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In Pursuit of the Molybdenum(III) Tris(thiolate) Fragment: Unusual Structure of a Dimolybdenum μ-Nitrido Complex

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The new molybdenum nitrido−thiolate complex $N{\equiv}Mo(SAd)_3$ (Ad = 1-adamantyl) was prepared by a ligand exchange route involving reaction of $Ti(SAd)(O^iPr)_3$ with Chisholm's nitrido−butoxide complex $N{\equiv}Mo(O^tBu)_3$. In an effort to abstract the nitrido nitrogen from $N{\equiv}Mo(SAd)_3$, the compound was treated with $Mo(N[^tBu]Ph)_3$, a three-coordinate molybdenum(III) complex. This resulted in formation of the unusual and thermally unstable (μ-nitrido)dimolybdenum complex $(AdS)_3Mo(\mu\text{-}N)Mo(N[^tBu]Ph)_3$, which was isolated and characterized. An X-ray study revealed $(AdS)_3Mo(\mu\text{-}N)Mo(N[^tBu]Ph)_3$ to possess an unsymmetrical Mo−(μ-N)−Mo linkage, the Mo−thiolate fragment exhibiting a substantially longer bond to the bridging nitrogen atom. The structure of $(AdS)_3Mo(\mu\text{-}N)Mo(N[^tBu]Ph)_3$ is noteworthy, displaying trigonal monopyramidal coordination at the (μ-N)−Mo−thiolate Mo center. Since $N{\equiv}Mo(N[^tBu]Ph)_3$ is a good leaving group, $(AdS)_3Mo(\mu\text{-}N)Mo(N[^tBu]Ph)_3$ should be a source of the reactive $Mo(SAd)_3$ fragment. In all the studied reactions of the (μ-nitrido)dimolybdenum complex one of the observed products was $N{\equiv}Mo(N[^tBu]Ph)_3$. Two products containing the $Mo(SAd)_3$ fragment were observed: $(AdS)_3Mo{\equiv}Mo(SAd)_3$ and $[(ON)Mo(\mu\text{-}SAd)(SAd)_2]_2$. Upon treatment with pyridine, the tris(thio-1-adamantyl)(nitrosyl)molybdenum dimer forms the pyridine adduct $(AdS)_3Mo(NO)(py)$, which is a monomer.

1. Introduction

The recent discovery[1,2] of dinitrogen reductive cleavage by *N-tert*-butylanilide complexes of molybdenum(III) has prompted us to search for other ancillary ligands capable of supporting such chemistry. Thiolate ligands are attractive in this context because Mo−thiolate linkages should be generally less susceptible to protolytic rupture than Mo−amido linkages.[3] Protolytic stability is desirable for the eventual development of N_2-splitting systems that function in the presence of Brønsted acids. Thus the class of (presently unknown) molybdenum(III) tris(thiolate) complexes represents an attractive synthetic challenge, and one which furthermore evokes the MoS_3 moiety of the FeMo-co component of the nitrogenase enzymes.[4−6]

Examples of $Mo_2(SR)_6$ complexes have been uncovered in the course of the maturation of Mo≡Mo triple bond chemistry.[7] One would therefore not expect simple $Mo(SR)_3$ complexes to persist in monomeric form. Carefully designed thiolate ligands likely will be required to stabilize the monomeric form of such complexes.[8] Nevertheless, it has been shown recently that access to sterically unencumbered, three-coordinate molybdenum(III) fragments (perhaps as transients) is available through N-atom abstraction chemistry. Such reactions utilize the azophilic $Mo(N[^tBu]\text{-}Ph)_3$ (**1**) and related derivatives as N-atom abstractors. In one manifestation Chisholm's nitrido−butoxide complex $N{\equiv}Mo(O^tBu)_3$ (**2**) provided access to the molybdenum(III) tris(butoxide) fragment "$Mo(O^tBu)_3$", which underwent dimerization or gave rise to N_2 chemistry, depending on the conditions.[9] A second manifestation involved the use of $N{\equiv}Mo(NMe_2)_3$ as an N-atom donor, chemistry resulting in the characterization of N-atom bridged dimolybdenum complexes, intermediates in the N-atom transfer process.[10]

The present work was undertaken with the specific goal of gaining access to the "$Mo(SAd)_3$" (Ad = 1-adamantyl) fragment by N-atom abstraction from the corresponding nitrido derivative $N{\equiv}Mo\text{-}(SAd)_3$ (**3**). Accordingly we report on the synthesis and characterization of the new molybdenum nitrido−thiolate $N{\equiv}Mo(SAd)_3$ (**3**) and describe the reaction of **3** with azophilic $Mo(N[^tBu]Ph)_3$ (**1**). The unsymmetrical (μ-nitrido)dimolybdenum complex $(AdS)_3Mo(\mu\text{-}N)Mo(N[^tBu]Ph)_3$ (**4**) was isolated, and its chemical properties were studied. The attemps to break the nitrido−$Mo(SAd)_3$ bond lead to the formation of compounds containing the $Mo(SAd)_3$ fragment. In this context, $(AdS)_3Mo{\equiv}Mo(SAd)_3$ (**5**) and $[(ON)Mo(\mu\text{-}SAd)(SAd)_2]_2$ (**6**) were prepared.

2. Experimental Procedure

2.1. General Considerations. Unless stated otherwise, all operations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen or using Schlenk techniques under an argon atmosphere. Anhydrous diethyl ether was purchased from Mallinckrodt; pentane, *n*-hexane, and tetrahydrofuran were purchased from EM Science. Diethyl ether, toluene, benzene, pentane, and *n*-hexane were dried and deoxygenated by the method of Grubbs.[11] THF was distilled

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under nitrogen from purple sodium benzophenone ketyl. Distilled solvents were transferred under vacuum into bombs before being pumped into a Vacuum Atmospheres drybox. TMS$_2$O was degassed and dried over 4 Å sieves. Benzonitrile was degassed, dried over 4 Å sieves, and filtered through activated alumina prior to use. C_6D_6 and pyridine-d_5 were purchased from Cambridge Isotopes and were degassed and dried over 4 Å sieves. The 4 Å sieves, alumina, and Celite were dried in vacuo overnight at a temperature just above 200 °C. 1-Adamantanethiol,[12] Mo$_2$Cl$_6$(dme)$_2$[13] (**7**), N≡Mo(O^{t}Bu)$_3$[14] (**2**), and Mo(N[^{t}Bu]Ph)$_3$[2] (**1**) were synthesized according to literature procedure. Ti(Cl)(O^{i}Pr)$_3$ was purchased from Aldrich and was used without further purification. Other chemicals were used as received. Solution infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR using KBr plates. Cyclic voltammetry measurements were collected with the assistance of a Eco-Chemie Autolab potentiostat (pgstat20) and the GPES 4.3 software. ^{1}H and ^{13}C NMR spectra were recorded on Varian XL-300 or Varian Unity-300 spectrometers at room temperature. Chemical shifts are reported with respect to internal solvent: 7.15 ppm and 128.38 (t) ppm (C_6D_6); 8.74, 7.58, 7.22 ppm, and 150.35 (t), 135.91 (t), 123.87 (p) ppm (pyridine-d_5). CHN analyses were performed by Microlytics, South Deerfield, MA, Canadian Microanalytical Service Ltd, Deeta, Canada, and H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

2.2. In-Situ Generation of Ti(SAd)(O^{i}Pr)$_3$ (8). 1-Adamantanethiol (21.80 g, 0.130 mol, 1 equiv) was dissolved in pentane (100 mL) in a 500 mL round-bottom flask. The solution was cooled to near freezing in an externally-cooled cold well inside a drybox. The mixture was stirred magnetically, and *n*-butyllithium (81 mL of a 1.6 M solution in hexanes, 0.130 mol, 1 equiv) was added via syringe. During the addition the mixture became cloudy. The mixture was allowed to warm to 25 °C, at which point the volatile components were removed in vacuo. The residue was slurried with diethyl ether (200 mL), and the slurry was cooled to near freezing in the cold well. The cold slurry was stirred magnetically and treated with Ti(Cl)(O^{i}Pr)$_3$ (33.76 g, 0.130 mol, 1 equiv) as a diethyl ether solution (1:1 by volume). Upon addition of the titanium reagent the mixture acquired a green color. After the mixture was stirred 1 h while being warmed to 25 °C, volatile components were removed in vacuo. The resulting viscous oil was extracted with pentane, and the extract was filtered through a bed of Celite on a fritted glass funnel. Removal of solvent from the filtrate gave **8** as a viscous oil. Crude **8** obtained in this manner was ≥90% pure as assayed by ^{1}H NMR spectroscopy. A similar procedure carried out on a 4.63 g scale of 1-adamantanethiol afforded 9.60 g of **8** (89% yield). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.24$ (d, 9H, CH*Me*$_2$), 1.59, 1.70 (br app doublets, 6H, Ad proximal *CH*$_2$), 1.99 (br app s, 3H, Ad C*H),* 2.39 (br app s, 6H, Ad distal C*H*$_2$), 4.54 (sept, 3H, C*H*Me$_2$).

2.3. Preparation of N≡Mo(SAd)$_3$ (3). To a magnetically stirred solution of Ti(SAd)(O^{i}Pr)$_3$ (**8**, 33.78 g, 86.08 mmol; 3.5 equiv; see section 2.2) in diethyl ether (150 mL) was added solid N≡Mo(O^{t}Bu)$_3$ (**2**, 8.10 g, 24.60 mmol, 1 equiv) in small portions. The mixture was stirred for 1.5 h at which point the volatile components were removed in vacuo. Pentane (ca. 50 mL) was added to the oily residue, precipitating a green-yellow solid. The solid was collected by filtration on a fritted glass funnel and washed with pentane until the filtrate was pale yellow. The solid **3** obtained in this manner amounted to 12.93 g (86% yield). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.44$, 1.57 (app doublets, 18H, Ad proximal C*H*$_2$), 1.90 (app s, 9H, Ad C*H),* 2.45 (app s, 18H, Ad distal C*H*$_2$). ^{13}C NMR (C_6D_6): $\delta = 55.31$, 47.87, 36.49, 31.89. Low resolution EIMS: *m/z* 613 (7.70%, M$^+$*)*. Anal. Calcd for $C_{30}H_{45}MoNS_3$: C, 58.89; H, 7.41; N, 2.29. Found: C, 59.16; H, 7.69; N, 2.26.

2.4. Preparation of (AdS)$_3$Mo(μ-N)Mo(N[^{t}Bu]Ph)$_3$ (4). To a thawing solution of N≡Mo(SAd)$_3$ (**3**, 0.311 g, 0.508 mmol, 1 equiv; see section 2.3) in toluene (14 mL) was added dropwise via pipet a cold toluene solution of Mo(N[^{t}Bu]Ph)$_3$ (**1**, 0.274 g, 0.508 mmol, 1 equiv). The mixture was allowed to warm to 25 °C, during which process its color changed from orange to dark green. Approximately 15 min after reaching 25 °C, volatile components were removed from the mixture in vacuo. The solid **4** thereby obtained was recrystallized from *n*-hexane at −35 °C, giving 225 mg of pure **4** as a black powder (38% yield). Anal. Calcd for $C_{60}H_{87}N_4S_3Mo_2$: C, 62.53; H, 7.61; N, 4.86. Found: C, 62.99; H, 7.88; N, 4.57. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 8.09$ ($\Delta\nu_{1/2} = 25$ Hz), 6.78 ($\Delta\nu_{1/2} = 18$ Hz), 6.52 ($\Delta\nu_{1/2} > 150$ Hz), 5.76 ($\Delta\nu_{1/2} = 30$ Hz), 4.84 ($\Delta\nu_{1/2} = 131$ Hz), 3.41 ($\Delta\nu_{1/2} = 129$ Hz), 1.96 ($\Delta\nu_{1/2} = 15$ Hz), 1.80 ($\Delta\nu_{1/2} = 11$ Hz). UV−vis (hexanes): 497 nm ($\epsilon = 4041$), 560 nm ($\epsilon = 3627$), 650 nm ($\epsilon = 3602$), 841 nm ($\epsilon = 3469$). SQuID solid-state magnetic susceptibility data obtained as reported previously: $\mu_{eff} = 1.69(2)\ \mu_B$; $\Theta = -0.03(14)$ K; $\chi_{tip} = 105(2) \times 10^{-2}$; *R* for least-squares fit of χ^{corr} vs *T* plot from 5 to 300 K, 0.997 51 (magnetic field = 1000 G). The data were corrected for diamagnetism using Pascal's constants and background from a similar run without sample.

2.5. Preparation of [(ON)Mo(μ-SAd)(SAd)$_2$]$_2$ (6). Compound **4** (200 mg, 0.180 mmol, 1 equiv) was dissolved in toluene (15 mL) in a septum-capped Schlenk flask. Nitric oxide gas (4.4 mL, 0.180 mmol, 1 equiv, 1 atm, 25 °C) was added via syringe over the magnetically-stirred solution. A gradual color change from green-brown to brown-yellow over 25 min was observed. After the mixture was stirred for a total of 40 min, volatile material was removed in vacuo. ^{1}H NMR spectra of the crude reaction mixture revealed the presence of N≡Mo(N[^{t}Bu]Ph)$_3$ (**9**) and [(ON)Mo(μ-SAd)(SAd)$_2$]$_2$. The crude yellow solid was extracted with pentane with stirring to remove nitride **9**, and the slurry was subjected to filtration on a sintered glass frit. The filter cake consisting largely of [(ON)Mo(μ-SAd)(SAd)$_2$]$_2$ was washed further with pentane to a pale yellow color. The total amount of **6** obtained in this way was 76 mg (0.061 mmol, 67%). Anal. Calcd for $C_{30}H_{45}NOMoS_3$: C, 57.39; H, 7.22; N, 2.23. Found: C, 57.29; H, 7.40; N, 2.20. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 1.46$ (app doublet, 6H, bridge SAd proximal C*H*$_2$), 1.55 (app doublet, 12H, terminal SAd proximal C*H*$_2$), 1.81 (app doublet, 18H, overlapping bridge SAd proximal C*H*$_2$ with terminal SAd proximal C*H*$_2$), 2.07 (app singlet, 18H, overlapping bridge SAd C*H* with terminal SAd C*H*), 2.58 (app singlet, 24H, terminal SAd distal C*H*$_2$), 3.04 (app singlet, 12H, bridge SAd distal C*H*$_2$). ^{13}C NMR (C_6D_6): $\delta = 31.98$, 32.57, 36.50, 36.76, 47.73, 48.08, 58.45, 63.82. ^{1}H NMR (300 MHz, pyridine-d_5, 25 °C): $\delta = 1.63$, 1.85 (app doublets, 18H, Ad proximal C*H*$_2$) 2.12 (app singlet, 9H, Ad C*H*) 2.59 (app singlet, 18H, Ad distal C*H*$_2$) ^{13}C NMR (pyridine-d_5): $\delta = 32.14$, 36.88, 48.66, 56.32. IR data (C_6H_6 solution, KBr plates, cm^{-1}): 2913 (br), 2848 (s), 1642 (vs, NO stretch), 1447 (m), 1342 (m), 1294 (s), 1101 (m), 955 (w), 823 (w).

2.6. Preparation of (AdS)$_3$Mo≡Mo(SAd)$_3$ (5). A solution of 1-adamantanethiol (974 mg, 5.80 mmol, 6 equiv) in pentane (40 ml) was cooled to near freezing in a cold-well inside the box. The mixture was stirred magnetically, and *n*-butyllithium (3.62 ml of a 1.6 M solution in hexanes, 5.80 mmol, 6 equiv) was added via syringe. The volatiles were removed in vacuo after 30 min of stirring. The white solid was dissolved in THF, and solid khaki Mo$_2$Cl$_6$(dme)$_2$ (**7**) (565 mg, 0.96 mmol, 1 equiv) was added in small portions over 10 min. Upon addition, the color of the colorless solution turned from bright-green at the beginning to green-brown, ending dark brown-red. After 3 h of stirring, the volatiles were removed in vacuo giving a brown-orange solid. Diethyl ether was added, and the suspension was stirred for 15 min and filtered through a bed of Celite on a sintered glass frit. The diethyl ether extraction was repeated once. The solvent was evacuated from the filtrate fraction, and the orange-brown powder was recrystallized from a mixture of diethyl ether and hexamethyldisiloxane, by cooling at −35 °C. Two crops of orange-brown (AdS)$_3$Mo≡Mo(SAd)$_3$ were collected summing up to 402 mg (0.34 mmol, 35.4%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 1.71$, 1.54 (app doublets, 18H, Ad proximal C*H*$_2$), 2.01 (app singlet, 9H, Ad C*H*), 2.54 (app singlet, 18H, Ad distal C*H*$_2$). ^{13}C NMR (C_6D_6): $\delta = 32.18$, 36.87, 48.78; 56.42. Anal. Calcd for $C_{60}H_{90}Mo_2S_6$: C, 60.27; H, 7.59. Found: C, 60.27; H, 7.44.

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2.7. Preparation of [(ON)Mo(μ-SAd)(SAd)$_2$]$_2$ (6) from (AdS)$_3$Mo$\equiv$Mo(SAd)$_3$ (5). Compound **5** (243 mg, 0.20 mmol, 1 equiv) was dissolved in 15 mL of toluene in a Schlenk flask capped with a septum. The gases were removed in vacuo, and the flask was taken out of the box. NO (9.8 mL, 0.40 mmol, 2 equiv, 1 atm, 25 °C) was added via syringe. The reaction mixture was stirred for 4 h. The color of the solution gradually changed from dark red-brown to yellow-brown. The solvent was removed in vacuo, and the flask was brought into the box. Pentane (40 mL) was added, and suspension was stirred for 1 h and then filtered through a sintered glass frit. The collected pale yellow-brownish solid was washed with diethyl ether to give the pure pale yellow [(ON)Mo(μ-SAd)(SAd)$_2$]$_2$, as determined by ^{1}H NMR and IR spectroscopy. The total amount of **6** obtained in this manner was 150 mg (0.12 mmol, 60%).

2.8. Preparation of (AdS)$_3$Mo(NO)(py) (10). Compound **6** (80 mg, 0.064 mmol) was dissolved in pyridine, and the solution was stirred for 15 min. The volatiles were removed in vacuo. The solid was washed briefly with cold pentane to remove a brownish impurity and then collected on a fritted glass funnel as a pale yellow solid pure by ^{1}H NMR spectroscopy. The solid **10** obtained using this procedure amounted to 79 mg (0.112 mmol, 87%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 1.57$, 1.85 (app doublets, 18H Ad proximal C*H*$_2$), 2.09 (app singlet, 9H Ad C*H*), 2.66 (app singlet, 18H, Ad distal C*H*$_2$), 6.45 (app triplet, 2H, Py *meta* C*H*), 6.70 (app triplet, 1H, Py *para* C*H*), 9.59 (app doublet, 2H, Py *ortho* C*H*). ^{13}C NMR (C_6D_6): $\delta = 32.13$, 36.96, 48.73, 56.18, 124.50, 138.70, 153.39. Anal. Calcd for $C_{35}H_{50}N_2OMoS_3$: C, 59.47; H, 7.13; N, 3.96. Found: C, 58.68; H, 7.01; N, 3.81. IR data (C_6H_6 solution, KBr plates, cm^{-1}): 2913 (br), 2848 (s), 1643 (vs, NO stretch), 1605 (w), 1444 (m), 1379 (w), 1342 (w), 1295 (m), 1227 (w), 1117 (m), 1101 (w), 1070 (w).

2.9. Reaction of (AdS)$_3$Mo(μ-N)Mo(N[^{t}Bu]Ph)$_3$ (4) with Benzonitrile To Give (AdS)$_3$Mo$\equiv$Mo(SAd)$_3$ (5). Neat benzonitrile (0.2 equiv) was added to a stirring solution of **4** in toluene, at room temperature. No color change was observed upon mixing. The color of the solution turned brown red over the next couple of hours. After being stirred overnight, the volatiles were removed in vacuo, and the crude mixture was analyzed by ^{1}H NMR spectroscopy. The NMR spectrum showed $N\equiv Mo(N[^tBu]Ph)_3$ (**9**) and (AdS)$_3$Mo$\equiv$Mo(SAd)$_3$ (**5**) in a ratio of approximatively 6 to 1. When benzonitrile is used in excess (3 equiv), the initial color change occured immediatly upon addition and the ratio of $N\equiv Mo(N[^tBu]Ph)_3$ (**9**) to (AdS)$_3$Mo$\equiv$Mo(SAd)$_3$ (**5**) was approximatively 5 to 2. Attempts were made to isolate (AdS)$_3$Mo$\equiv$Mo(SAd)$_3$ (**5**) from the mixture with $N\equiv Mo(N[^tBu]Ph)_3$ (**9**) for recording a yield but were unsuccessful.

2.10. X-ray Crystal Data. Crystals grown from concentrated ether solutions at −35 °C quickly were moved from a scintillation vial to a microscope slide containing Paratone N (an Exxon product). Samples were selected and mounted on a glass fiber in wax and Paratone. The data collections were carried out at a sample temperature of 188 K on a Siemens Platform three-circle goniometer with a CCD detector using Mo Kα radiation ($\lambda = 0.710\,73$ Å). The data were processed and reduced by utilizing the program SAINT supplied by Siemens Industrial Automation, Inc. The structures were solved by direct methods (SHELXTL v5.03, Sheldrick, G. M., and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically, except atoms C(28) and C(48) of **10**, both which were refined isotropically. Hydrogen atoms were placed in calculated ($d_{CH} = 0.96$ Å) positions. Some details regarding reduced data and cell parameters are available in Table 1. In addition, selected bond distances and angles are supplied in the figure captions of the ORTEP drawings.

2.11. Density Functional Calculations. Calculations were carried out with the ADF program, employing scalar relativistic corrections for the non-hydrogen atoms in the context of the frozen core approximation. The local density approximation functional used was that of Vosko, Wilk, and Nusair, while the functionals for the generalized gradient approximations took the form of Becke (exchange) and Perdew (correlation).

Table 1. Crystallographic Data for $N\equiv Mo(SAd)_3$ (**3**), (AdS)$_3$Mo(μ-N)Mo(N[^{t}Bu]Ph)$_3$ (**4**), and (AdS)$_3$Mo(NO)(py) (**10**)

	3	**4**	**10**
formula	$C_{35}H_{57.5}MoN_3O_{1.25}S_3$	$C_{40}H_{58}Mo_{1.33}N_{2.67}S_2$	$C_{35}H_{50}Mo_1N_2S_3O$
fw	701.42	728.26	706.89
space group	$P\bar{1}$	$P\bar{3}$	$P\bar{1}$
a, Å	12.423(7)	15.677(3)	12.5627(6)
b, Å	16.795(11)	15.677(3)	16.9028(9)
c, Å	17.746(11)	16.021(2)	17.5580(9)
α, deg	91.951(14)	90	98.0140(10)
β, deg	94.11(2)	90	108.6950(10)
λ, deg	102.95(2)	120	90.7040(10)
V, Å^3	3495(4)	3410.1(9)	3490.7(3)
Z	4	3	4
cryst color/habit	yellow plate	black plate	yellow plate
D_{calcd}, g·cm^{-3}	1.296	1.122	1.345
μ, mm^{-1}	0.567	0.494	0.585
$F(000)$	1486	1214	1488
GOF^a on F^2	1.404	1.110	1.328
$R_1(F_0)^b$ for $I > 2\sigma(I)$	0.1374	0.0588	0.1261
$wR_2(F_0^2)^c$ for $I > 2\sigma(I)$	0.2847	0.1823	0.2361

^{a} $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. ^{b} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} $wR_2 = [\sum[F_o^2 - F_c^2)^2]/[\sum w(F_c^2)^2]]^{1/2}$.

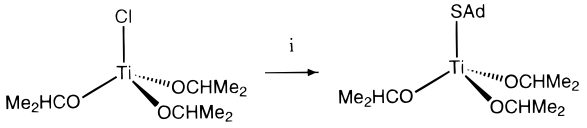

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Figure 1. Synthetic protocol for the preparation of Ti(SAd)(O^{i}Pr)$_3$ (**8**). i: Li(SAd), Et$_2$O, −90 → 25 °C, −LiCl.

3. Results and Discussion

3.1. Synthesis and Characterization. In order to carry out the desired N-atom transfer reaction, the molybdenum(VI) nitrido−thiolate $N\equiv Mo(SAd)_3$ (**3**) was required. Although many molybdenum(VI) nitrido complexes are known, relatively few of them employ thiolate ancillary ligands, and we could discern none that possess exclusively thiolates as supporting ligands. The new compound **3** therefore initiates a previously unexplored class of nitridomolybdenum complexes.

Chisholm's nitrido−butoxide compound $N\equiv Mo(O^tBu)_3$ (**2**) is turning out to be pivotal in molybdenum(VI) nitrido chemistry, in that it has recently served as the precursor to nitridomolybdenum tris(hydrocarbyl) systems.[15,16] The latter are under study as polymerization catalyst precursors. Also, compound **2** served as the precursor to $N\equiv Mo(NMe_2)_3$ in a ligand exchange process involving titanium tetrakis(dimethylamide).[10]

Here again we show that **2**[14] serves as a versatile source of the nitridomolybdenum(VI) fragment, undergoing reaction with the in-situ generated (Figure 1) titanium(IV) thiolate Ti(SAd)(O^{i}Pr)$_3$ (**8**) to provide **3** in 86% yield (Figure 2). It is worth noting that our attempts to utilize the Li(SAd) reagent[12] directly with in-situ generated [Mo(N)Cl$_3$]$_x$[17] failed to provide appreciable quantities of the desired nitrido−thiolate **3**, while the titanium−thiolate route of Figure 2 is rapid and efficient. Separation of the tetraalkoxytitanium(IV) byproduct poses no problem because of its high lipophilicity vis-à-vis the molybdenum nitrido−thiolate complexes.

One would likely expect $N\equiv Mo(SAd)_3$ (**3**) to be monomeric in view of the presence both of strong π-donors and bulky

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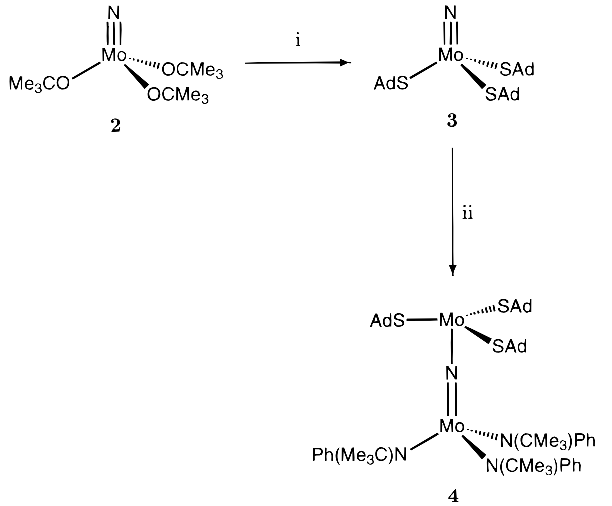

Figure 2. Synthetic protocol for the preparation of $(AdS)_3Mo(\mu\text{-}N)Mo(N[^tBu]Ph)_3$ (**4**). i: $Ti(SAd)(O^iPr)_3$ (**8**, 3 equiv), Et_2O, 25 °C. ii: $Mo(N[^tBu]Ph)_3$ (**1**), toluene, $-90 \rightarrow 25$ °C.

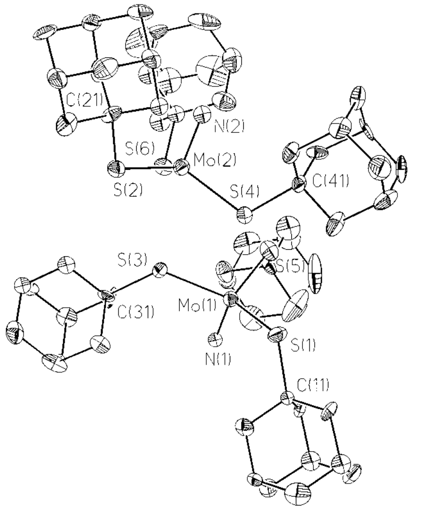

Figure 3. Drawing of the two molecules of $N{\equiv}Mo(SAd)_3$ (**3**) present in the asymmetric unit (35% probability ellipsoids). Solvent molecules of crystallization are omitted. Selected distances (Å) and angles (deg): Mo(1)−N(1), 1.63(2); Mo(1)−S(5), 2.305(7); Mo(1)−S(1), 2.311(7); Mo(1)−S(3), 2.345(6); Mo(1)−S(4), 3.115(7); Mo(2)−N(2), 1.62(2); Mo(2)−S(2), 2.304(7); Mo(2)−S(6), 2.307(7); Mo(2)−S(4), 2.335(6); Mo(2)−S(3), 3.077(7); N(1)−Mo(1)−S(5), 105.6(6); N(1)−Mo(1)−S(1), 104.0(6); S(5)−Mo(1)−S(1), 113.3(3); N(1)−Mo(1)−S(3), 102.8(6); S(5)−Mo(1)−S(3), 114.3(3); S(1)−Mo(1)−S(3), 115.1(2); N(2)−Mo(2)−S(2), 102.2(7); N(2)−Mo(2)−S(6), 103.1(7); S(2)−Mo(2)−S(6), 115.1(2); N(2)−Mo(2)−S(4), 102.2(7); S(2)−Mo(2)−S(4), 113.9(2); S(6)−Mo(2)−S(4), 117.4(2); C(11)−S(1)−Mo(1), 117.8(7); C(21)−S(2)−Mo(2), 113.3(8); C(31)−S(3)−Mo(1), 118.2(7); C(41)−S(4)−Mo(2), 115.6(8); C(51)−S(5)−Mo(1), 115.9(8); C(61)−S(6)−Mo(2), 114.1(8).

substituents. Accordingly, an X-ray diffraction study (Figure 3) reveals at most a very weak interaction between the two molecules present in the asymmetric unit. Each molecule of **3** exhibits pseudotetrahedral coordination about Mo. The molecules are distorted such that the N−Mo−S angles are compressed ca. 5° relative to the tetrahedral angle, while the S−Mo−S angles are enlarged by ca. 5°. Although no crystallographic symmetry is imposed on the molecule, **3** displays near-C_{3v} symmetry. The Mo−S and Mo≡N bond lengths (see caption to Figure 3) are unremarkable with the exception of the putative intermolecular contacts defined by Mo(2)···S(3) and Mo(1)···S(4). These contacts, oriented trans to the Mo≡N linkages, are in excess of three Å and, as such, likely represent a negligible bonding interaction. By way of comparison, the dative S···Mo bond distances in the compounds $MoCl_4(SEt_2)_2$ and $MoCl_4(PhC{\equiv}CSeC_4H_9)(SEt_2)$ are respectively 2.534(2) and 2.668(2) Å.[18,19]

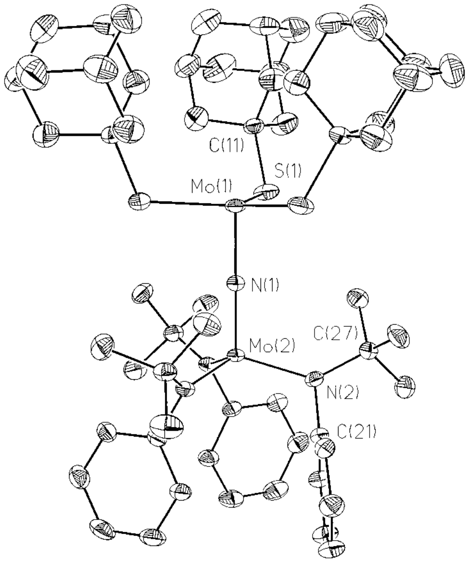

Figure 4. Drawing of $(AdS)_3Mo(\mu\text{-}N)Mo(N[^tBu]Ph)_3$ (**4**) with ellipsoids at the 35% probability level. The molecule possesses crystallographic 3-fold symmetry. Selected distances (Å) and angles (deg): Mo(1)−N(1), 1.882(7); Mo(1)−S(1), 2.308(2); Mo(2)−N(1), 1.771(7); Mo(2)−N(2), 1.977(5); N(1)−Mo(1)−S(1), 93.71(4); S(1)−Mo(1)−S(1)′, 119.585(9); N(2)−Mo(2)−N(2)′, 112.77(11); N(1)−Mo(2)−N(2), 105.93(13); C(11)−S(1)−Mo(1), 115.5(2); Mo(2)−N(1)−Mo(1), 180.0; C(21)−N(2)−C(27), 114.3(4); C(21)−N(2)−Mo(2), 111.7(3); C(27)−N(2)−Mo(2), 133.8(3).

The solid-state conformation of **3** is such that the metal−nitrogen triple bond is tightly flanked by the three adamantyl substituents, but as will be shown below, the fragment can access other conformations. The "three-up" conformation observed in the solid-state structure of **3** contrasts with the "two-up, one-down" structure observed in several cases for trigonal bipyramidal compounds possessing three equatorial thiolate ligands.[20−23]

Having in hand nitride **3**, we investigated its reaction with $Mo(N[^tBu]Ph)_3$ (**1**). Mixing equimolar amounts of **3** and **1** in toluene gave rise to a dark green mixture. Removal of toluene and recrystallization (hexane, −35 °C) gave $(AdS)_3Mo(\mu\text{-}N)Mo(N[^tBu]Ph)_3$ (**4**) as an analytically pure black powder in moderate (38%) yield. Although the compound is paramagnetic (μ_{eff} ca. 1.7 μ_B), it exhibits the expected number (8) of broad ^1H NMR signals in the 1−10 ppm range. The degree of paramagnetism, as assayed from 5 to 300 K by SQuID magnetometry, is consistent with a doublet ground state for the complex.

Structural information from an X-ray diffraction study (Figure 4) reveals that $(AdS)_3Mo(\mu\text{-}N)Mo\text{-}(N[^tBu]Ph)_3$ (**4**) possesses a linear yet unsymmetrical μ-nitrido linkage. Indeed, the N−

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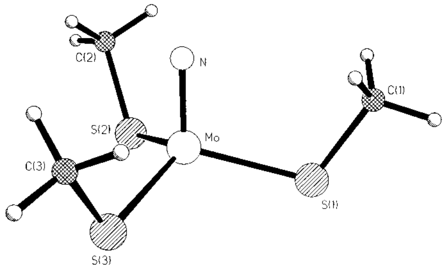

Figure 5. Structure of $N{\equiv}Mo(SMe)_3$ (**11**) as optimized by ADF with scalar relativistic corrections, the constraint of C_{3v} symmetry, and in its lowest-lying singlet state. Bond lengths (Å) and angles (deg): N−Mo, 1.674; Mo−S, 2.340; S−C, 1.861; N−Mo−S, 105.7; Mo−S−C, 108.2. Overlap populations: N−Mo, 0.4595; S−Mo, 0.2267; S−C, 0.3044. Hirschfield charges: N, −0.2928; Mo, 0.4607; S, −0.0926.

$Mo_{thiolate}$ distance (1.882(7) Å) is significantly longer than the $N{-}Mo_{amide}$ distance (1.771(7) Å). This is in contrast to the situation for the related (μ-nitrido)dimolybdenum hexakis(amide) complexes that have been characterized; the latter display linear but symmetrical μ-nitrido linkages.[10]

3.2. Bonding in the *μ*-Nitrido Complex. It is tempting to speculate that the asymmetry in the μ-nitrido linkage for **4** is a consequence of the disparity in donor sets (N- versus S-donors) on the two molybdenum centers. The compound is a mixed-valence species, Mo(V)/Mo(IV), and in view of the direction of the asymmetry of the μ-nitrido bridge, one may assign the $Mo(N[^tBu]Ph)_3$ fragment as containing the more highly oxidized of the two molybdenum centers. In the limiting case the structure of **4** suggests that it ultimately may fragment to "$Mo(SAd)_3$" and the stable nitrido derivative $N{\equiv}Mo(N[^tBu]Ph)_3$ (**9**).

Some of the foregoing notions are borne out by the results of density functional calculations on the model compounds $N{\equiv}Mo(SMe)_3$ (**11**) and $(HS)_3Mo(\mu\text{-}N)Mo(NH_2)_3$ (**12**). Geometry optimizations for the two model compounds were in reasonably good agreement with the experimental data especially with respect to bond distances. For example, the calculated Mo≡N distance for **11** was 1.674 Å (Figure 5), compared with the experimental value of 1.63(2) Å for **3**; note that the latter value has a high esd associated with it and that a more typical distance for a terminal molybdenum nitrido is 1.658(5) Å as found for **9**. Also, for $(HS)_3Mo(\mu\text{-}N)Mo(NH_2)_3$ (**12**), the $\mu\text{-}N{-}Mo_{thiolate}$ bond length is 1.857 Å (Figure 6) and the $\mu\text{-}N{-}Mo_{amide}$ bond length is 1.786 Å, compared to experimental values in **4** of 1.882(7) and 1.771(7) Å, respectively.

3.3. Reactions of the *μ*-Nitrido Complex. The chemistry of $(AdS)_3Mo(\mu\text{-}N)Mo(N[^tBu]Ph)_3$ (**4**) confirmed the speculation that the bond between the nitride and the metal atom supported by thiolate ligands is more susceptible to be broken, forming $N{\equiv}Mo(N[^tBu]Ph)_3$ (**9**) and species containing the "$Mo(SAd)_3$" fragment (Figure 7).

In an attempt to generate the molybdenum(III) tris(thiolate) fragment by thermal decomposition, the μ-nitrido complex was allowed to sit in benzene at room temperature for several days. Under these conditions, **4** decomposes, generating $N{\equiv}Mo(N[^tBu]Ph)_3$ (**9**), as expected. A well-defined product containing the thiolate ligands was not isolated. Access to a species containing the molybdenum(III) tris(thiolate) fragment was made possible by adding benzonitrile to a toluene solution of **4** at room temperature. Besides **9**, $(AdS)_3Mo{\equiv}Mo(SAd)_3$ (**5**) was formed in this reaction. The reaction follows this route when benzonitrile is used in excess (3 equiv) as well as when it is used in substoichiometric amounts (0.2 equiv). Benzonitrile probably promotes the decomposition of **4** by forming an adduct with the metal center supported by thiolate ligands, an adduct which subsequently dimerizes to give the metal−metal triple bond. This idea is substantiated by the fact that the reaction is faster when an excess of benzonitrile is used. Also, the ratio of $(AdS)_3Mo{\equiv}Mo(SAd)_3$ (**5**) to $N{\equiv}Mo(N[^tBu]Ph)_3$ (**9**) (1:2.5, as determined by ^{1}H NMR spectroscopy) is close to the theoretical case (1:2) when excess PhCN (3 equiv) is used. For comparison, when a substoichiometric amount of PhCN (0.2 equiv) was used, the ratio of $(AdS)_3Mo{\equiv}Mo(SAd)_3$ (**5**) to $N{\equiv}Mo(N[^tBu]Ph)_3$ (**9**) was significantly smaller (1:6). In the described reactions, the presence of $(AdS)_3Mo{\equiv}Mo(SAd)_3$ was detected by ^{1}H NMR spectroscopy, but separation of **5** from **9** was unsuccessful. For characterization, compound **5** was prepared independently using $Mo_2Cl_6(dme)_2$ (**7**), previously shown to be a good starting material for the synthesis of molybdenum(III) dimers.[13] $(AdS)_3Mo{\equiv}Mo(SAd)_3$ (**5**) was prepared by adding solid **7** to 6 equiv of Li(SAd) dissolved in THF. The isolated yield of **5**, an orange-brown solid, was 35%.

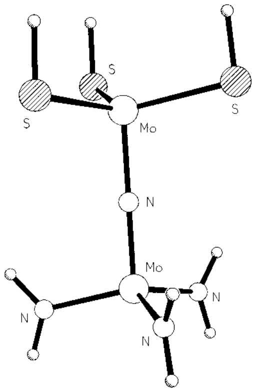

Figure 6. Structure of $(HS)_3Mo(\mu\text{-}N)Mo(NH_2)_3$ (**12**) as optimized by ADF with scalar relativistic corrections, the constraint of C_{3v} symmetry, and in its lowest-lying doublet state. Bond lengths (Å) and angles (deg): $\mu\text{-}N{-}Mo_{thiolate}$, 1.857; $\mu\text{-}N{-}Mo_{amide}$, 1.786; Mo−S, 2.331; Mo−N, 1.978; μ-N−Mo−S, 101.2; μ-N−Mo−N, 102.1. Overlap populations: $\mu\text{-}N{-}Mo_{thiolate}$, 0.1335; $\mu\text{-}N{-}Mo_{amide}$, 0.1918; Mo−S, 0.1867; Mo−N, 0.0914. Hirschfield charges: $Mo_{thiolate}$, +0.4134; Mo_{amide}, +0.6612; μ-N, −0.3352; S, −0.1622; N_{amide}, −0.3223.

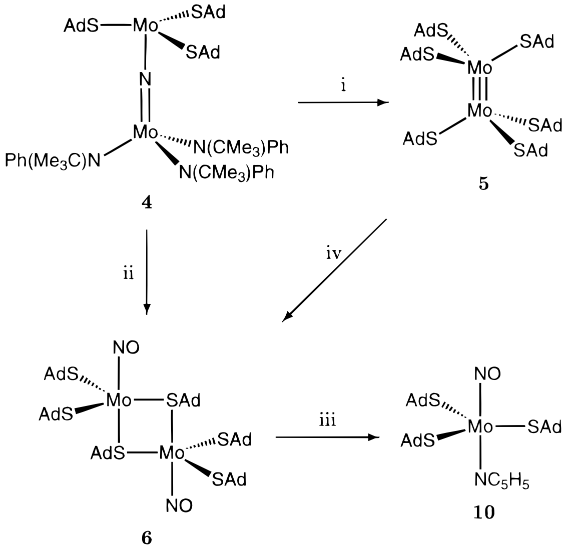

Figure 7. Reactions of $(AdS)_3Mo(\mu\text{-}N)Mo(N[^tBu]Ph)_3$ (**4**) involving loss of $N{\equiv}Mo(N[^tBu]Ph)_3$ (**9**). i: Benzonitrile, 0.2−3 equiv, toluene, 25 °C. ii: NO gas, 1 equiv, toluene, 25 °C, 67%. iii: Pyridine, excess, 25 °C, 87%. iv: NO gas, 2 equiv, toluene, 25 °C, 60%.

The reaction of **4** with gaseous NO was explored to gain more information about the two different nitrido−molybdenum bonds.

Reaction of $(AdS)_3Mo(\mu\text{-}N)Mo(N[^tBu]Ph)_3$ (**4**) with gaseous NO in toluene solution gave $[(ON)Mo(\mu\text{-}SAd)(SAd)_2]_2$ (**6**) in addition to 1 equiv of **9**. It is important to note that the ^{1}H NMR spectrum of the crude mixture did not present any peaks assignable to $Mo(NO)(N[^tBu]Ph)_3$, showing that the bond between the nitride and the molybdenum supported by amide ligands has no tendency to break even in the presence of reactive agents such as NO. The proposed dimeric structure of **6** (see Figure 7) is confirmed by ^{1}H NMR data revealing two distinct thiolate ligand environments. This tendency toward dimerization was previously reported for molybdenum nitrosyl complexes suported by alkoxide ligands.[24,25] The strong nitrosyl stretch in the IR spectum (1642 cm^{-1}) for **6** is similar to the NO stretch reported for the related compound with isopropoxide ligands (1640 cm^{-1})[25] suggesting a very small influence of changing the sets of ligands on the Mo−NO bonding. In order to confirm the assigned structure, $[(ON)Mo(\mu\text{-}SAd)(SAd)_2]_2$ (**6**) was independently prepared by treating a toluene solution of $(AdS)_3Mo{\equiv}Mo(SAd)_3$ (**5**) with 2 equiv of gaseous NO, a reaction characteristic of metal−metal triple-bonded systems.[25]

Treatment of **6** with excess pyridine gave yellow $(AdS)_3Mo(NO)(py)$ (**10**), which was readily obtained in crystalline form. The solid-state conformation of **10** incorporates a trigonal-bipyramidal molybdenum center, with the thiolate ligands lying in the equatorial position and the adamantyl groups surrounding the nitrosyl group (Figure 8). Five-coordinated complexes with three arylthiolate ligands forming a cavity around the nitrosyl group have been described previously.[23] $(AdS)_3Mo(NO)(py)$ is structurally related to Chisholm's tri-*tert*-butoxy(nitrosyl)(pyridine)tungsten.[26] Compound $(^tBuO)_3W(NO)(py)$ presents M−N and N−O bond lengths close to the ones reported here for **10**. The Mo−S bond lengths are comparable with the bond lengths for the equatorial thiolate ligands in other molybdenum−nitrosyl complexes exhibiting a trigonal-bipyramidal geometry, such as $Mo(SC_6H_2{}^iPr_3\text{-}2,4,6)_3(NH_3)(NO)$ and $[NHEt_3][Mo(SPh)_4(NO)]$.[23]

4. Concluding Remarks

For the first time, a $Mo(SR)_3$ fragment has been transferred via intermetal N-atom transfer. It is of interest that Mo≡Mo bond formation occurs in a benzonitrile mediated reaction, as opposed to nitrile cleavage or coupling. Furthermore, despite the success described here with respect to N-atom abstraction from $N{\equiv}Mo(SAd)_3$, no binding of dinitrogen by the $Mo(SR)_3$ fragment is in evidence. On the basis of the observed chemistry, a tentative conclusion is that the $Mo(SR)_3$ fragment is substantially less π-basic (reducing) than corresponding $Mo(N[R]Ar)_3$ complexes.

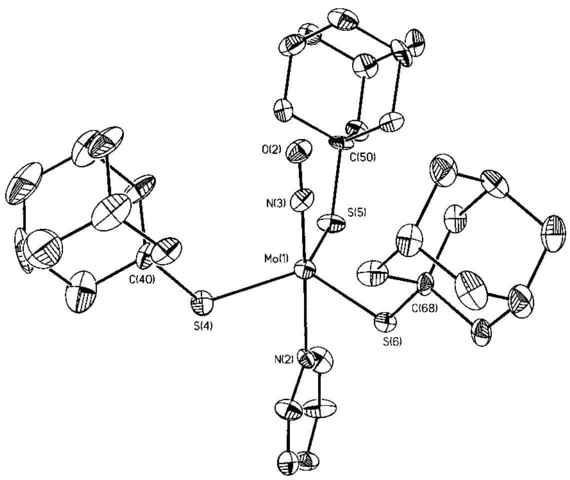

Figure 8. Drawing of the molecule of $(AdS)_3Mo(NO)(py)$ (**10**) present in the asymmetric unit (35% probability ellipsoids). Only one molecule is showed for clarity. Two crystallographically independent molecules are present in the asymmetric unit. Selected distances (Å) and angles (deg): Mo(1)−S(4), 2.313(5); Mo(1)−S(5), 2.319(4); Mo(1)−S(6), 2.311(4); Mo(1)−N(3), 1.769(13); Mo(1)−N(2), 2.350(12); N(3)−O(2), 1.21(2); N(2)−Mo(1)−S(5), 85.8(3); N(2)−Mo(1)-S(6), 81.3(3); S(5)−Mo(1)−S(4), 120.1(2); N(2)−Mo(1)−S(4), 79.6(3); S(5)−Mo(1)−S(6), 116.9(2); S(4)−Mo(1)−S(6), 117.6(2); O(2)−N(2)−Mo(1), 178.4(12); N(3)−Mo(1)−S(5), 96.8(4); N(3)−Mo(1)−S(6), 97.9(4); N(3)−Mo(1)−S(4), 98.5(4); N(3)−Mo(1)−N(2), 177.3(5); Mo(1)−S(4)−C(40), 118.0(6); Mo(1)−S(5)−C(50), 118.2(5); Mo(1)−S(6)−C(68), 118.6(5).

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Supporting Information Available: Text discussing other reactions of complex **4**, a cyclic voltammogram for **4**, X-ray crystallographic files for **3** and **10** not available in CIF format, and an X-ray crystallographic file in CIF format for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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