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Molybdenum, Tungsten, and Rhenium d^2 Complexes That Contain the $[(C_6F_5NCH_2CH_2)_2NMe]^{2-}$ Ligand

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Summary: The reaction between $(C_6F_5NHCH_2CH_2)_2NH$ and methyl iodide in the presence of base leads to $(C_6F_5NHCH_2CH_2)_2NMe$ ($H_2[Ar_FNMe]$) in good yield. Reactions between $H_2[Ar_FNMe]$ and MCl_4 (M = Mo or W) in the presence of NEt_3 yield pseudooctahedral paramagnetic compounds of the type $[Et_3NH]\{[Ar_FNMe]MCl_3\}$. The reaction between 3 equiv of MeMgCl and $[Et_3NH]\{[Ar_FNMe]MoCl_3\}$ produced paramagnetic trigonal bipyramidal $[Ar_FNMe]MoMe_2$. The reaction between $H_2[Ar_FNMe]$ and $Mo(NMe_2)_4$ produced paramagnetic seven-coordinate $[(C_6F_4(NMe_2)NCH_2CH_2)_2NMe]MoF_2$ instead of five-coordinate $[(C_6F_5NCH_2CH_2)_2NMe]Mo(NMe_2)_2$, while the reaction between $H_2[Ar_FNMe]$, $[NEt_4]_2[Re(O)Cl_5]$, and NEt_3 produced diamagnetic trigonal bipyramidal $[Ar_FNMe]Re(O)Cl$. X-ray studies confirmed the structures of $[Et_3NH]\{[Ar_FNMe]MoCl_3\}$, $[Ar_FNMe]MoMe_2$, $[(C_6F_4(NMe_2)NCH_2CH_2)_2NMe]MoF_2$, and $[Ar_FNMe]Re(O)Cl$.

We have been interested in complexes that contain triamidoamine ligands, $[(RNCH_2CH_2)_3N]^{3-}$ (R = $SiMe_3$ or C_6F_5), in part because of their ability to define and sterically protect a trigonal coordination pocket.[1−6] Triamidoamine ligands have also allowed us to explore relatively rare middle oxidation states (2^+, 3^+, 4^+) of Mo and W, particularly with regard to dinitrogen activation and reduction.[10−13] Related trigonal planar[14] molybdenum complexes that contain monodentate amido ligands have recently displayed dramatic success in terms of cleaving strong multiple bonds, in particular that of molecular nitrogen.[15] Although we are continuing to prepare new types of triamidoamine ligands, most recently those that contain various aryl substituents on the amido nitrogens,[16] we have also begun to explore the synthesis and chemistry of diamidoamine complexes in the hopes of making the metal center more accessible. (Complexes that contain planar diamido donor ligands with a central pyridine donor of the type $[C_5H_3N(CH_2NAryl)_2]^{2-}$ also have been described.[7−9]) Interestingly, in vanadium chemistry involving the $[(Me_3SiNCH_2CH_2)_2NSiMe_3]^{2-}$ ligand, dinitrogen recently has been cleaved between two vanadium centers to yield a $V_2(\mu\text{-}N)_2$ complex.[17] Two examples of structurally characterized Mo(IV) diamidoamine complexes exist,[11] but no general route to Mo, W, or Re complexes containing such ligands has been reported. Here we report examples of Mo, W, and Re complexes that contain the $[(C_6F_5NCH_2CH_2)_2NMe]^{2-}$ ($[Ar_FNMe]^{2-}$) ligand.

The reaction between diethylenetriamine and C_6F_6 in the presence of K_2CO_3 has been reported to yield $(C_6F_5NHCH_2CH_2)_2NH$.[18] The fact that the central nitrogen can be deprotonated to produce a planar trianionic ligand[18] is a potential complication that we would like to avoid. We have found that the central nitrogen can be methylated with methyl iodide in CH_3CN (eq 1).[19] Pure $H_2[Ar_FNMe]$ can be readily made by this route in good yield on a 6−7 g scale.

$$(C_6F_5NHCH_2CH_2)_2NH \xrightarrow[CH_3CN,\ 15\ h]{1.3\ CH_3I,\ K_2CO_3} \underset{H_2[Ar_FNMe]}{(C_6F_5NHCH_2CH_2)_2NMe} \quad (1)$$

The reaction between $MoCl_4(THF)_2$, $H_2[Ar_FNMe]$, and NEt_3 in THF gave a paramagnetic, burgundy red powder (eq 2).[20] The ^{19}F NMR spectrum of this product

$$H_2[Ar_FNMe] + MoCl_4(THF)_2 \xrightarrow[22\ °C,\ 2\ h]{2.2\ NEt_3,\ THF} [Et_3NH]\{[Ar_FNMe]MoCl_3\} \quad (2)$$

in THF displayed five resonances at −95.5, −119.3, −131.3, −135.0, and −169.3 ppm, consistent with

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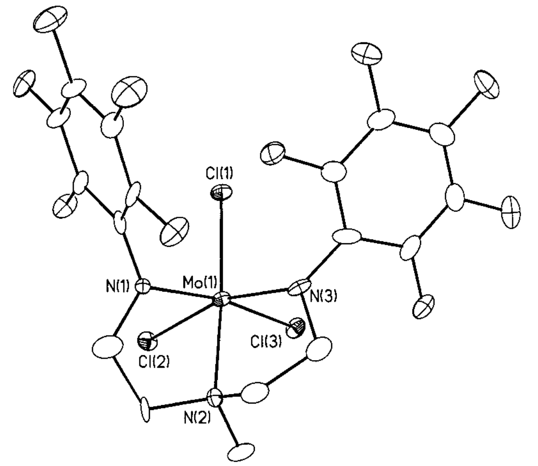

Figure 1. ORTEP drawing (30% probability) of the structure of the anion in $[HNEt_3]\{[(C_6F_5NCH_2CH_2)_2NMe]MoCl_3\}$ (bond lengths in Å, angles in deg): Mo−N(1) = 1.991(8), Mo−N(2) = 2.216(8), Mo−N(3) = 2.019(9), Mo−Cl(1) = 2.410(3), Mo−Cl(2) = 2.480(3), N(1)−Mo−N(3) = 102.9(3), N(1)−Mo−N(2) = 77.9(3), N(1)−Mo−Cl(1) = 94.6(2), N(2)−Mo−Cl(1) = 171.5(2), N(1)−Mo−Cl(3) = 167.8(2). [$C_{23}H_{27}Cl_3F_{10}MoN_4$, monoclinic, $P2_1/c$, $Z = 4$, $a = 11.811(3)$ Å, $b = 17.123(4)$ Å, $c = 17.325(4)$ Å, $\beta = 95.233(4)°$, $T = 180(2)$ K, R1 = 0.0807, wR2 = 0.1833 (all data).]

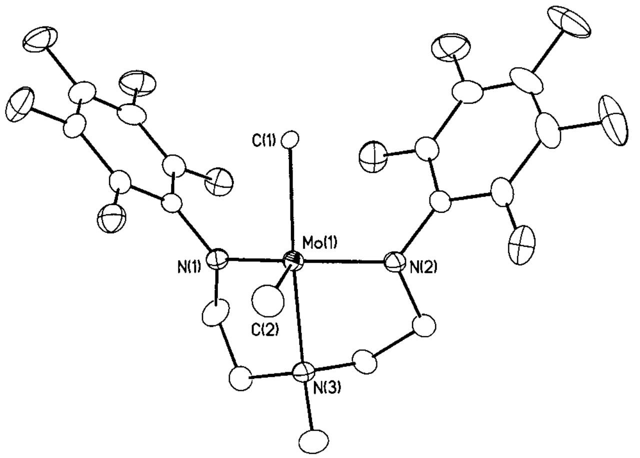

Figure 2. ORTEP drawing (30% probability) of the structure of $[(C_6F_5NCH_2CH_2)_2NMe]MoMe_2$ (bond lengths in Å, angles in deg): Mo−N(1) = 1.970(4), Mo−N(2) = 1.957(4), Mo−N(3) = 2.325(4), Mo−Cl(1) = 2.269(4), Mo−C(2) = 2.134(6), N(2)−Mo−N(1) = 123.3(2), N(2)−Mo−C(2) = 114.9(2), N(2)−Mo−C(1) = 96.4(2), N(3)−Mo−C(1) = 171.4(2). N(3)−Mo−C(2) = 96.7(2), N(3)−Mo−N(2) = 78.7(2). [$C_{19}H_{17}F_{10}MoN_3$, monoclinic, $P2_1/n$, $Z = 2$, $a = 11.7234(4)$ Å, $b = 12.0802(4)$ Å, $c = 16.2635(5)$ Å, $\beta = 110.599(1)°$, R1 = 0.0496, wR2 = 0.1127.]

equivalent, but not rapidly rotating pentafluorophenyl rings. A single-crystal X-ray study revealed the product to be $[Et_3NH]\{[Ar_FNMe]MoCl_3\}$ (Figure 1). (X-ray data were collected on a Bruker CCD diffractometer with Mo Kα = 0.71073 Å and solved using a full-matrix least-squares refinement on F^2.) The coordination geometry is approximately octahedral, with the $[Ar_FNMe]^{2-}$ ligand arranged in a *fac* manner (N(1)−Mo−N(3) = 102.9(3)°). The Mo−N(1) and Mo−N(3) bond lengths are those expected for metal−amido bonds, and the Mo−N(2) bond length is that expected for a dative interaction between the amine donor and the metal. A toluene-soluble tetrabutylammonium salt was prepared in quantitative yield by treating $[Et_3NH]\{[Ar_FNMe]MoCl_3\}$ with $[Bu_4N]Cl$ in THF.

A reaction similar to that shown in eq 2 between $WCl_4(dme)$, $H_2[Ar_FNMe]$, and NEt_3 in diethyl ether gave $[Et_3NH]\{[Ar_FNMe]WCl_3\}$ in 60% yield. An X-ray study (to be reported later) showed the structure to be analogous to that of $[Et_3NH]\{[Ar_FNMe]MoCl_3\}$. A tetrabutylammonium salt could be prepared in the same manner as noted above for $[Bu_4N]\{[Ar_FNMe]MoCl_3\}$.

Addition of 3 equiv of MeMgCl to $[Et_3NH]\{[Ar_FNMe]MoCl_3\}$ in THF led to a deep forest green, paramagnetic product in 50% yield[21] with ^{19}F NMR resonances (in THF) at −57.2, −73.0, −106.0, −147.4, and −149.0 ppm. An X-ray study revealed this species to be $[Ar_FNMe]MoMe_2$ (Figure 2). The geometry is approximately trigonal bipyramidal with "equatorial" L−M−L angles of 123.3°, 114.9°, and 118.8°. The Mo−N$_{amido}$ and Mo−N$_{amine}$ bond lengths are normal. Addition of 2,6-lutidinium chloride to $[Ar_FNMe]MoMe_2$ in diethyl ether yielded a paramagnetic blue-green product that we formulate as $[Ar_FNMe]MoMeCl$ on the basis of elemental analysis (C, H, N, Cl).

The reaction between $H_2[Ar_FNMe]$ and $Mo(NMe_2)_4$ (toluene, 22 °C, 12 h) gave a paramagnetic green product in relatively low isolated yield (23%) that had only four approximately equally intense resonances in the ^{19}F NMR spectrum (in THF) at −70.8, −122.3, −124.9, and −145.2 ppm. An X-ray study showed this product to be one in which an ortho fluorine on each ring was replaced with a dimethylamido group. This transformation led to the product being seven-coordinate $[(C_6F_4(NMe_2)NCH_2CH_2)_2NMe]MoF_2$ instead of five-coordinate $[(C_6F_5NCH_2CH_2)_2NMe]Mo(NMe_2)_2$ (Figure 3). The N(5)−Mo−N(2) angle is only 95.19(19)°, as a consequence of the high coordination number. The Mo−N(1) and Mo−N(3) bond lengths are slightly longer than the Mo−N(4) bond length, presumably for steric reasons. The mechanism of this unusual reaction is not known. The favored proposal at this stage is nucleophilic attack on the ortho carbon of the C_6F_5 ring by a coordinated amide or free amine, followed by loss of F^- or direct transfer of the ortho fluoride to Mo. In any case, this result reveals the potential complications that might arise through the use of C_6F_5-substituted amides in the presence of strong nucleophiles. The yield of $[(C_6F_4(NMe_2)NCH_2CH_2)_2NMe]$-

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(19) Methyl iodide (1.86 mL, 29.9 mmol) was added dropwise to a stirred mixture of $(C_6F_5NHCH_2CH_2)_2NH$ (10 g, 23.0 mmol) and K_2CO_3 (17.5 g, 126 mmol) in CH_3CN (120 mL). After 15 h the volatile components were removed in vacuo and the residue was washed with water (200 mL) and extracted into ethyl acetate (200 mL). The product was isolated from the ethyl acetate layer.

(20) $MoCl_4(THF)_2$ (2.55 g, 6.67 mmol) was added as a solid to a stirred solution of $(C_6F_5NHCH_2CH_2)_2NMe$ (3 g, 6.67 mmol) in THF (50 mL) at room temperature. After 30 min NEt_3 (2.0 mL, 14.35 mmol) was added. After an additional 2 h the reaction mixture was filtered through Celite and the filtrate was added to 100 mL of rapidly stirred pentane. The burgundy product was filtered off; yield 4.70 g (83%).

(21) A solution of MeMgCl (3.2 M in THF) was added to a solution of $[HNEt_3]\{[(C_6F_5NCH_2CH_2)_2NMe]MoCl_3\}$ (0.75 g, 1.01 mmol) in THF (20 mL) at −30 °C. The reaction was allowed to warm to room temperature as it was stirred. After 30 min, the solution was concentrated to dryness in vacuo. The residue was extracted into ether (20 mL), and 1,4-dioxane (0.28 mL) was added. The mixture was filtered through Celite, and the filtrate was added dropwise to rapidly stirred volume of pentane (100 mL). A small amount of brown solid was filtered off, and the filtrate was concentrated to approximately 15 mL to produce green crystalline product; yield 0.29 g (50%).

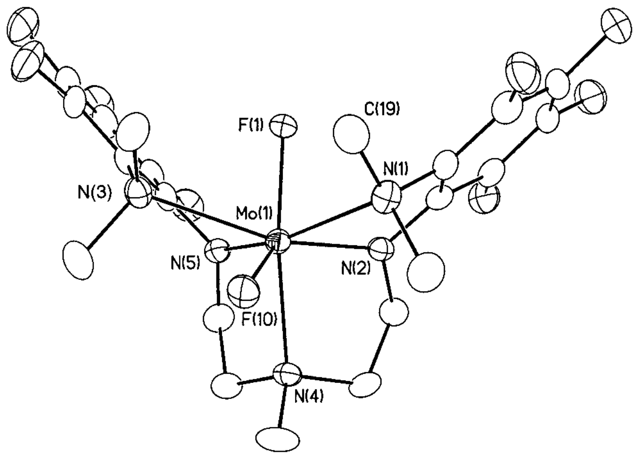

Figure 3. ORTEP drawing (30% probability) of the structure of $[(C_6F_4(NMe_2)NCH_2CH_2)_2NMe]MoF_2$ (bond lengths in Å, angles in deg): Mo−F(1) = 1.968(3), Mo(1)−F(10) = 1.933(3), Mo−N(5) = 2.008(5), Mo−N(2) = 2.013(5), Mo−N(4) = 2.330(5), Mo−N(1) = 2.440(5), Mo−N(3) = 2.482(5), F(10)−Mo−F(1) = 120.45(14), F(10)−Mo−N(5) = 123.20(16), F(1)−Mo−N(5) = 90.99(16), N(5)−Mo−N(2) = 95.19(19), N(5)−Mo−N(4) = 76.46(18). $[C_{48}H_{46}F_{10}MoN_5$, monoclinic, $P2_1/n$, $a = 11.237(8)$ Å, $b = 13.674(9)$ Å, $c = 17.159(12)$ Å, $\beta = 99.936(12)°$, $T = 293(2)$ K, R1 = 0.0914, wR2 = 0.1110 (all data).]

MoF_2 probably is not high, as evidenced by a substantial amount of free ligand produced along with other unknown paramagnetic products.

We have reported that the reaction between $(C_6F_5NHCH_2CH_2)_3N$, $[NEt_4]_2[Re(O)Cl_5]$, and NEt_3 produces a five-coordinate oxo chloro Re(V) species in which the $[(C_6F_5NCH_2CH_2)_2N(CH_2CH_2NHC_6F_5)]^{2-}$ ligand is present; this complex was not structurally characterized.[22] A similar reaction between $H_2[Ar_FNMe]$, $[NEt_4]_2[Re(O)Cl_5]$, and NEt_3 produced an aquamarine-colored diamagnetic product that is virtually insoluble in all common solvents with the exception of pyridine, in which it displays only moderate solubility (eq 3). Allowing pentane to diffuse into a pyridine solution of the complex over several hours yielded crystals of suitable quality for X-ray diffraction. The complex was found to be a trigonal bipyramid with the oxo ligand in the equatorial position (Figure 4). The relatively short Re−O(1) distance (1.675(9) Å) reflects the pseudo triple bond character of this moiety. The Re−N(2), Re−N(3), and Re−N(1) distances are all somewhat shorter than in the other Mo compounds presented here, perhaps as a consequence of the higher formal oxidation state of the metal.

$$H_2[Ar_FNMe] + [NEt_4][Re(O)Cl_5] \xrightarrow[22\ °C,\ 30\ min]{2.2\ NEt_3,\ CH_3CN} [Ar_FNMe]Re(O)Cl \quad (3)$$

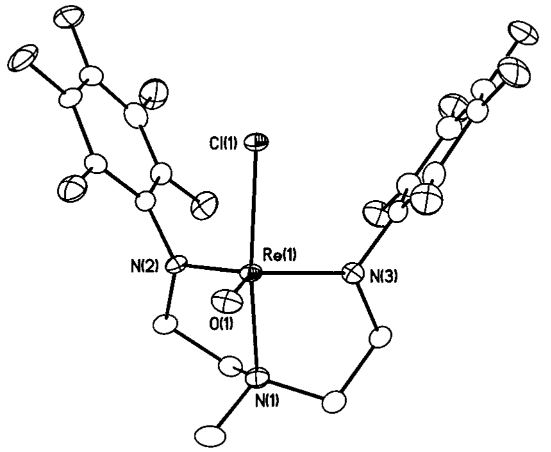

Figure 4. ORTEP drawing (30% probability) of the structure of $[(C_6F_5NCH_2CH_2)_2NMe]Re(O)Cl$ (bond lengths in Å, angles in deg): Re−O(1) = 1.675(9), Re−N(2) = 1.951(7), Re−N(3) = 1.960(7), Re−N(1) = 2.154(8), Re−Cl(1) = 2.362(2), O(1)−Re−N(2) = 118.9(3), N(2)−Re−N(3) = 119.7(3), O(1)−Re−N(1) = 97.7(4), N(2)−Re−N(1) = 80.4(3), O(1)−Re−Cl(1) = 102.8(3), N(2)−Re−Cl(1) = 89.9(2), N(1)−Re−Cl(1) = 159.5(3). $[C_{17}H_{11}ClF_{10}N_3ORe$, monoclinic, $P2_1/n$, $a = 7.923(3)$ Å, $b = 19.766(4)$ Å, $c = 13.182(4)$ Å, $\beta = 106.182(19)°$, R1 = 0.0435, wR2 = 0.1084 (all data).]

We conclude that five-coordinate or six-coordinate complexes of Mo, W, and Re that contain the $[(C_6F_5NCH_2CH_2)NMe]^{2-}$ ligand can be prepared from d^2 Mo, W, or Re halides by relatively “direct” routes. We are currently exploring the chemistry of these new species, in particular with regard to dinitrogen fixation and reduction. We are also exploring the possibility of synthesizing similar complexes that contain less electron-withdrawing aryl substituents on the amido nitrogens, as well as complexes that contain bulkier aryl rings to better protect the metal center against bimolecular reactions.

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Supporting Information Available: Experimental details, labeled ORTEP drawings, crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for $[Et_3NH]\{[Ar_FNMe]MoCl_3\}$, $[Ar_FNMe]MoMe_2$, $[(C_6F_4(NMe_2)NCH_2CH_2)_2NMe]MoF_2$, and $[Ar_FNMe]Re(O)Cl$. This material is available free of charge via the Internet at http://pubs.acs.org.

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