py 6), 141.5 (py 4), 138.3 (py 4), 126.4 (py 3,5), 125.7 (py 3,5), 125.4 (py 3,5), 124.7 (py 3,5), 64.7 (NCH_2), 63.7 (NCH), 63.5 (NCH), 63.4 (NCH_2), 42.0 (CH_3), 41.3 (CH_3), 24.3 (cyclohexyl), 24.2 (cyclohexyl), 23.7 (cyclohexyl), 23.6 (cyclohexyl), CO carbon not observed. IR (CH_3CN): 1889 (CO), 1602 (NO). CV: E_{pa} = 0.56 V. *Anal.* Calc. for $C_{21}H_{28}F_6MoN_5O_2P$: C, 40.46; H, 4.53; N, 11.23. Found: C, 40.72; H, 4.55; N, 11.37%. The structure of **12** was confirmed by single-crystal X-ray diffraction.

2.4.3. [(cis-β-Imchxn)Mo(NO)(CO)]PF$_6$ (**13**), mixture of 4 diastereomers

A mixture of sodium nitrite (0.031 g, 0.449 mmol), potassium hexafluorophosphate (0.106 g, 0.576 mmol), compound **8** (0.214 g, 0.444 mmol), and methanol (5 mL) was stirred while hydrochloric acid (12 M, 0.3 mL, 4 mmol) was added over 30 s. Aqueous potassium hydroxide (2 M, 2.3 mL, 4.6 mmol) was added over 2 min, giving a brown solution which turned to a purple mixture within a few hours. After four days of stirring at ambient temperature, precipitate was collected by filtration, rinsed with water (45 mL) and diethyl ether (45 mL), and dried *in vacuo* to give a light purple solid (**13A**, **13B**, **13C**, and **13D**; in a ratio of ~1:20:trace: trace based on integrations of ^1H resonances at 6.56, 6.44, 6.13 and 5.92 ppm; 0.132 g; 49.5%). ^1H NMR (CD_3CN, δ, **13A**, select resonances): 7.15 (d, J = 1.6, 1H, Im), 7.08 (d, J = 1.2, 1H, Im), 7.06 (d, J = 1.6, 1H, Im), 6.56 (1H, d, J = 1.6, Im), 5.14 (dd, J = 8.4, 5.2, 1H, NH), 4.34 (dd, J = 14.8, 1H, NCH_2), 4.31 (d, J = 17.6, 1H, NCH_2), 3.91 (dd, J = 16.0, 5.2, NCH_2), 3.66 (s, 3H, CH_3), 3.64 (s, 3H, CH_3), 3.25 (td, J = 11.6, 4.8, 1H, NH), 3.12 (dd, J = 15.6, 1H, NCH_2), 2.77 (qd, J = 11.2, 4.0, NCH); (**13B**): 7.13 (d, J = 1.6, 1H, Im), 7.12 (d, J = 2.0, 1H, Im), 7.00 (d, J = 1.6, 1H, Im), 6.44 (d, J = 1.2, 1H, Im), 4.67 (dd, J = 7.6, 5.2, 1H, NH), 4.54 (dd, J = 14.4, 1.6, 1H, NCH_2), 4.33 (d, J = 16.0, 1H, NCH_2), 4.06 (dd, J = 16.0, 4.8, 1H, NCH_2), 3.80 (dd, J = 14.8, 11.2, 1H, NCH_2), 3.70 (s, 3H, CH_3), 3.61 (s, 3H, CH_3), 3.33 (td, J = 11.2, 4.8, 1H, NH), 2.94 (qd, J = 11.2, 4.0, 1H, NCH), 2.29 (m, 3H, NCH, cyclohexyl), 1.81 (d, J = 11.6, 1H, cyclohexyl), 1.73 (d, J = 12.4, 1H, cyclohexyl), 1.46 (qd, J = 12.8, 3.2, 1H, cyclohexyl), 1.25 (m, 2H, cyclohexyl), 1.03 (qd, J = 12.0, 3.6, 1H, cyclohexyl); (**13C**, select resonances): 7.18 (d, J = 1.2, 1H, Im), 7.05 (d, J = 1.2, 1H, Im), 6.98 (d, J = 1.6, 1H, Im), 6.13 (d, J = 1.6, 1H, Im), 5.49 (bs, 1H, NH), 4.50 (d, J = 17.2, 1H, NCH_2), 4.37 (dd, J = 16.0, 6.8, 1H, NCH_2), 3.67 (s, 3H, CH_3), 3.62 (s, 3H, CH_3); (**13D**, select resonances): 7.17 (d, J = 1.2, 1H, Im), 7.03 (d, J = 1.2, 1H, Im), 6.96 (d, J = 1.2, 1H, Im), 5.92 (d, J = 1.2, 1H, Im), 5.25 (bs, 1H, NH), 3.64 (s, 3H, CH_3). ^{13}C NMR (CD_3CN, δ, **13B**): 151.9 (Im 2), 150.2 (Im 2), 131.9 (Im 3,5), 126.8 (Im 3,5), 123.9 (Im 3,5), 123.7 (Im 3,5), 69.8 (NCH), 66.1 (NCH), 50.2 (NCH_2), 45.8 (NCH_2), 34.8 (CH_3), 34.5 (CH_3), 31.5 (cyclohexyl), 31.4 (cyclohexyl), 25.3 (cyclohexyl), 24.2 (cyclohexyl), CO carbon not observed. IR (CH_3CN): 1871 (CO), 1579 (NO). CV: E_{pa} = 0.30 V. *Anal.* Calc. for $C_{17}H_{26}F_6MoN_7O_2P$: C, 33.95; H, 4.36; N, 16.30. Found: C, 34.31; H, 4.60; N, 16.44%.

2.4.4. [(cis-β-ImchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (**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 layering 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 1:20 ratio was obtained by layering with diethyl ether an acetonitrile solution of **14A**:**14B**:**14D** in an ~1:16:trace ratio. ^1H NMR (CD_3CN, δ, **14A**, [(*syn-cis-β*-ImchxnMe$_2$)Mo(NO)(CO)]PF$_6$ 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, NCH_2), 4.02 (d, J = 15.6, 1H, NCH_2), 3.90 (d, J = 16.8, 1H, NCH_2), 3.69 (s, 3H, $ImCH_3$), 3.65 (s, 3H, $ImCH_3$), 3.45 (d, J = 16.0, 1H, NCH_2), 3.18 (s, 3H, NCH_3), 2.60 (s, 3H, NCH_3), 1.45 (qd, J = 12.0, 3.6, 1H, cyclohexyl); (**14B**, [(*syn-cis-β*-ImchxnMe$_2$)Mo(NO)(CO)]PF$_6$ 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, NCH_2), 4.13 (d, J = 15.6, 1H, NCH_2), 3.93 (d, J = 16.8, 1H, NCH_2), 3.66 (s, 3H, $ImCH_3$), 3.65 (s, 3H, $ImCH_3$), 3.41 (d, J = 15.6, 1H, NCH_2), 3.34 (td, J = 11.2, 3.6, 1H, NCH), 3.15 (s, 3H, NCH_3), 2.74 (s, 3H, NCH_3), 2.21 (m, 1H, cyclohexyl), 2.10 (td, J = 11.6, 4.0, 1H, NCH), 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, NCH_2), 3.93 (d,

J = 16.0, 1H, NCH_2), 3.03 (d, J = 15.2, 1H, NCH_2), 2.98 (s, 3H, NCH_3), 2.72 (s, 3H, NCH_3).; (**14D**, select resonances): 7.21 (d, J = 1.6, 1H, Im), 7.04 (d, J = 1.2, 1H, Im), 6.97 (d, J = 1.2, 1H, Im), 5.52 (d, J = 1.6, 1H, Im), 4.55 (d, J = 15.6, 1H, NCH_2), 4.01 (d, J = 15.6, 1H, NCH_2), 3.87 (d, J = 14.8, 1H, NCH_2), 3.70 (s, 3H, $ImCH_3$), 3.60 (s, 3H, $ImCH_3$), 2.88 (s, 3H, NCH_3), 2.81 (s, 3H, NCH_3). ^{13}C NMR (CD_3-CN, δ, **14B**): 149.5 (Im 2), 149.3 (Im 2), 132.1 (Im 4,5), 126.1 (Im 4,5), 124.7 (Im 4,5), 124.7 (Im 4,5), 72.3 (NCH), 69.4 (NCH), 56.9 (NCH_2), 53.7 (NCH_2 and NCH_3), 44.0 (NCH_3), 35.0 ($ImCH_3$), 34.9 ($ImCH_3$), 26.1 (cyclohexyl), 26.2 (cyclohexyl), 25.1 (cyclohexyl), 24.4 (cyclohexyl). IR (CH_3CN): 1877 (CO), 1586 (NO). CV: E_{pa} = 0.34 V. *Anal.* Calc. for $C_{19}H_{30}F_6MoN_7O_2P$: C, 36.26; H, 4.80; N, 15.58. Found: C, 36.29; H, 4.78; N, 15.27%. The structures of **14A** and **14B** cocrystallized and **14B** alone were confirmed by single-crystal X-ray diffraction.

2.5. [(cis-α-N_4)Mo(NO)X]PF_6 compounds

2.5.1. [(cis-α-picchxn)Mo(NO)I]PF_6 (**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 (600 mL). Precipitate was collected by filtration, rinsed with diethyl ether (5 × 10 mL), and dried *in vacuo* to give a bright yellow solid (**15**, 3.502 g, quantitative). IR (CH_3CN): 1622 (NO). CV (100 mV/s): $E_{1/2}$ = −1.00 V, ΔE_p = 0.08 V. *Anal.* Calc. for $C_{18}H_{24}F_6IMoN_5OP$: C. 31.14, H. 3.48, N. 10.09. Found: C. 31.59, H. 3.75, N. 10.08%.

2.5.2. [(cis-α-picchxnMe_2)Mo(NO)Br]PF_6 (**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 green solid (**16**, 0.5120 g, 92.6%). X-ray quality crystals were obtained by layering an acetonitrile solution of **16** with diethyl ether. IR (CH_3CN): 1622 (NO). CV (100 mV/s): $E_{1/2}$ = −0.89 V, ΔE_p = 0.05 V. *Anal.* Calc. for $C_{18}H_{24}F_6BrMoN_5OP$: 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

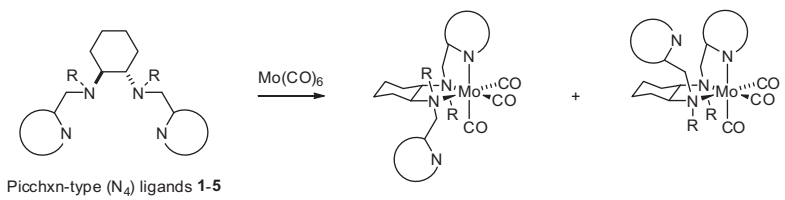
3.1. Synthesis and characterization of fac-(κ^3-N_4)Mo(CO)$_3$ complexes

Reported and novel picchxn-type (N_4) 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*-(κ^3-N_4)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*-(κ^3-ImchxnMe_2)Mo(CO)$_3$ results mainly from use of a Soxhlet extraction to obtain analytically pure samples.

The ^1H NMR spectra of *fac*-(κ^3-N_4)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*-(κ^3-N_4)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 pK_a 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 descreases the σ-basicity of N-donor tetradentate ligands [75]. This effect was attributed to steric interactions weaking the MoN bonds, but interestingly, MoN bond lengths for the solved structure of (κ^3-ImchxnMe_2)Mo(CO)$_3$ (**9**) do not show an obvious increase compared to those for the two complexes in the unit cell of (κ^3-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 π-acidic carbonyl groups *trans* to a substantially σ-basic amine group, *fac*-(κ^3-N_4)Mo(CO)$_3$ complexes **6**–**10** show a great deal of stability toward further intramolecular substitution of carbonyl groups, and attempts to produce (κ^4-N_4)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 each of the complexed nitrogens was part



fac-(κ^3-picchxn)Mo(CO)$_3$, **6**, 99%, dr = >20:1
fac-(κ^3-picchxnMe_2)Mo(CO)$_3$, **7**, 74%, dr = 5:1
fac-(κ^3-Imchxn)Mo(CO)$_3$, **8**, 94%, dr = 10:1
fac-(κ^3-ImchxnMe_2)Mo(CO)$_3$, **9**, 34%, dr = 2.5:1
fac-(κ^3-Thzchxn)Mo(CO)$_3$, **10**, 55%, dr = 7:1

Scheme 1. Reactions of picchxn-type (N_4) ligands to give (κ^3-N_4)Mo(CO)$_3$ complexes.

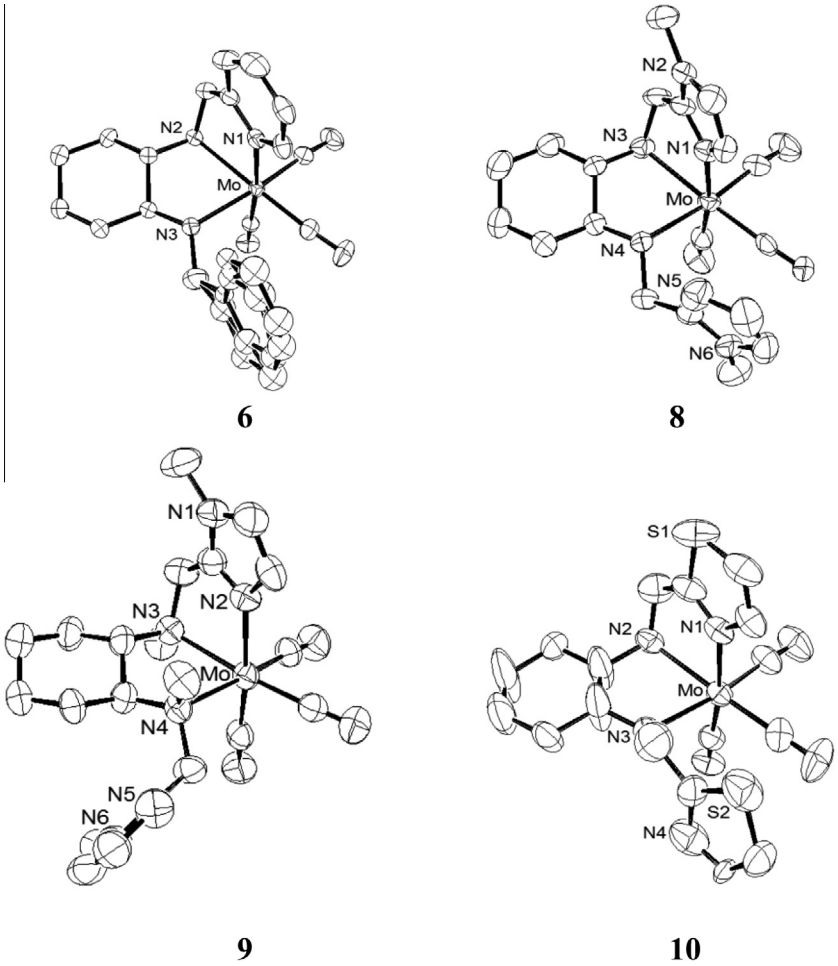


Fig. 3. X-ray crystal structures (ORTEP, 50% probability ellipsoids) of (κ^3-picchxn)Mo(CO)$_3$ (**6**), (κ^3-Imchxn)Mo(CO)$_3$ (**8**), (κ^3-ImchxnMe$_2$)Mo(CO)$_3$ (**9**), and (κ^3-Thzchxn)Mo(CO)$_3$ (**10**) [69].

Table 1
IR, electrochemical, and crystal data for *fac*-(κ^3-N$_4$)Mo(CO)$_3$ complexes (**6–10**).

Complex	υ_{CO} (cm^{-1})	E_{pa}[a]	MoN (Å)	CO (Å)
(κ^3-picchxn)Mo(CO)$_3$ (**6**)	1898, 1766	0.09	2.26, 2.30, 2.33	1.18, 1.18, 1.16
(κ^3-picchxnMe$_2$)Mo(CO)$_3$ (**7**)	1900, 1767	0.21	–	–
(κ^3-Imchxn)Mo(CO)$_3$ (**8**)	1896, 1756	0.00	2.27, 2.32, 2.33 2.24, 2.33, 2.36	1.18, 1.17, 1.16 1.17, 1.20, 1.17
(κ^3-ImchxnMe$_2$)Mo(CO)$_3$ (**9**)	1900, 1761	0.11	2.25, 2.33, 2.39	1.17, 1.20, 1.15
(κ^3-Thzchxn)Mo(CO)$_3$ (**10**)	1901, 1766	0.12	2.27, 2.31, 2.35	1.17, 1.19, 1.19

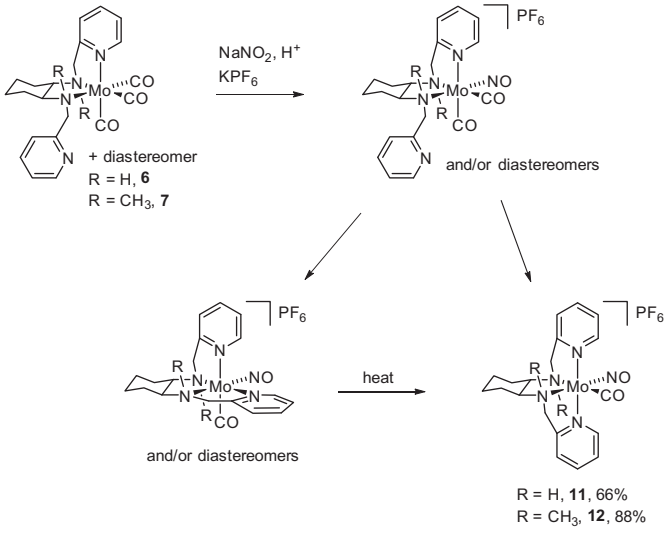
[a] Potential of anodic peak (V) vs. NHE.

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)]PF$_6$ 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*-(κ^3-N$_4$)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*-toluenesulfonamide (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*-(κ^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; υ_{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*-(κ^3-picchxn)Mo

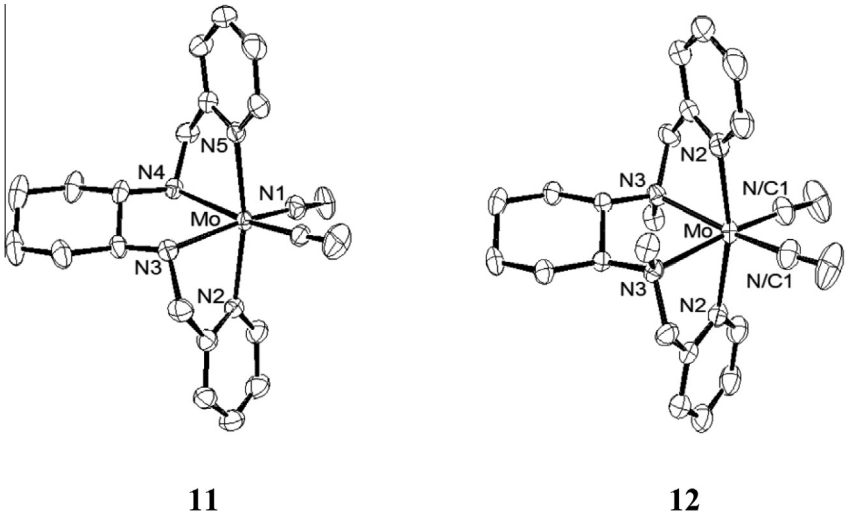
$(NO)(CO)_2]PF_6$ diastereomers, and data for molybdenum complexes bearing four amine groups and *cis* carbonyl and nitrosyl ligands, such as Tp(MeIm)Mo(NO)(CO) (MeIm = 1-methylimidazole, υ_{CO} = 1865 cm^{-1}) [59,61], strongly suggest that the latter peak corresponds to the CO stretch of one or more [(*cis*-picchxn)Mo(NO)(CO)]PF_6 diastereomers. Moderate heating causes the 2023 cm^{-1} and 1933 cm^{-1} set to recede and the 1883 cm^{-1} peak to grow, eventually giving samples of [(*cis*-α-picchxn)Mo(NO)(CO)]PF_6 (**11**, Scheme 2), which has been isolated in analytically pure form and fully characterized. ^1H NMR spectra of [(*cis*-α-N_4)Mo(NO)(CO)]PF_6 compounds are distinctive in that the peaks appear in pairs, reflecting the C_2 symmetry of the {(*cis*-α-N_4)Mo} fragment. However, prior to the complete formation of **11**, ^1H NMR spectra of *fac*-(κ^3-picchxn)Mo$(CO)_3$ (**6**) nitrosylation products show a different compound that lacks such pairings but likewise corresponds to IR stretches at 1884 cm^{-1} (υ_{CO}) and 1598 cm^{-1} (υ_{NO}). These observations are taken as strong evidence that **6** initially undergoes a nitrosylation reaction to give one or more [*fac*-(κ^3-picchxn)Mo$(NO)(CO)_2]PF_6$ diastereomers (Scheme 2). The kinetically favored intramolecular substitution product of [*fac*-(κ^3-picchxn)Mo$(NO)(CO)_2]PF_6$ is one or more [(*cis*-β-picchxn)Mo(NO)(CO)]PF_6 diastereomers, but under the conditions that promote this substitution [(*cis*-β-picchxn)Mo(NO)(CO)]PF_6 diastereomers convert to the thermodynamically favored [(*cis*-α-picchxn)Mo(NO)(CO)]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 [*fac*-(κ^3-picchxn)Mo$(NO)(CO)_2]PF_6$ diastereomers is also a possibility.



Scheme 2. Reactions of (κ^3-picchxn)Mo$(CO)_3$ (**6**) and (κ^3-picchxnMe$_2$)Mo$(CO)_3$ (**7**) to give [(*cis*-α-picchxn)Mo(NO)(CO)]PF_6 (**11**) and [(*cis*-α-picchxnMe$_2$)Mo(NO)(CO)]PF_6 (**12**).

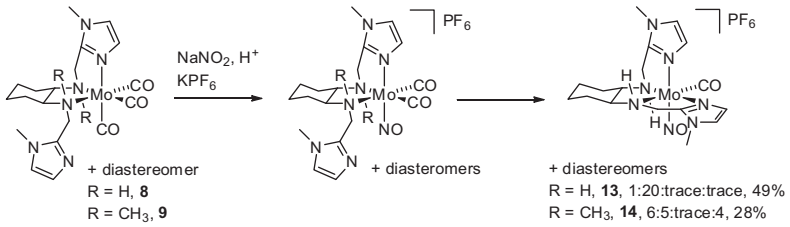
Nitrosylation of *fac*-(κ^3-picchxnMe$_2$)Mo$(CO)_3$ (**7**) proceeds in a fashion similar to that of (κ^3-picchxn)Mo$(CO)_3$ (**6**), with IR peaks attributed to CO stretches of [*fac*-(κ^3-picchxnMe$_2$)Mo$(NO)(CO)_2$]PF_6 diastereomers being observed at 2025 and 1937 cm^{-1} and ^1H NMR data indicating the formation of multiple [(*cis*-picchxnMe$_2$)Mo(NO)(CO)]PF_6 diastereomers before equilibration to [(*cis*-α-picchxnMe$_2$)Mo(NO)(CO)]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*-α configuration and Λ helicity for both (*S,S*)-picchxn (in *S,S*-**11**) and (*S,S*)-picchxnMe$_2$ (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 [(*cis*-α-PDP)Mo(NO)(CO)]PF_6 (PDP = 2-[[2-(1(pyridine-2-ylmethyl)pyrrolidin-2-yl)pyrrolidin-1-yl]methyl]pyridine) from [(κ^3-PDP)Mo$(CO)_3]PF_6$, for which [(*cis*-β-PDP)Mo(NO)(CO)]PF_6 is isolable but converts to [(*cis*-*a*-PDP)Mo(NO)(CO)]PF_6 with moderate heating [59].

Nitrosylation sequences of (κ^3-Imchxn)Mo$(CO)_3$ (**8**) and (κ^3-ImchxnMe$_2$)Mo$(CO)_3$ (**9**) proceed initially in a fashion analogous to those of (κ^3-picchxn)Mo$(CO)_3$ (**6**) and (κ^3-picchxnMe$_2$)Mo$(CO)_3$ (**7**), showing CO stretches in the IR spectrum attributed to respective [*fac*-(κ^3-Imchxn)Mo$(NO)(CO)_2]PF_6$ (2023 and 1932 cm^{-1}) and [*fac*-(κ^3-ImchxnMe$_2$)Mo$(NO)(CO)_2]PF_6$ (2024 and 1931 cm^{-1}) diastereomers before proceeding to tetradentate complexes. However, NMR monitoring experiments have given no evidence of either [(*cis*-α-Imchxn)Mo(NO)(CO)]PF_6 or [(*cis*-α-ImchxnMe$_2$)Mo(NO)(CO)]PF_6, indicating that, unlike tetradentate complexes of picchxn (**1**) and picchxnMe$_2$ (**2**), those of Imchxn (**3**) and ImchxnMe$_2$



11 **12**

Fig. 4. X-ray crystal structures (ORTEP, 50% probability ellipsoids) of [(Λ-*S,S*-*cis*-α-picchxn)Mo(NO)(CO)]PF_6 (**11**) and [(Λ-*S,S*-*cis*-α-picchxnMe$_2$)Mo(NO)(CO)]PF_6 (**12**) with PF_6^- anions omitted.



Scheme 3. Reactions of (κ^3-Imchxn)Mo(CO)$_3$ (**8**) and (κ^3-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**).

(**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.

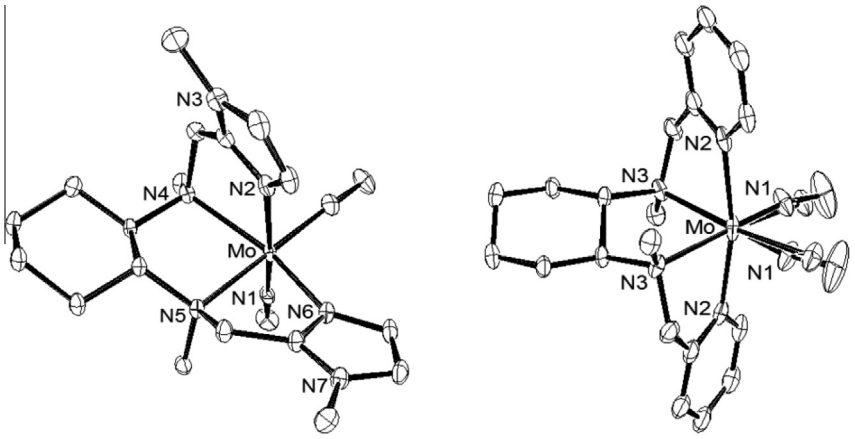
The four observed diastereomers of **14** each show a single markedly shielded imidazolyl (Im) proton signal between 6.25 and 5.50 ppm. This shift of a single heterocycle ^{1}H signal in *cis*-β complexes such as **14** has long been ascribed to the positioning of a heterocycle ring proton above the face of the other heterocycle ring [84], and diastereomers of **13** likewise each show one Im proton signal between 6.60 and 5.90 ppm. Layering with diethyl ether an acetonitrile solution of [(*cis*-β-ImchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (**14**) containing a 6 (6.24 ppm, **14A**): 5 (6.04 ppm, **14B**): trace (5.70 ppm, **14C**): 4 (5.52 ppm, **14D**) ratio of diastereomers resulted in selective cocrystallization of a sample showing **14A** and **14B** in an ~1:1 ratio in the ^{1}H NMR spectrum, and a solved X-ray structure showed two diastereomers cocrystallized in a 2:3 ratio. From a sample showing a 1:16 ratio of **14A** and **14B** in the ^{1}H NMR spectrum, the same procedure yielded crystals consisting of **14A** and **14B** cocrystallized in a 1:20 ratio, as evidenced by both ^{1}H NMR spectral data and a solved X-ray structure (Fig. 5). ^{1}H NMR monitoring experiments in which samples containing [*fac*-(κ^3-Imchxn)Mo(NO)(CO)$_2$]PF$_6$ and [*fac*-(κ^3-ImchxnMe$_2$)Mo(NO)(CO)$_2$]PF$_6$ were subjected to mild heating indicate little, if any, kinetic preference either among [(*cis*-β-Imchxn)Mo(NO)(CO)]PF$_6$ (**13**) diastereomers or among [(*cis*-β-ImchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (**14**) diastereomers, but if the solved X-ray structures of **14** reflect the major species observed in ^{1}H NMR spectra of the bulk crystalline samples then the thermodynamically favored diastereomers of [(*cis*-β-ImchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (**14A** and **14B**) have a *syn* relationship between the *N*-methyl groups on the central chelate ring and (*R,R*)-ImchxnMe$_2$ (*R,R*-**4**) gives the Δ 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^3-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

Table 2
IR and electrochemical data for [(κ^4-N$_4$)Mo(NO)(CO)]PF$_6$ compounds.

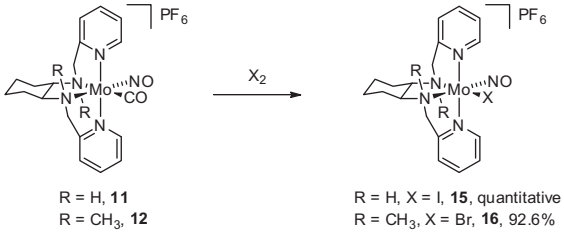
Compound	υ_{CO} (cm^{-1})	υ_{NO} (cm^{-1})	E_{pa}[a]
[(*cis*-α-picchxn)Mo(NO)(CO)]PF$_6$ (**11**)	1884	1598	0.45
[(*cis*-α-picchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (**12**)	1889	1602	0.56
[(*cis*-β-Imchxn)Mo(NO)(CO)]PF$_6$ (**13**)	1871	1579	0.30
[(*cis*-β-ImchxnMe$_2$)Mo(NO)(CO)]PF$_6$ (**14**)	1877	1586	0.34

[a] Potential of anodic peak (V) vs. NHE.



14 **16**

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



Scheme 4. Oxidations of [(*cis*-α-picchxn)Mo(NO)(CO)]PF_6 (**11**) and [(*cis*-α-picchxnMe_2)Mo(NO)(CO)]PF_6 (**12**) to give [(*cis*-α-picchxn)Mo(NO)I]PF_6 (**15**) and [(*cis*-α-picchxnMe_2)Mo(NO)Br]PF_6 (**16**).

subsequent lower oxidation potentials and lower CO and NO stretching frequencies for [(*cis*-β-Imchxn)Mo(NO)(CO)]PF_6 (**13**) and [(*cis*-β-ImchxnMe_2)Mo(NO)(CO)]PF_6 (**14**) as compared to those of [(*cis*-α-picchxn)Mo(NO)(CO)]PF_6 (**11**) and [(*cis*-α-picchxnMe_2)Mo(NO)(CO)]PF_6 (**12**). As with *fac*-(κ^3-N_4)Mo$(CO)_3$ complexes **6**–**9**, IR and electrochemical data for [(*cis*-α-N_4)Mo(NO)(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 $[(N_4)Mo(NO)X]PF_6$ compounds

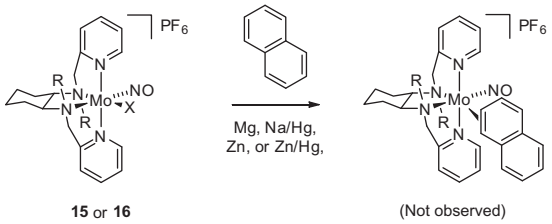
In previous work, substitution of the carbonyl ligand of Tp(MeIm)Mo(NO)(CO) for a dihapto-bound aromatic was effected via a two-step oxidation–reduction sequence in which the complex was first reacted with elemental bromine to give the 17-electron Mo(I) complex Tp(MeIm)Mo(NO)Br [61]. In order to assess the ability of $\{N_4Mo(NO)\}^+$ fragments to form similar complexes with aromatics, we first sought to remove the CO ligands from $[(N_4)Mo(NO)(CO)]^+$ complexes through similar oxidations. Reaction of [(*cis*-α-picchxn)Mo(NO)(CO)]PF_6 (**11**) with bromine proceeds vigorously, and collected products show IR peaks in the 1610–1630 cm^{-1} range, consistent with the expected NO stretch of [(*cis*-α-picchxn)Mo(NO)Br]PF_6, but these reactions did not proceed cleanly, with products showing residual ^{1}H NMR signals from **11** and IR spectra indicating NO ligands in multiple environments. When elemental iodine was instead used as the oxidant, the analogous reaction gave a quantitative yield of [(*cis*-α-picchxn)Mo(NO)I]PF_6 (**15**, Scheme 4) as evidenced by loss of the 1884 cm^{-1} CO stretch of [(*cis*-α-picchxn)Mo(NO)(CO)]PF_6 (**11**), shifting of the NO stretch from 1598 to 1622 cm^{-1}, disappearance of ^{1}H NMR signals for **11**, and replacement of the E_{pa} at 0.45 V for **11** with an $E_{1/2}$ at −1.00 V for **15**. Consistent with the larger steric profile of picchxnMe_2, reaction of [(*cis*-α-picchxnMe_2)Mo(NO)(CO)]PF_6 (**12**) with iodine proceeded more slowly than that of **11**, and while evidence of [(*cis*-α-picchxnMe_2)Mo(NO)I]PF_6 formation was observed, in this instance bromine proved the more effective oxidant, giving [(*cis*-α-picchxnMe_2)Mo(NO)Br]PF_6 (**16**, Scheme 4, υ_{NO} = 1619 cm^{-1}, $E_{1/2}$ = −0.89 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 [(*cis*-β-Imchxn)Mo(NO)(CO)]PF_6 (**13**) and [(*cis*-β-ImchxnMe_2)Mo(NO)(CO)]PF_6 (**14**) samples likely produced [(*cis*-β-Imchxn)Mo(NO)I]PF_6 (υ_{NO} = 1607 cm^{-1}) and [(*cis*-β-ImchxnMe_2)Mo(NO)Br]PF_6 (υ_{NO} = 1616 cm^{-1}) respectively, but owing to the tendency of Imchxn (**3**) and Imchxn (**4**) to give the undesired non-C_2-symmetric *cis*-β configuration, these compounds were not thoroughly characterized or extensively pursued.

3.4. Evaluations of $\{(cis\text{-}\alpha\text{-}N_4)Mo(NO)\}^+$ fragments as potential dearomatizing π-bases

Attempts to form dihapto complexes with π-acids such as naphthalene, furan, and cyclohexene through chemical reductions of [(*cis*-α-picchxn)Mo(NO)I]PF_6 (**15**) and [(*cis*-α-picchxnMe_2)Mo(NO)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** (υ_{NO} = 1622 cm^{-1}, $E_{1/2}$ = −1.00 V) and **16** (υ_{NO} = 1619 cm^{-1}, $E_{1/2}$ = −0.89 V) suggest that the $\{(cis\text{-}\alpha\text{-picchxn})Mo(NO)\}^+$ and $\{(cis\text{-}\alpha\text{-picchxn}Me_2)Mo(NO)\}^+$ 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 ({Tp(1-methylimidazole)Mo(NO)}) has a corresponding Mo(I) υ_{NO} of 1610 cm^{-1} and $E_{1/2}$ of −1.33 V [61]. Under comparable reaction conditions, {Tp(PMe_3)Mo(NO)} (from Tp(PMe_3)Mo(NO)Br, υ_{NO} = 1617 cm^{-1} and $E_{1/2}$ = −1.19 V) failed to give evidence of dihapto complex formation.[61] Electronic parameters have served as a useful guide in the development of π-basic dearomatization 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 phosphite ligand. The possibility that other aspects of these systems are essential for dearomatization 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 π-basic molybdenum dearomatization 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 (κ^3) example, a dimethylamino-substituted variant on a 5-coordinate Fe(II) center [89]. In contrast, we find octahedral (κ^3-N_4)Mo$(CO)_3$ 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



Scheme 5. Intended dihapto complexation reactions of naphthalene. Analogous experiments using furan and cyclohexene were likewise unsuccessful.

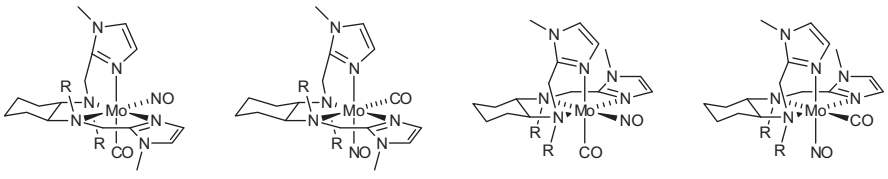


Fig. 6. Proposed configurations of observed [(*cis*-β-Imchxn)Mo(NO)(CO)]$^+$ (**13**) and [(*cis*-β-Imchxn)Mo(NO)(CO)]$^+$ (**14**) diastereomers.

identical, nitrosylation of (κ^3-N_4)Mo(CO)$_3$ complexes is expected to give a complicated mixture of diastereomers, so while strong evidence of [(κ^3-N_4)Mo(NO)(CO)$_2$]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 tetradentate (κ^4) 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*-α picchxn configuration can form, with the *trans*-diaminocyclohexyl group's chiral centers limiting the configuration of the metal center such that the *S,S* enantiomer of picchxn gives Λ helicity (as depicted in Scheme 2) and the *R,R* enantiomer gives Δ helicity [47]. This configuration is favored by picchxn on Cr(III) [8,46,47] and Cd(II) [54,55], by picchxnMe$_2$ 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), PicchxnMe$_2$ can give the *cis*-α configuration under some reaction conditions [22,23]. Ru(II) does not show a strong preference, but *cis*-α-picchxn and picchxnMe$_2$ complexes have been isolated from diastereomeric mixtures [7,49]. In the current study of Mo(0) and Mo(I) complexes, the only tetradentate configuration observed for picchxn (**1**) and picchxnMe$_2$ (**2**) is the *cis*-α with helicity as predicted by Yamamoto. When the two heterocycle groups of a picchxn-type ligand are *cis* to one another, one of two *cis*-β diastereomers is observed. In one of these, the heterocycle-2-ylmethyl groups are *anti* on the central chelate ring and the *S,S* N_4 enantiomer gives Δ helicity (Fig. 6). This *anti-cis*-β 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 picchxnMe$_2$ derivative with 6-methylpyridyl groups can adopt the *anti-cis*-β 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*-α-picchxn diastereomer [7]. In the other *cis*-β diastereomer, the heterocycle-2-ylmethyl groups are *syn* on the central chelate ring and the *S,S* N_4 enantiomer gives Λ helicity (Fig. 6). This *syn-cis*-β configuration is favored by the picchxnMe$_2$ derivative with 6-methylpyridyl groups on Fe(III) [27] and can also form on Fe(II) [23]. A Ru(II) complex with picchxnMe$_2$ in this configuration can be isolated from a mixture with the corresponding *cis*-α-picchxnMe$_2$ diastereomer [7,48,49], and in the current study it was the favored and solved configuration for [(*cis*-β-ImchxnMe$_2$)Mo(NO)(CO)]PF_6 diastereomers (**14A** and **14B**). Because the *cis*-β configuration breaks the C_2 symmetry of the N_4 ligand, toggling the positions of the CO and NO$^+$ ligands accounts for four [(*cis*-β-N_4)Mo(NO)(CO)]$^+$ diastereomers, consistent with ^{1}H NMR data for isolated [(*cis*-β-Imchxn)Mo(NO)(CO)]$^+$ (**13**) and [(*cis*-β-Imchxn)Mo(NO)(CO)]$^+$ (**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*-α 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(I) 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 [(*cis*-α-picchxn)Mo(NO)(CO)]PF_6 (**11**) measuring 2.20, 2.27, 2.27, and 2.19 Å, only slightly longer than the CrN bonds of [(*cis*-α-picchxn)$CrCl_2$]ClO_4 (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 [(*cis*-α-picchxn)CdI_2 measuring 2.40, 2.44, 2.44, and 2.40 Å [54].

4. Conclusion

Picchxn-type (N_4) ligands form (κ^3-N_4)Mo(CO)$_3$, [(κ^4-N_4)Mo(NO)(CO)]PF_6, and [(κ^4-N_4)Mo(NO)X]PF_6 (X = Br, I) compounds analogous to other Mo(0) and Mo(I) examples. The π-basicity of {(N_4)Mo(NO)}$^+$ fragments can by 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*-β configurations while picchxn and picchxnMe$_2$ form {(*cis*-α-N_4)Mo(NO)}$^+$ fragments that do not appear to be sufficiently electron-rich to serve as dearomatization agents. Ongoing studies in our lab are addressing both the corresponding tungsten examples and similar complexes bearing 2,2′-bispyrrolidine-based ligands, which may have a greater tendency to adopt the *cis*-α configuration [34,59].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2015.09.005.

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