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Topological Variations of the PDP Ligand and Its Prospects in Molybdenum(0) Dearomatization Agents

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S *Supporting Information*

ABSTRACT: The compounds *fac*-(κ^3-PDP)Mo(CO)$_3$ {**1**; PDP = 2-[[2-(1-(pyridin-2-ylmethyl)pyrrolidin-2-yl)pyrrolidin-1-yl]methyl]pyridine}, [(*cis-β*-PDP)Mo(NO)(CO)]PF$_6$ ([*cis-β*-**3**]PF$_6$), [(*cis*-α-PDP)Mo(NO)(CO)]PF$_6$ ([*cis*-α-**3**]PF$_6$), [(*cis*-α-PDP)Mo(NO)Br]PF$_6$ ([**4**]PF$_6$), [(*trans*-PDP)Cu](BF$_4$)$_2$·CH$_3$CN ([**5**](BF$_4$)$_2$·CH$_3$CN), and [(*trans*-PDP)Cu](OSO$_2$CF$_3$)$_2$ ([**5**](OSO$_2$CF$_3$)$_2$) have been synthesized and structurally characterized by single-crystal X-ray diffraction. These are the first reported complexes of PDP on metal centers other than iron(II). The observed configurations indicate a broader range of accessible PDP topologies than has been reported. The {(*cis*-α-PDP)Mo(NO)}$^+$ fragment is found to be less π-basic than the dearomatizing {Tp(MeIm)Mo(NO)} fragment [Tp = hydridotris(1-pyrazolyl)borato; MeIm = 1-methylimidazole].

Chiral C_2-symmetric ligands have the potential to create well-defined chiral environments about metal centers and as such have long held a special place in catalysis.[1,2] Following from investigations directed at nonheme dioxygenase models, many studies have addressed the use of chiral C_2-symmetric *trans*-1,2-diaminocyclohexane-based N$_2$/Py$_2$ tetradentate ligands such as *N,N*′-bis(pyridin-2-ylmethyl)-*trans*-1,2-diaminocyclohexane (hcp; Figure 1),[3] *N,N*′-bis(pyridin-2-ylmethyl)-*N,N*′-dimethyl-*trans*-1,2-diaminocyclohexane (bpmcn),[4−10] and *N,N*′-bis-(6-methylpyridin-2-ylmethyl)-*N,N*′-dimethyl-*trans*-1,2-diaminocyclohexane (6-Me$_2$-bpmcn)[4,5,9] in iron(II) oxidation catalysts. These N$_2$/Py$_2$ examples are flexible, with bpmcn giving cis-α,[4,5,8,11] cis-β,[5,8,12] and trans[8] topologies on iron(II) and 6-Me$_2$-bpmcn giving two cis-β geometries differing in the relative configurations of the bound amine nitrogen atoms.[4,13,14] On other metal centers, additional geometrical variability is observed. For example, on copper(I) and copper(II), 6-Me$_2$-bpmcn adopts a highly distorted tetrahedral geometry,[15] while hcp on copper(II) gives a distorted-tetrahedral geometry, the bond angles of which can also be described as distorted trans.[16] Recently, iron(II) catalysts involving 2-[[2-(1-(pyridin-2-ylmethyl)pyrrolidin-2-yl)pyrrolidin-1-yl]methyl]pyridine (PDP)[7,10,17−19] and 2-[[2-[1-(6-methylpyridin-2-ylmethyl)pyrrolidin-2-yl]pyrrolidin-1-yl]methyl]-6-methylpyridine (6-Me$_2$-PDP)[9] were observed to give remarkable selectivity in a series of oxidations, with the former showing activity in the C−H activation of alkanes. Published examples of PDP complexes have been limited to the iron(II) metal center, and in each, the ligand adopts exclusively the cis-α topology.[7,9,18] This arrangement has been described as resulting from limitations imposed by the bis(pyrrolidinyl) group.[9]

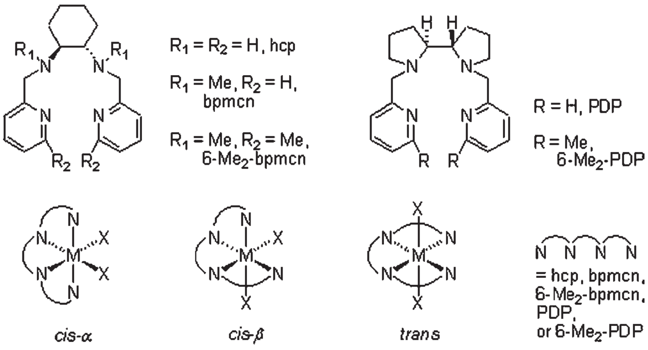

Figure 1. Chiral C$_2$-symmetric N$_2$/Py$_2$ ligands and potential tetradentate topologies in an octahedral coordination sphere.

Our interest in N$_2$/Py$_2$ ligands stems from ongoing studies of low-valent group 6 complexes with potential applications in dearomatization. Given the success of {Tp(L)M(NO)} (L = MeIm and M = Mo or L = PMe$_3$ and M = W) fragments in effecting the otherwise inaccessible transformation of aromatics,[20−25] we have been exploring electronically similar systems in which the Tp(L) portion has been replaced with other N-heterocycle and amine groups.[26−28] While studying various {(N$_2$/Py$_2$)M(NO)} systems, we observed a surprising range of topologies for PDP.

Heating PDP with Mo(CO)$_6$ gives *fac*-(κ^3-PDP)Mo(CO)$_3$ (**1**; Scheme 1). Upon exposure to sodium nitrite and hydrochloric acid, **1** gives a product in which the N$_2$/Py$_2$ ligand is complexed in a tetradentate fashion to the {Mo(NO)(CO)}$^+$ fragment. When this reaction is run at ambient temperature, the isolated complex shows exclusively the cis-β topology (*cis-β*-**3**). This selectivity is clearly kinetic in nature because moderate heating gives complete conversion to the cis-α topology (*cis*-α-**3**). This shape is retained upon oxidation with bromine, which gives [(*cis*-α-PDP)Mo(NO)Br]PF$_6$ ([**4**]PF$_6$). The structures of **1**, [*cis-β*-**3**]PF$_6$, [*cis*-α-**3**]PF$_6$, and [**4**]PF$_6$ have been confirmed by single-crystal X-ray diffraction (Figure 2).[29] The unit cell of [*cis*-α-**3**]PF$_6$ includes two independent [(*cis*-α-PDP)Mo(NO)(CO)]$^+$ groups. Whereas the CO and NO$^+$ positions in *cis*-α-**3** are disordered, *cis-β*-**3** is observed as a single isomer in which the linear nitrosyl group is exclusively trans to one of the

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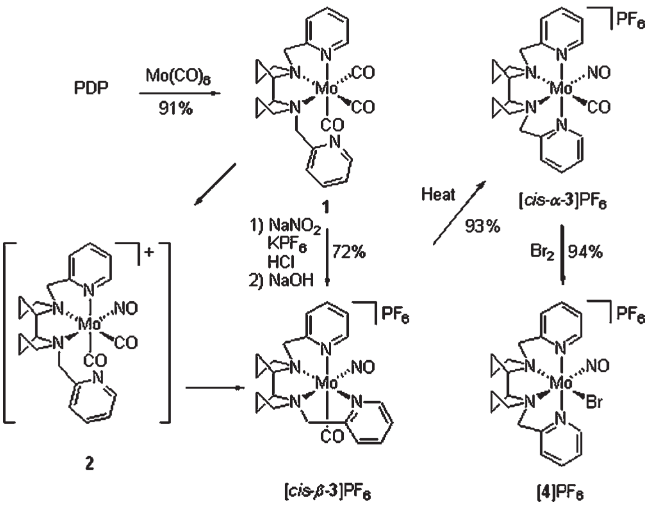
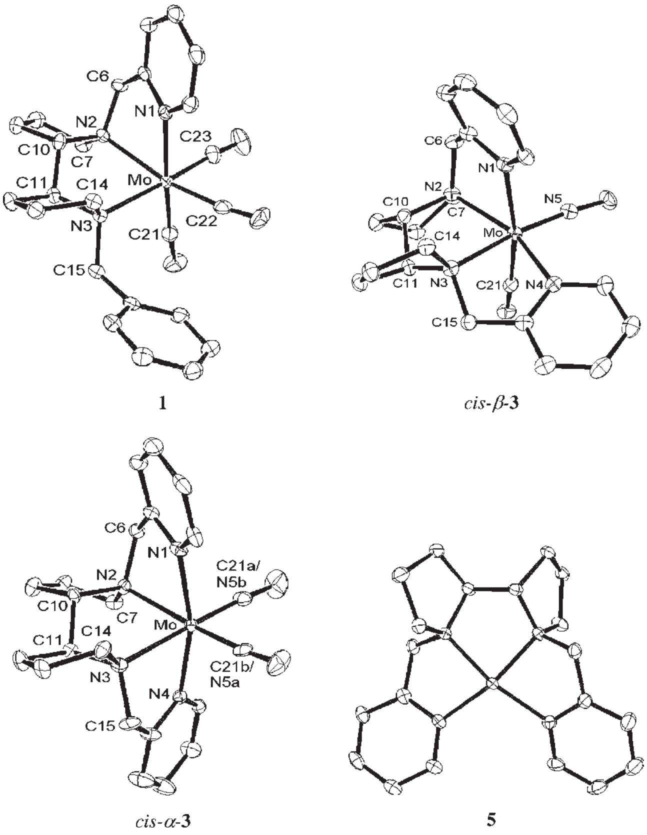
Scheme 1. Synthesis of 1, [*cis*-β-3]PF_6, [*cis*-α-3]PF_6, and [4]PF_6



aliphatic nitrogen atoms. The ^{1}H NMR spectra of *cis*-β-**3** and *cis*-α-**3** are markedly different, with that of *cis*-α-**3** showing pairs of peaks reflecting C_2 symmetry of the {(*cis*-α-PDP)Mo} fragment. The spectrum of *cis*-β-**3** shows no such pattern. Taken together, these spectra suggest that the solution-state structures of *cis*-β-**3** and *cis*-α-**3** likely correspond to the observed solid-state structures. The 17-electron complex **4** is NMR-silent. It shows an NO$^+$ stretch at 1616 cm^{-1}, an $E_{p,a}$ at 1.01 V (vs NHE), an $E_{1/2}$ at −0.96 V, and disordered NO$^+$ and Br positions in the crystalline state.



1

cis-β-3

cis-α-3

5

Figure 2. ORTEP diagrams (50% probability ellipsoids) of **1**, *cis*-β-**3**, *cis*-α-**3**, and **5**.

In spite of the free pyridyl nitrogen atom on the pendant PDP arm of **1**, solvated samples show no propensity to undergo substitution for a fourth CO group to give a κ^4-dicarbonyl complex either with further heating or upon exposure to acid alone. The synthesis of *cis*-β-**3** almost certainly proceeds through a κ^3-dicarbonyl mononitrosyl intermediate (**2**; Scheme 1), the formation of which is substantially associative and therefore precludes rearrangement of a five-coordinate intermediate. The Mo−C21, Mo−C22, and Mo−C23 bond lengths of **1** (1.942 (3), 1.925(3), and 1.944(3) Å, respectively) suggest that the Mo−C23 bond is not substantially weaker than the Mo−C21 or Mo−C22 bonds, so the observed selectivity for the NO$^+$ placement in *cis*-β-**3** more likely follows from a steric influence of the unbound PDP pyridin-2-ylmethyl arm on the C21 and C22 carbonyl positions that leaves the C23 site more available for NO$^+$ substitution. The reasons for the kinetic favorability of *cis*-β-**3** over *cis*-α-**3** are less clear. Angles about the aliphatic amines of **1** range from 102.44° (C11−N3−C14) to 120.06° (Mo−N2−C7). If these angles remain fairly constant in the generation of **2**, then the formation of *cis*-β-**3** imposes additional angle strain about N3 (Mo−N3−C14 angle = 124.2°), while leaving the N2 angles largely unchanged. Conversion to *cis*-α-**3** relieves much of this strain (Mo−N3−C14 = 118.5° and 116.7°) with minimal additional perturbation of the angles about N2.

Having observed the initially unexpected cis-β geometry for PDP, we wondered whether the restrictions imposed by the bis(pyrrolidinyl) group would prohibit its complexation in a trans topology. The reaction of PDP with $Cu(BF_4)_2\cdot 6H_2O$, $Cu(OSO_2CF_3)_2$, and $CuBr_2$ yields the corresponding $[(PDP)Cu]^{2+}$ ([**5**]) salts (70, 81, and 30%). Slow crystal growth from an acetonitrile/ether solution of [**5**]$(BF_4)_2\cdot{}^1/_2C_2H_5OH$ yields [**5**]$(BF_4)_2\cdot CH_3CN$, the solved structure of which indeed shows the ligand in a configuration similar to that observed for $[(hcp)Cu]^{2+}$ (Figure 2).[16] The copper(II) center of **5** is in a square-planar coordination sphere with a tetrahedral twist of 8.6°, while the four independent $[(hcp)Cu]^{2+}$ groups in the unit cell of $[(hcp)Cu]CuCl_4$ show twists of 6.9, 13.0, 13.5, and 12.6°.[16,30] A disordered X-ray structure of [**5**]$(OSO_2CF_3)_2$ suggests a distorted trans ligand topology and long bonds to the trifluoromethanesulfonate anions in the remaining octahedral coordination sites.

The observed range of ligand topologies in **1** and **3**−**5** has implications for the potential applications of PDP. The cis-α topology is desirable because it reduces the potential number of complex stereoisomers by retaining the C_2 symmetry of the chiral ligand. The mechanisms and outcomes of oxidations catalyzed by nonheme iron(II) systems have been shown to vary dramatically with the topologies of the N_2/Py_2 ligands,[5,6,8] and the major reason for the use of PDP in such reactions is its perceived rigidity.[7,9] Evidence of topological isomerization has been reported for other N_2Py_2 ligands on iron(II),[8] and while the metal centers of *cis*-β-**3** and **5** are obviously very different from iron(II), data from these complexes clearly demonstrate that the inherent structure of PDP does not limit it to the cis-α configuration.

Studies of the reaction chemistry of [**4**]PF_6 are ongoing, but initial attempts to bind aromatics have been unsuccessful. Samples exposed to amalgamated zinc and furan or naphthalene develop an anodic pulse at 0.20 V, indicating reduction of the metal, but numerous NO$^+$ stretches are observed in the IR spectrum, and ^{1}H NMR spectra show no evidence of aromatic incorporation. Available data suggest that the $\{(cis\text{-}\alpha\text{-PDP})Mo(NO)\}^+$ fragment is probably not sufficiently electron-rich for the desired activation of aromatics. Examples of metal fragments that form stable dihapto complexes with aromatics are quite limited,[22,31,32] and thus the necessary criteria for such fragments are not well understood. One method that has been used with some success has been to match NO^+ stretching frequencies and electrochemical potentials of potential surrogates to those of established systems.[20−22,26,32−34] Upon one-electron reduction, the complex Tp(MeIm)Mo(NO)Br (ν_{NO^+} = 1610 cm^{-1} and $E_{1/2}$ = −1.33 V) yields {Tp(MeIm)Mo(NO)}, which forms stable dihapto complexes with a range of polycyclic arenes and aromatic heterocycles.[20,35] In contrast, [(Tpm)(MeIm)Mo(NO)Br]$^+$ [Tpm = tris(1-pyrazolyl)methane; ν_{NO^+} = 1629 cm^{-1} and $E_{1/2}$ = −0.94 V],[26] the reduction of which would be expected to yield the isosteric {Tpm(MeIm)Mo(NO)}$^+$ fragment, fails to give stable complexes with aromatics. $E_{1/2}$ of [**4**]PF_6 (−0.96 V) suggests electronic properties similar to those of [(Tpm)(MeIm)Mo(NO)Br]$^+$, and its NO^+ stretch (1616 cm^{-1}) is similar to that of Tp(PMe_3)Mo(NO)Br (1617 cm^{-1}),[26] which likewise proved unsuitable for dearomatization reactions. A more direct assessment of the π basicity of the {(*cis*-α-PDP)Mo(NO)}$^+$ fragment can be made by looking at the stretching frequency of a bound carbonyl. Comparing the CO stretch of [*cis*-α-**3**]PF_6 (1888 cm^{-1}) to that of Tp(MeIm)Mo(NO)(CO) (1865 cm^{-1})[35] indicates that {(*cis*-α-PDP)Mo(NO)}$^+$ is markedly less π-basic than {Tp(MeIm)Mo(NO)}.

The current range of PDP applications is quite limited, but given the remarkable outcomes of those that have been reported, it is likely that complexes of PDP and its derivatives will receive extensive study. The current work illustrates that while PDP may be less flexible than other N_2Py_2 variations, it is not restricted to the cis-α topology. Because the {(*cis*-α-PDP)Mo(NO)}$^+$ fragment seems insufficiently π-basic for use in dearomatization sequences, further studies in our laboratory will likely involve more electron-donating variations of the PDP ligand and investigations of tungsten analogues.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Full experimental details and CIF files for **1**, [*cis*-β-**3**]PF_6, [*cis*-α-**3**]PF_6, [**4**]PF_6, [**5**]$(BF_4)_2$·CH_3CN, and [**5**]$(OSO_2CF_3)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581–1590.

(2) Pfaltz, A.; Drury, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5723–5726.

(3) Lyakin, O. Y.; Bryliakov, K. P.; Britovsek, G. J. P.; Talsi, E. P. *Inorg. Chem.* **2009**, *131*, 10798–10799.

(4) Costas, M.; Tipton, A. K.; Chen, K.; Jo, D.; Que, L., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 6722–6723.

(5) Costas, M.; Que, L., Jr. *Angew. Chem., Int. Ed.* **2002**, *41*, 2179–2181.

(6) Mas-Balleste, R.; Costas, M.; van den Berg, T.; Que, L. *Chem.—Eur. J.* **2006**, *12*, 7489–7500.

(7) Chen, M. S.; White, M. C. *Science* **2007**, *318*, 783–787.

(8) England, J.; Davies, C. R.; Banaru, M.; White, A. J. P.; Britovsek, G. J. P. *Adv. Synth. Catal.* **2008**, *350*, 883–897.

(9) Suzuki, K.; Oldenburg, P. D.; Que, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 1887–1889.

(10) Gomez, L.; Garcia-Bosch, I.; Company, A.; Benet-Buchholz, J.; Polo, A.; Sala, X.; Ribas, X.; Costas, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5720–5723.

(11) Stubna, A.; Jo, D.-H.; Costas, M.; Brenessel, W. W.; Andres, H.; Bominaar, E. L.; Munck, E.; Que, L., Jr. *Inorg. Chem.* **2004**, *43*, 3067–3079.

(12) Costas, M.; Rohde, J.-U.; Stubna, A.; Ho, R. Y. N.; Quaroni, L.; Munck, E.; Que, L. J. *J. Am. Chem. Soc.* **2001**, *123*, 12931–12932.

(13) Reynolds, M. F.; Costas, M.; Ito, M.; Jo, D.-H.; Tipton, A. A.; Whiting, A. K.; Que, L. *J. Biol. Inorg. Chem.* **2003**, *8*, 263–272.

(14) Jo, D.-H.; Chiou, Y.-M.; Que, L. J. *Inorg. Chem.* **2001**, *40*, 3181–3190.

(15) Company, A.; Guell, M.; Popa, D.; Benet-Buchholz, J.; Parella, T.; Fontrodona, X.; Llobet, A.; Sola, M.; Ribas, X.; Luis, J. M.; Costas, M. *Inorg. Chem.* **2006**, *45*, 9643–9645.

(16) Zhang, Y.; Xiang, L.; Wang, Q.; Duan, X.-F.; Zi, G. *Inorg. Chim. Acta* **2008**, *361*, 1246–1254.

(17) Christmann, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2740–2742.

(18) Vermeulen, N. A.; Chen, M. S.; White, M. C. *Tetrahedron* **2009**, *65*, 3078–3084.

(19) Chen, M. S.; White, M. C. *Science* **2010**, *327*, 566–571.

(20) Meiere, S. H.; Keane, J. M.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2003**, *125*, 2024–2025.

(21) Graham, P.; Meiere, S. H.; Sabat, M.; Harman, W. D. *Organometallics* **2003**, *22*, 4364–4366.

(22) Keane, J. M.; Harman, W. D. *Organometallics* **2005**, *24*, 1786–1798.

(23) Graham, P. M.; Delafuente, D. A.; Liu, W.; Myers, W. H.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2005**, *127*, 10568–10572.

(24) Kosturko, G. W.; Harrison, D. P.; Sabat, M.; Myers, W. H.; Harman, W. D. *Organometallics* **2009**, *28*, 387–389.

(25) Harrison, D. P.; Sabat, M.; Myers, W. H.; Harman, W. D. *J. Am. Chem. Soc.* **2010**, *132*, 17282–17295.

(26) Ha, Y.; Dilsky, S.; Graham, P. M.; Liu, W.; Reichart, T. M.; Sabat, M.; Keane, J. M.; Harman, W. D. *Organometallics* **2006**, *25*, 5184–5187.

(27) Dilsky, S.; Palomaki, P. K. B.; Rubin, J. A.; Saunders, J. E.; Pike, R. D.; Sabat, M.; Keane, J. M.; Ha, Y. *Inorg. Chim. Acta* **2007**, 2387–2396.

(28) Saunders, J. E.; Ley, A. N.; Palomaki, P. K. B. *J. Undergrad. Res. Chem.* **2009**, *8*, 98–101.

(29) Full details of all reported crystallographic studies are available in the Supporting Information. Nonracemic PDP samples were used in this study, and in all cases, observed absolute configurations reflect those of the specific PDP sample used. ORTEP diagrams in Figure 2 have been inverted to give consistent orientations and configurations across the schemes and figures.

(30) Calculated from the reported CIF data.

(31) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953–1978.

(32) Brooks, B. C.; Gunnoe, T. B.; Harman, W. D. *Coord. Chem. Rev.* **2000**, 3–61.

(33) Brooks, B. C.; Chin, R. M.; Harman, W. D. *Organometallics* **1998**, *17*, 4716–4723.

(34) Surendranath, Y.; Harman, W. D. *J. Chem. Soc., Dalton Trans.* **2006**, 3957–3965.

(35) Mocella, C. J.; Delafuente, D. A.; Keane, J. M.; Warner, G. R.; Friedman, L. A.; Sabat, M.; Harman, W. D. *Organometallics* **2004**, *23*, 3772–3779.