

9-2005

# 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](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](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>.

---

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact [digirep@iastate.edu](mailto:digirep@iastate.edu).

---

# 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 = C<sub>6</sub>H<sub>5</sub> (**1a**), *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> (**1b**), 2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**1c**), and 2,6-(*i*-Pr)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**1d**), can be prepared by the reaction of (TTP)MoCl<sub>2</sub> with 2 equiv of LiNHR in toluene. Upon treatment of the imido complexes with pyridine derivatives, NC<sub>5</sub>H<sub>4</sub>-*p*-X (X = CH<sub>3</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, C:N), new six-coordinate complexes, (TTP)MoNR·NC<sub>5</sub>H<sub>4</sub>-*p*-X, were observed. The reaction between the molybdenum imido complexes, (TTP)MoNC<sub>6</sub>H<sub>5</sub> or (TTP)MoNC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, and (TTP)Ti(η<sup>2</sup>-PhC:CPh) resulted in complete imido group transfer and two-electron redox of the metal centers to give (TTP)Mo(η<sup>2</sup>-PhC:CPh) and (TTP)TiNC<sub>6</sub>H<sub>5</sub> or (TTP)TiNC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>.

## Disciplines

Chemistry

## Comments

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

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

Lisa M. Berreau,<sup>†</sup> Jinyuan Chen,<sup>‡</sup> and L. Keith Woo\*<sup>‡</sup>

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111, and Department of Chemistry, Utah State University, Logan, Utah 84322-0300

Received July 1, 2005

The imido(*meso*-tetra-*p*-tolylporphyrinato)molybdenum(IV) complexes, (TTP)Mo=NR, where R = C<sub>6</sub>H<sub>5</sub> (**1a**), *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> (**1b**), 2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**1c**), and 2,6-(*i*-Pr)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**1d**), can be prepared by the reaction of (TTP)MoCl<sub>2</sub> with 2 equiv of LiNHR in toluene. Upon treatment of the imido complexes with pyridine derivatives, NC<sub>5</sub>H<sub>4</sub>-*p*-X (X = CH<sub>3</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, C≡N), new six-coordinate complexes, (TTP)Mo=NR·NC<sub>5</sub>H<sub>4</sub>-*p*-X, were observed. The reaction between the molybdenum imido complexes, (TTP)Mo=NC<sub>6</sub>H<sub>5</sub> or (TTP)Mo=NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, and (TTP)Ti(η<sup>2</sup>-PhC≡CPh) resulted in complete imido group transfer and two-electron redox of the metal centers to give (TTP)Mo(η<sup>2</sup>-PhC≡CPh) and (TTP)Ti=NC<sub>6</sub>H<sub>5</sub> or (TTP)Ti=NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>.

The transfer of an oxygen atom from transition-metal-oxo complexes to organic or nonmetal substrates is a well-documented process.<sup>1</sup> The related reaction of intermetal oxygen atom transfer continues to be an area of intense research and has been extensively reviewed.<sup>2</sup> However, fewer examples involving the isoelectronic imido group transfer have been reported.<sup>3–8</sup> Furthermore, imido group transfer processes reported to date have largely involved transfer to nonmetal substrates, e.g., phosphines, alkanes, and alkenes. 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.<sup>9</sup>

Metalloporphyrin complexes have been extremely useful in investigating a variety of inner-sphere redox processes involving intermetal halogen,<sup>10</sup> oxygen,<sup>11</sup> nitrogen,<sup>12</sup> sulfur,<sup>13</sup> and selenium atom transfer reactions.<sup>13</sup> However, extension of this system to intermetal imido transfer has not materialized, even though metalloporphyrin complexes containing organoimido ligands are becoming more common.<sup>14–18</sup> Surprisingly, the only imidomolybdenum porphyrin examples are Mo(V) complexes, and only one has been structurally characterized.<sup>8,19</sup> We previously reported that treatment of (TTP)MCl<sub>2</sub> (M = Ti, Zr, Hf; TTP = *meso*-tetra-*p*-tolylporphyrinato) with various lithium amides results in the formation of M(IV) organoimido complexes.<sup>20,21</sup> By extension of this synthetic method to molybdenum chemistry, we have been able to prepare new organoimidomolybdenum(IV)

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

<sup>†</sup> Utah State University.

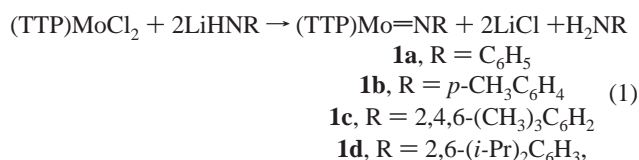
<sup>‡</sup> Iowa State University.

- (1) (a) Ostovic, D.; Bruice, R. *Acc. Chem. Res.* **1992**, *25*, 314. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (c) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571. (d) Jorgensen, K. A. *Chem. Rev.* **1989**, *89*, 431.
- (2) Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125.
- (3) Holm, R. H.; Harlan, E. W. *J. Am. Chem. Soc.* **1990**, *112*, 186.
- (4) Dobbs, D. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 3836.
- (5) Rovis, T.; Evans, D. A. *Prog. Inorg. Chem.* **2001**, *50*, 1.
- (6) Mahy, J.-P.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1986**, *108*, 1079.
- (7) Perez, P. J.; White, P. S.; Brookhart, M.; Templeton, J. L. *Inorg. Chem.* **1994**, *33*, 6050.
- (8) Eikey, R. A.; Abu-Omar, M. M. *Coord. Chem. Rev.* **2003**, *243*, 83.

- (9) Jolly, M.; Mitchell, J. P.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 1331.
- (10) (a) Chapman, R. D.; Fleischer, E. B. *J. Am. Chem. Soc.* **1982**, *104*, 1582. (b) Cohen, I. A.; Jung, C.; Governo, T. *J. Am. Chem. Soc.* **1972**, *94*, 3003. (c) Reed, C. A.; Kouba, J. K.; Grimes, C. J.; Cheung, S. K. *Inorg. Chem.* **1978**, *17*, 2666.
- (11) (a) Woo, L. K.; Goll, J. G.; Berreau, L. M.; Weaving, R. *J. Am. Chem. Soc.* **1992**, *114*, 7411. (b) Woo, L. K.; Hays, J. A.; Goll, J. G. *Inorg. Chem.* **1990**, *29*, 3916.
- (12) (a) Woo, L. K.; Goll, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3755. (b) Woo, L. K.; Czaplá, D. J.; Goll, J. *Inorg. Chem.* **1990**, *29*, 3915. (c) Woo, L. K.; Goll, J. G.; Czaplá, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478. (d) Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1989**, *111*, 5955.
- (13) (a) Woo, L. K.; Hays, J. A. *Inorg. Chem.* **1993**, *32*, 2228. (b) Berreau, L. M.; Woo, L. K. *J. Am. Chem. Soc.* **1995**, *117*, 1314.
- (14) (a) Smieja, J. A.; Omberg, K. M.; Breneman, G. L. *Inorg. Chem.* **1994**, *33*, 614. (b) Smieja, J. A.; Shirzad, K.; Roy, M.; Kittilstved, K.; Twamley, B. *Inorg. Chim. Acta* **2002**, *335*, 141. (c) Au, S. M.; Fung, W. H.; Huang, J. S.; Cheung, K. K.; Che, C. M. *Inorg. Chem.* **1998**, *37*, 6564.
- (15) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073.
- (16) (a) Che, C. M.; Huang, J. S.; Li, Z. Y.; Poon, C. K. *Inorg. Chim. Acta* **1991**, *190*, 161. (b) Huang, J. S.; Che, C. M.; Poon, C. K. *J. Chem. Soc., Chem. Commun.* **1992**, 161.
- (17) Elliot, R. L.; Nichols, P. J.; West, B. O. *Polyhedron* **1987**, *12*, 2191.
- (18) Buchler, J. W.; Pfeifer, S. Z. *Naturforsch. B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 1362.
- (19) (a) Kim, J. C.; Rees, W. S.; Goedken, V. L. *Inorg. Chem.* **1995**, *34*, 2483. (b) Kim, J. C.; Rees, W. S.; Goedken, V. L. *Inorg. Chem.* **1994**, *33*, 3191.
- (20) (a) Berreau, L. M.; Young, V. G., Jr.; Woo, L. K. *Inorg. Chem.* **1995**, *34*, 527. (b) Gray, S. D.; Thorman, J. L.; Berreau, L. M.; Woo, L. K. *Inorg. Chem.* **1997**, *36*, 278.
- (21) Thorman, J. L.; Guzei, I. A.; Young, V. G., Jr.; Woo, L. K. *Inorg. Chem.* **1999**, *38*, 3814.

porphyrin complexes. These compounds undergo a two-electron intermetal redox process mediated by imido group transfer. Specifically, treatment of (TTP)Mo=NR (R = C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>) with a low-valent titanium porphyrin complex, (TTP)Ti( $\eta^2$ -PhC≡CPh), resulted in complete intermetal imido group transfer, a formal two-electron redox process.

We previously showed that (TTP)MoCl<sub>2</sub> is a useful precursor for the preparation of a number of new molybdenum porphyrin complexes.<sup>22</sup> This practical starting material can be readily converted into new metalloporphyrin imido complexes. As illustrated in eq 1, anaerobic treatment of (TTP)MoCl<sub>2</sub><sup>23</sup> with LiNHR resulted in the formation of molybdenum(IV) organoimido complexes. Relatively pure (TTP)Mo=N-Ph (**1a**) could be obtained by recrystallization



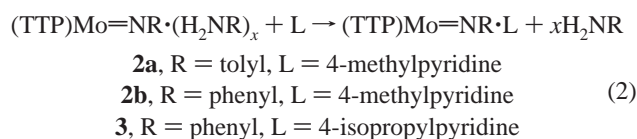
from a minimal amount of toluene/hexane (ca. 1:3) on cooling to -20 °C for 1 h. An orange-red solid was isolated in approximately 60% yield after filtration, washing with hexanes, and drying in vacuo.<sup>24</sup> A similar method was used to prepare tolyl,<sup>25</sup> mesityl,<sup>26</sup> and 2,6-diisopropylphenyl<sup>27</sup> 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**·(H<sub>2</sub>NR)<sub>x</sub>. Only in the case of the mesitylimido complex, **1c**, was an analytically pure material obtained after several recrystallizations.<sup>26</sup>

- (22) Berreau, L. M.; Young, V. G., Jr.; Woo, L. K. *Inorg. Chem.* **1995**, *34*, 3485.
- (23) Berreau, L. M.; Hays, J. A.; Young, V. G., Jr.; Woo, L. K. *Inorg. Chem.* **1994**, *33*, 105.
- (24) Analytical data for **1a**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, ppm) 8.73 (s, 8H, β-H), 7.96 (d, 8H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.24 (m, 8H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 6.0 (t, 1H, *p*-H), 5.88 (t, 2H, *m*-H), 4.77 (d, 2H, *o*-H), 2.36 (s, 12H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>); UV-vis (toluene) 432 (Soret), 454 (sh), 552, 614 nm; MS (FAB, CH<sub>3</sub>-CN, positive ion) *m/e* 857 (857); IR (KBr, cm<sup>-1</sup>) bands associated with the porphyrin ligand, 1475, 1332, 1208, 1182, 1109, 1069, 1005, 844, 800, 724, 523; bands for Mo=NPh, 753, 686.
- (25) Analytical data for **1b**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, ppm) 8.39 (s, 8H, β-H), 7.88 (d, 8H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.27 (m, 8H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 5.81 (d, 2H, =NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 5.01 (d, 2H, =NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 2.34 (s, 12H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.37 (s, 3H, =NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>); UV-vis (toluene, nm) 302, 430 (Soret), 452 (sh), 550, 570 (sh); MS (FAB, positive ion) *m/e* 870 (M<sup>+</sup>, 870).
- (26) Analytical data for **1c**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, ppm) 8.65 (s, 8H, β-H), 7.95 (d, 8H, *o*-tolyl), 7.23 (m, 8H, *m*-tolyl), 5.65 (s, 2H, *m*-mesityl), 2.36 (s, 12H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.42 (s, 3H, *p*-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 0.03- (s, 6H, *o*-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>); UV-vis (toluene) 430 (Soret), 551, 629 nm; MS (EI, positive ion) *m/e* 899.2 (M<sup>+</sup>, 899.3). Anal. Calcd for C<sub>57</sub>H<sub>47</sub>MoN<sub>5</sub>·0.4C<sub>7</sub>H<sub>8</sub>: C, 76.83; H, 5.41; N, 7.49. Found: C, 76.18; H, 5.48; N, 6.88. The toluene solvate (0.4 equiv) was observed in the <sup>1</sup>H NMR spectrum of the sample submitted for elemental analysis.
- (27) Analytical data for **1d**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, ppm) 8.79 (s, 8H, β-H), 8.08 (d, 4H, -C<sub>6</sub>H<sub>4</sub>Me), 7.96 (d, 4H, -C<sub>6</sub>H<sub>4</sub>Me), 7.26 (d, 4H, -C<sub>6</sub>H<sub>4</sub>Me), 7.21 (d, 4H, -C<sub>6</sub>H<sub>4</sub>Me), 6.31 (t, 1H, *p*-C<sub>6</sub>H<sub>3</sub>(*i*-Pr)<sub>2</sub>), 6.01 (d, 2H, *m*-C<sub>6</sub>H<sub>3</sub>(*i*-Pr)<sub>2</sub>), 2.37 (s, 12H, -C<sub>6</sub>H<sub>4</sub>Me), 0.01 (d, 12H, -CHMe<sub>2</sub>), -0.15 (m, 2H, -CHMe<sub>2</sub>). A total of 0.3 equiv of free (2,6-diisopropylphenyl)amine also existed in the product: <sup>1</sup>H NMR of (2,6-diisopropylphenyl)amine (C<sub>6</sub>D<sub>6</sub>) 7.05 (d, 2H, *m*-H), 6.89 (t, 1H, *p*-H), 3.12 (s, 2H, -NH), 2.62 (m, 2H, -CHMe<sub>2</sub>), 1.13 (d, 12H, -CHMe<sub>2</sub>). Purification to remove free amine failed because of the high solubility of the imido product in Et<sub>2</sub>O.

The new porphyrin complexes were characterized by <sup>1</sup>H NMR, UV-vis, mass, and IR spectroscopy. Although the IR spectrum of **1** contains a band at 753 cm<sup>-1</sup> that may correspond to a Mo=N stretch,<sup>19a</sup> coupling with a N-C stretching mode and/or other vibrations of the organoimido group complicates the assignment.<sup>28</sup> Molybdenum(IV) porphyrins have been shown to exhibit both paramagnetic ([TTP]MoCl<sub>2</sub>)<sup>29</sup> and diamagnetic ([TTP]Mo=O) properties.<sup>29</sup> The <sup>1</sup>H NMR spectra of the imido complexes exhibit sharp resonances that are diagnostic of diamagnetic porphyrin compounds. For example, the <sup>1</sup>H NMR spectrum of the five-coordinate imido complex (TTP)Mo=NC<sub>6</sub>H<sub>5</sub> exhibits a singlet for the β-pyrrole hydrogens at 8.73 ppm, multiplets for the *o*- 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. Particularly characteristic is the ring current effect on the imido phenyl protons. These hydrogens exhibit upfield shifts ranging from 0.7 to 1.9 ppm relative to the free amine: 6.00 (t, 1H, *p*-H), 5.88 (t, 2H, *m*-H), and 4.77 (d, 2H, *o*-H) ppm.<sup>30</sup>

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, CH<sub>3</sub>) ppm.<sup>30</sup>

The initial amine adducts were labile. Thus, treatment of the imido complexes **1a**·(H<sub>2</sub>NR)<sub>x</sub> and **1b**·(H<sub>2</sub>NR)<sub>x</sub> with pyridine derivatives resulted in the loss of the coordinated amine and the formation of new six-coordinate adducts, (TTP)Mo=NR·L.<sup>31</sup>



The <sup>1</sup>H 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.
- (29) Diebold, T.; Chevrier, B.; Weiss, R. *Inorg. Chem.* **1979**, *18*, 1193.
- (30) Data for aniline: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm) 7.17 (m, 2H, *m*-H), 6.70 (m, 2H, *o*-H), 6.77 (m, 1H, *p*-H). Data for *p*-toluidine: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm) 6.99 (d, 2H, *m*-H), 6.33 (d, 2H, *o*-H), 2.26 (s, 3H, CH<sub>3</sub>).
- (31) Data for (TTP)Mo=N-tolyl·4-methylpyridine: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, ppm) 8.32 (d, 2H, *pic*), 7.51 (m, 8H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.09 (m, 8H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 6.92 (s, 8H, β-H), 6.2–6.4 (m, 6H, =N-tolyl, *pic*), 2.24 (s, 12H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.86 (s, 3H, =NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.63 (s, 3H, *pic*). Data for (TTP)Mo=NPh·4-methylpyridine: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, ppm) 7.94 (m, 2H, *pic*), 7.51 (m, 8H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.10 (m, 8H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 6.95 (s, 8H, β-H), 6.2–6.6 (m, 6H, =NPh, *pic*), 2.23 (s, 12H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.58 (s, 3H, *pic*).

## COMMUNICATION

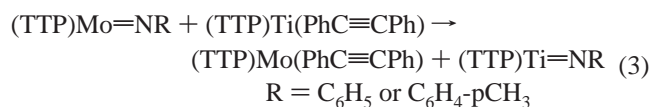
fragment. Significant shifts are observed for all resonances associated with the porphyrin ligand for the picoline complexes. For example, the  $\beta$ -pyrrole resonance has been shifted upfield and is observed as a sharp singlet at 6.92 ppm. Resonances corresponding to the tolyl groups of the porphyrin 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**·(H<sub>2</sub>NR)<sub>x</sub> 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).<sup>32</sup>

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 PPh<sub>3</sub> to form X=PPh<sub>3</sub>.<sup>22</sup> The resulting Mo(II) intermediate was trapped with an alkyne. In contrast to this, (TTP)Mo=NPh does not transfer its imido ligand to PPh<sub>3</sub> after 3 days at ambient temperature. This is also different from the chemistry of the lighter congener (TPP)Cr=NPh complex, which does transfer its imido ligand to PPh<sub>3</sub> to form the phosphine imine.<sup>33</sup>

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=NC<sub>6</sub>H<sub>5</sub> (**1a**) with a titanium(II)  $\eta^2$ -acetylene complex, (TTP)Ti( $\eta^2$ -PhC≡CPh),<sup>34</sup> resulted in complete intermetal imido group

transfer, yielding a known titanium porphyrin organoimido



complex, (TTP)Ti=NR,<sup>20</sup> and a known molybdenum(II)  $\eta^2$ -alkyne complex, (TTP)Mo( $\eta^2$ -PhC≡CPh).<sup>35</sup> Both the six-coordinated complexes **1**·(H<sub>2</sub>NR)<sub>x</sub> and the amine-free complexes, **1**, participate in the imido transfer reactions. The amine-free reactions produce cleaner NMR spectra and are reported here. In a typical, ambient-temperature reaction, an NMR tube containing a C<sub>6</sub>D<sub>6</sub> solution of (TTP)Mo=NPh was treated with a slight excess of (TTP)Ti(PhC≡CPh). The reaction was monitored over a period of 3 days. After 14 h, new  $\beta$ -pyrrole resonances corresponding to (TTP)Ti=NPh (9.21 ppm)<sup>20</sup> and (TTP)Mo(PhC≡CPh) (8.99 ppm) began to appear. Over the course of the reaction, the resonances of the starting materials diminish, while those of the products intensify, yielding a final spectrum composed of the resonances of (TTP)Mo(PhC≡CPh) and (TTP)Ti=NPh. The overall time required for the reaction to go to completion is approximately 2 weeks. The slow nature of this reaction could be due to steric problems associated with a possible  $\mu$ -imido intermediate. Further studies involving the synthesis and reactivity of early-transition-metal porphyrinatoimido complexes are underway.

**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

- (32) Mo=NPh·4-*i*-Prpy: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, ppm) 8.12 (br, 2H, *py*), 7.67 (d, 8H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.54 (s, 8H,  $\beta$ -H), 7.15 (m, 8H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 6.5 (br, 2H, *py*), 6.34 (m, 2H, =NPh), 6.09 (t, 1H, =NPh), 5.74 (m, 2H, =NPh), 2.28 (s, 12H, -C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 0.780 (m, 7H, *py*).
- (33) Boujemaa, M.; Murray, K. S.; Nichols, P. J.; Thompson, S.; West, B. O. *Polyhedron* **1994**, *13*, 485.

- (34) Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102.
- (35) De Cian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1850.