Imidomolybdenum(IV) Porphyrin Complexes: Synthesis, Characterization, and Intermetal Imido Transfer Reactivity

Lisa Mary Berreau
Iowa State University

Jinyuan Chen
Utah State University

L. Keith Woo
Iowa State University, kwoo@iastate.edu

Follow this and additional works at: http://lib.dr.iastate.edu/chem_pubs
Part of the Chemistry Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/chem_pubs/781. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Imidomolybdenum(IV) Porphyrin Complexes: Synthesis, Characterization, and Intermetal Imido Transfer Reactivity

Abstract
The imido(meso-tetra-p-tolylporphyrinato)molybdenum(IV) complexes, (TTP)MoNR, where R = C6H5 (1a), p-CH3C6H4 (1b), 2,4,6-(CH3)3C6H2 (1c), and 2,6-((i-Pr)2C6H4 (1d), can be prepared by the reaction of (TTP)MoCl2 with 2 equiv of LiNHR in toluene. Upon treatment of the imido complexes with pyridine derivatives, NC5H4-p-X (X = CH3, CH(CH3)2, C⋮N), new six-coordinate complexes, (TTP)MoNR-NC5H4-p-X, were observed. The reaction between the molybdenum imido complexes, (TTP)MoNC6H5 or (TTP)MoNC6H4CH3, and (TTP)Ti(η2-PhC⋮CPh) resulted in complete imido group transfer and two-electron redox of the metal centers to give (TTP)Mo(η2-PhC⋮CPh) and (TTP)TiNC6H5 or (TTP)TiNC6H4CH3.

Disciplines
Chemistry

Comments
Reprinted (adapted) with permission from Inorganic Chemistry 44 (2005): 7304, doi:10.1021/ic051100e. Copyright 2005 American Chemical Society.

This article is available at Iowa State University Digital Repository: http://lib.dr.iastate.edu/chem_pubs/781
The imido(meso-tetra-p-tolylporphinato)molybdenum(IV) complexes, (TTP)Mo=NR, where R = C₂H₅ (1a), p-CH₃C₆H₄ (1b), 2,4,6-(CH₃)₃C₆H₂ (1c), and 2,6-(t-Pr)₂C₆H₄ (1d), can be prepared by the reaction of (TTP)MoCl₂ with 2 equiv of LiNHR in toluene. Upon treatment of the imido complexes with pyridine derivatives, NC₆H₄-p-X (X = CH₂, CH(CH₃)₂), nN, new six-coordinate complexes, (TTP)Mo=NR-NC₆H₄-p-X, were observed. The reaction between the molybdenum imido complexes, (TTP)Mo=NC₆H₅ or (TTP)Mo=NC₆H₃CH₃, and (TTP)Ti(η²-PhC≡CPh) resulted in complete imido group transfer and two-electron redox of the metal centers to give (TTP)Mo(η²-PhC≡CPh) and (TTP)Ti=NC₆H₅ or (TTP)Ti=NC₆H₃CH₃.

The transfer of an oxygen atom from transition-metal–oxo complexes to organic or nonmetal substrates is a well-documented process.¹ The related reaction of intermetal oxygen atom transfer continues to be an area of intense research and has been extensively reviewed.² However, fewer examples involving the isoelectronic imido group transfer have been reported.³–⁸ Furthermore, imido group transfer processes reported to date have largely involved transfer to nonmetal substrates, e.g., phosphines, alkanes, and alkynes. Examples of intermetal pairwise exchange reactions involving oxo, imido, and alkylidene ligands were reported by Gibson et al. In these latter reactions, no net redox change occurs.⁹

Metalloporphyrin complexes have been extremely useful in investigating a variety of inner-sphere redox processes involving intermetal halogen,¹⁰ oxygen,¹¹ nitrogen,¹² sulfur,¹³ and selenium atom transfer reactions.¹⁴ However, extension of this system to intermetal imido transfer has not materialized, even though metalloporphyrin complexes containing organoimido ligands are becoming more common.¹⁴–¹⁸ Surprisingly, the only imidomolybdenum porphyrin examples are Mo(V) complexes, and only one has been structurally characterized.⁸,¹⁹ We previously reported that treatment of (TTP)MCl₂ (M = Ti, Zr, Hf; TTP = meso-tetra-p-tolylporphinato) with various lithium amides results in the formation of (IV) organoimido complexes.²⁰,²¹ By extension of this synthetic method to molybdenum chemistry, we have been able to prepare new organoimidomolybdenum(IV) complexes.²²

(17) Elliott, R. L.; Nichols, P. J.; West, B. O. Polyhedron 1987, 12, 2191.

To whom correspondence should be addressed. E-mail: kwoo@iastate.edu.

† Utah State University.
‡ Iowa State University.


Received July 1, 2005
porphyrin complexes. These compounds undergo a two-electron intermetal redox process mediated by imido group transfer. Specifically, treatment of (TTP)Mo==NR (R = C6H5, C6H4-p-CH3) with a low-valent titanium porphyrin complex, (TTP)Ti(n°-PhC≡CPh), resulted in complete intermetal imido group transfer, a formal two-electron redox process.

We previously showed that (TTP)MoCl3 is a useful precursor for the preparation of a number of new molybdenum porphyrin complexes.22 This practical starting material can be readily converted into new metallolporphyrin imido complexes. As illustrated in eq 1, anerobic treatment of (TTP)MoCl3 with LiNHR resulted in the formation of molybdenum(IV) organoimido complexes. Relatively pure (TTP)Mo==N—Ph (1a) could be obtained by recrystallization from a minimal amount of toluene/hexane (ca. 1:3) on cooling to −20 °C for 1 h. This orange-red solid was isolated in approximately 60% yield after filtration, washing with hexanes, and drying in vacuo.24 A similar method was used to prepare tolyl,25 mesityl,26 and 2,6-disopropylphenyl27 analogues. In all cases, analytically pure samples were difficult to obtain because of the inclusion of varying amounts of amine adduct produced as a side product, 1 (H2NR). Only in the case of the mesitylimidyl complex, 1c, was an analytically pure material obtained after several recrystallizations.26

The new porphyrin complexes were characterized by 1H NMR, UV−vis, mass, and IR spectroscopy. Although the IR spectrum of 1 contains a band at 753 cm−1 that may correspond to a Mo==N stretch,19 coupling with a N−C stretching mode and/or other vibrations of the organoimido group complicates the assignment.28 Molybdenum(IV) porphyrins have been shown to exhibit both paramagnetic ([TTP]MoCl2)29 and diamagnetic ([TTP]Mo==O) properties.29

The 1H NMR spectra of the imido complexes exhibit sharp resonances that are diagnostic of diamagnetic porphyrin compounds. For example, the 1H NMR spectrum of the five-coordinate imido complex (TTP)Mo==NC6H5 exhibits a singlet for the β-pyrrole hydrogens at 8.73 ppm, multiplets for the α- and p-tolyl protons at 7.96 (d, 8H) and 7.24 (m, 8H) ppm, and a tolyl methyl signal at 2.36 (s, 12H) ppm.

When excess amine is present, the formation of six-coordinate complexes is observed. As noted above, this was a complication during the initial imido synthesis because neutral amine was produced as a byproduct. The initially isolated imido complexes would have up to 1 equiv of the parent amine, bound as a sixth ligand. NMR studies showed that the position of the β-pyrrole proton resonance of these adducts depended upon the amount of amine present, with the signal shifting upfield with an increasing amount of coordinated amine. A range of 8.4−8.7 ppm has been observed for the β-pyrrole resonances. Signals for the coordinated p-toluidine in complex 2 are shifted upfield as well, appearing at 6.81 (d, 2H, m-H), 6.09 (d, 2H, o-H), and 2.12 (s, 3H, CH3) ppm.

The initial amine adducts were labile. Thus, treatment of the imido complexes 1a(H2NR) and 1b(H2NR), with pyridine derivatives resulted in the loss of the coordinated amine and the formation of five-coordinate adducts, (TTP)Mo==NR:L.31

(TTP)Mo==NR(H2NR) + L → (TTP)Mo==NR-L + H2NR

The 1H NMR spectrum of 2b clearly exhibited a new methyl signal at 1.63 (s, 3H) ppm corresponding to the new picoline

(28) Nugent, W. A.; Mayer, J. M. Metal−Ligand Multiple Bonds; Wiley: New York, 1988; Chapter 4, pp 123−125.


(30) Data for aniline: 1H NMR (C6D6, ppm) 8.71 (d, 2H, m-H), 6.70 (m, 2H, o-H), 6.77 (m, 1H, p-H). Data for p-toluidine: 1H NMR (C6D6, ppm) 6.99 (d, 2H, m-H), 6.33 (d, 2H, o-H), 2.26 (s, 3H, CH3).

(31) Data for (TTP)Mo==N-tolyl-4-methylpyridine: 1H NMR (C6D6, ppm) 8.32 (d, 2H, pic), 7.51 (m, 8H, −CH2CH3), 7.09 (m, 8H, −CH2CH3), 6.92 (s, 8H, β-H), 6.2−6.4 (s, 6H, −N-tolyl, pic), 2.24 (s, 12H, −CH2CH3), 1.86 (s, 6H, −NC6H4CH3), 1.63 (s, 3H, pic). Data for (TTP)Mo==Np4-4-methylpyridine: 1H NMR (C6D6, ppm) 7.94 (m, 2H, pic), 7.51 (m, 8H, −CH2CH3), 7.10 (m, 8H, −CH2CH3), 6.95 (s, 8H, β-H), 6.2−6.6 (s, 6H, −Npic, pic), 2.23 (s, 12H, −CH2CH3), 1.58 (s, 3H, pic).
fragment. Significant shifts are observed for all resonances associated with the porphyrin ligand for the picoline complexes. For example, the β-pyrole resonance has been shifted upfield and is observed as a sharp singlet at 6.92 ppm. Resonances corresponding to the tolyl groups of the porphyrin ligand are also shifted upfield, with the methyl resonance now appearing at 2.24 ppm. The signals associated with the tolyl group of the imido ligand are instead shifted downfield slightly, appearing in the region of 6.2–6.4 ppm. Similar shifts are observed for the picoline derivative of the phenylimido complex, 1a.

Other pyridine derivatives also produce new six-coordinate imido complexes. The addition of 4-isopropylpyridine to 1a-(H2NR) affords the molybdenum imido complex trans-(4-i-Prpy)(TTP)Mo=NPh (3), which is isolated in 61% yield after recrystallization from toluene/hexane (1:3).

Molybdenum porphyrin complexes bearing multiply bonded ligands are capable of transferring these terminal ligands to other species. For example, (TTP)Mo=X (X = S, Se) is reduced by PPh3 to form X=PPh3. The resulting Mo(II) intermediate was trapped with an alkyne. In contrast to this, (TTP)Mo=NPh does not transfer its imido ligand to PPh3 after 3 days at ambient temperature. This is also different from the chemistry of the lighter congener (TTP)Cr=NPh complex, which does transfer its imido ligand to PPh3 to form the phosphine imine.

In an extension of our work with intermetal inner-sphere reactions, a net two-electron redox process, mediated by imido group transfer, occurs with these metalloporphyrin complexes. As shown in eq 3, treatment of (TTP)Mo=NCS (1a) with a titanium(II) η2-acetylene complex, (TTP)Ti(η2-PhC≡CPh), resulted in complete intermetal imido group transfer, yielding a known titanium porphyrin organoimido complex, (TTP)Mo=NPh + (TTP)Ti(PhC≡CPh) → (TTP)Mo(PhC≡CPh) + (TTP)Ti=NPh. (3)

Acknowledgment. Financial support for this work was provided in part by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

Supporting Information Available: Experimental procedures for base-free complexes 1a–d. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051100E


