Inorg. Chem. **2008**, *47*, 10226−10228

Inorganic Chemistry
Communication

Molybdenum Tris(2,5-dimethylpyrrolide), a Rare Homoleptic Molybdenum(III) Monomer

Keith M. Wampler and Richard R. Schrock*

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received September 3, 2008

The monomeric, homoleptic molybdenum(III) complex molybdenum tris(2,5-dimethylpyrrolide) has been prepared. Reduction with KC_8 in THF yields the molybdenum(II) complex potassium [molybdenum tris(2,5-dimethylpyrrolide)], while protonation with $[H(OEt_2)_2][BAr^F_4]$ yields a cationic species that contains an η^1-3*H*-pyrrole ligand.

Transition-metal pyrrolide complexes ($NC_4H_4^-$ and substituted versions) have been of interest for decades largely because they are aza analogues of the ubiquitous cyclopentadienyl ion.[1] We have found that molybdenum[2] and tungsten[3] bispyrrolide and bis(2,5-dimethylpyrrolide)imido alkylidene complexes can be prepared readily and that they may be converted into bisalkoxide metathesis catalysts upon the addition of alcohols or diols or into new monoalkoxide monopyrrolide catalysts of the type M(NR)(CHR′)(OR″)(pyrrolide).[4] Well-defined silica-supported catalysts may also be prepared using these precursors.[5] We then became interested in the possibility of preparing a tetrapyrrolide species analogous to $Mo(NMe_2)_4$[6] that could serve as a precursor to new molybdenum(IV) species through protonation of the pyrrolide ligands with relatively mild HX reagents. Here we report the facile and high-yield synthesis of monomeric $Mo(Me_2Pyr)_3$, where Me_2Pyr is 2,5-dimethylpyrrolide.

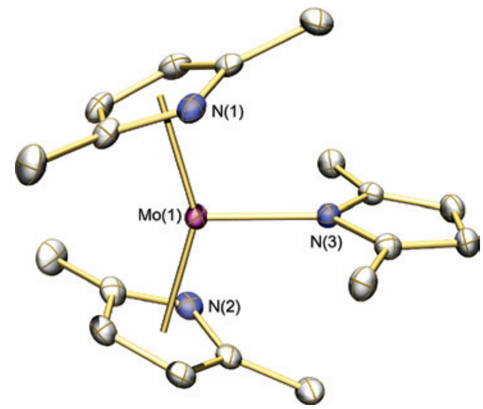

Figure 1. Thermal ellipsoids of **1** are displayed at the 50% probability level. Hydrogen atoms are omitted.

The first attempt to prepare $Mo(Me_2Pyr)_4$ consisted of the addition of 4 equiv of $LiMe_2Pyr$ to $MoCl_4(THF)_2$.[7] A paramagnetic product ($\mu_{eff} = 1.70\ \mu_B$, the Evans method) was obtained in 76% yield (vs $MoCl_4(THF)_2$). Elemental analyses suggested that the product has the formula $Mo(Me_2Pyr)_3$, not $Mo(Me_2Pyr)_4$. Therefore, $Mo(Me_2Pyr)_3$ is also obtained through the addition of 3 equiv of $LiMe_2Pyr$ to $MoCl_3(THF)_3$[7] (eq 1). In retrospect, the reduction of molybdenum(IV) should not be surprising because pyrroles are susceptible to oxidation and oxidative polymerization[8] and because the reduction of molybdenum(IV) to molybdenum(III) is relatively facile.

$$MoCl_3(THF)_3 + 3Li(Me_2Pyr) \xrightarrow[\text{THF, 23 °C}]{-3LiCl} \underset{\mathbf{1}}{Mo(Me_2Pyr)_3} \qquad (1)$$

An X-ray structural study of $Mo(Me_2Pyr)_3$ (Figure 1) shows it to be 17-electron $Mo(\eta^5\text{-}Me_2Pyr)_2(\eta^1\text{-}Me_2Pyr)$ (**1**) in which the centroids of the η^5-Me_2Pyr ligands and the Mo−η^1-Me_2Pyr bond form a trigonal arrangement about Mo. (The average sum of angles around Mo for the two

---

* To whom correspondence should be addressed. E-mail: rrs@mit.edu.

[1] (a) Kershner, D. L.; Basolo, F. *Coord. Chem. Rev.* **1987**, *79*, 279. (b) DuBois, M. R. *Coord. Chem. Rev.* **1998**, *174*, 191. (c) Senge, M. O. *Angew. Chem., Int. Ed.* **1996**, *35*, 1923. (d) Odom, A. L. *Dalton Trans.* **2005**, 225.

[2] Hock, A.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 16373.

[3] Kreickmann, T.; Arndt, S.; Schrock, R. R.; Müller, P. *Organometallics* **2007**, *26*, 5702.

[4] Singh, R.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2007**, *129*, 12654.

[5] (a) Blanc, F.; Berthoud, R.; Salameh, A.; Basset, J.-M.; Copéret, C.; Singh, R.; Schrock, R. R. *J. Am. Chem. Soc.* **2007**, *129*, 8434. (b) Blanc, F.; Berthoud, R.; Copéret, C.; Lesage, A.; Emsley, L.; Singh, R.; Kreickmann, T.; Schrock, R. R. *Proc. Natl. Acad. Sci.* **2008**, *105*, 12123.

[6] (a) Bradley, D. C.; Chisholm, M. H. *J. Chem. Soc. A* **1971**, 2741. (b) Chisholm, M. H.; Cotton, F. A.; Extine, M. W. *Inorg. Chem.* **1978**, *17*, 1329.

[7] Stoffelbach, F.; Saurenz, D.; Poli, R. *Eur. J. Inorg. Chem.* **2001**, 2699.

[8] Cross, M. G.; Walton, D.; Morse, N. J.; Mortimer, R. J.; Rosseinsky, D. R.; Simmonds, D. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *189*, 389.

10.1021/ic801695j CCC: $40.75

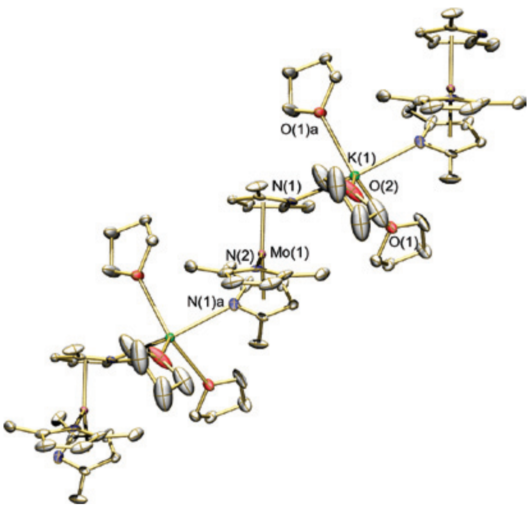

Figure 2. Portion of the structure of polymeric **2**. Thermal ellipsoids are displayed at the 50% probability level. Hydrogen atoms are omitted.

independent molecules in the asymmetric unit is 357°.) The average Mo−C and Mo−N distances to the η^5-Me_2Pyr ring (~2.3 Å) are ~0.1 Å shorter than the average in η^5-pyrrolides in several recent crystallographically characterized molybdenum and tungsten complexes such as Mo(NAd)(CHCMe$_2$Ph)(η^1-Me_2Pyr)(η^5-Me_2Pyr) (Ad = 1-adamantyl),[9] while the average Mo−N distance to the η^1-Me_2Pyr ligand (average = 2.12 Å) is almost identical with that in the recently reported species.

The bonding in **1** can be described in a manner analogous to that employed for a bent metallocene.[10] (Rapid rotation of the η^5-pyrrolide ligands about the M−centroid bonds gives **1** nominal C_{2v} symmetry in solution, the same as that for an analogous bent metallocene.) The Mo−N bond is formed using the $2a_1$ orbital that is pointed along the Mo(1)−N(3) bond. The three electrons therefore must be located in the $1a_1$ and b_2 orbitals that lie perpendicular to the trigonal plane or in the two hybrids formed from those orbitals. The variable-temperature ^1H NMR spectra of **1** (see the Supporting Information) suggest that in solution the η^5-Me_2Pyr and η^1-Me_2Pyr rings remain distinct on the NMR time scale between −10 and +110 °C.

A cyclic voltammetry (CV) study suggests that **1** is reduced reversibly with $i_a/i_c = 1.04$ ($E_{1/2} = -1.36$ V vs Ag/Ag$^+$) in a THF solution using [Bu$_4$N][PF$_6$] as an electrolyte. Bulk chemical reduction of **1** with KC$_8$ in THF yields 18-electron diamagnetic KMo(η^5-Me_2Pyr)$_2$(η^1-Me_2Pyr) (**2**). NMR studies of **2** confirm that the η^5-Me_2Pyr ligands and the η^1-Me_2Pyr ligand do not interconvert on the NMR time scale. An X-ray study of **2** (Figure 2) shows it to be polymeric in the solid state, with each K being bound to three molecules of THF and two η^5-pyrrolide nitrogen atoms. The K−O distances are quite long (~2.7 Å), although the K−N distance of 2.829(4) Å is ~0.15 Å shorter than those typical for other K−N$_{\text{pyrrolide}}$ donor interactions.[11] The average Mo-η^5-bound pyrrolide distance is 2.28 Å, which is similar to that observed in compound **1**. The Mo−η^1-pyrrolide bond length is 0.05 Å longer than that observed in compound **1**. The three THF molecules per K may be removed in vacuo as indicated by elemental analysis and NMR spectra of samples that have been exposed to a good vacuum for 1 day.

CV studies suggest that oxidation of **1** ($E_{1/2} = 380$ mV vs Ag/Ag$^+$) is irreversible under a variety of conditions with $i_a/i_c = 3.47$. (See the Supporting Information.) Attempts at one-electron bulk oxidation with a variety of oxidants (Ag$^+$, Fc$^+$, etc.) did not lead to any tractable material. We presume that oxidation of **1** to **1**$^+$ is followed by ill-defined decomposition that is likely to involve a 2,5-dimethylpyrrolide radical.

The reaction of **1** with 1 equiv of [H(Et$_2$O)$_2$][BAr$^F{}_4$][12] at −30 °C in a THF solution leads to paramagnetic cationic **3** in 86% yield after crystallization from a mixture of ether and pentane at −30 °C. Compound **3** has a solution (CD$_2$Cl$_2$) magnetic moment of 1.72 μ_B (the Evans method), consistent with low-spin Mo^{III}. IR spectra (solution or Nujol) of **3** reveal no NH stretch (above 3050 cm^{-1}) or Mo−H stretch between 1500 and 2800 cm^{-1}, and these spectra are essentially identical with those of the product (**3**-d_1) prepared from **1** and [D(Et$_2$O)$_2$][BAr$^F{}_4$]. The ^2H NMR spectrum of **3**-d_1 reveals two resonances in the ratio of 1:2 at 8.30 and 3.34 ppm that are observed in the same ratio in the relatively complex ^1H NMR spectrum of **3**.

The solid-state structure of **3** is shown in Figure 3a. The "Mo(Me$_2$Pyr)$_3$" framework observed in **1** and **2** persists in **3**. The molybdenum center is trigonally ligated, with the sum of the angles at the metal being 360°. The average Mo−η^5-pyrrolide bond length is virtually identical with that observed in **1**. The best structural solution (there is a slight "side-to-side" disorder of the η^1 ring over two positions; see the Supporting Information) places a proton on the β-carbon atom of what was η^1-pyrrolide in **1** to yield an η^1-3*H*-pyrrole ligand in **3**; the Mo−N(pyrrole) bond length [2.185(11) Å] in **3** is longer than the Mo−N bond length to the η^1-pyrrolide in **1** [2.1213(19) Å], consistent with the 3*H*-pyrrole ligand in **3** being datively bound to Mo. The distances within the 3*H*-pyrrole ring in one of the two positions are shown in Figure 3b. The "olefinic" and "aliphatic" resonances in the ^2H NMR spectrum of **3**-d_1 in a ratio of 1:2 must result from random H/D exchange at the two β-carbon atoms in 3*H*-pyrrole. We believe that protonation of the α-carbon[3,13] is disfavored because the methyl group on the protonated α-carbon would then be forced to point toward an η^5-pyrrolide ring.[3]

To our knowledge, no homoleptic pyrrolide complex of Mo (or W) and no X-ray structure of a complex that contains a 3*H*-pyrrole ligand have been published. Compound **1** is a member of the small class of monomeric homoleptic complexes of molybdenum(III), which includes several variations of the extensively studied trigonal-planar Mo(N-

---

(9) Marinescu, S. C.; Singh, R.; Hock, A. S.; Wampler, K. M.; Schrock, R. R.; Müller, P. *Organometallics* **2008**, in press.

(10) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(11) Freckmann, D. M. M.; Dube, T.; Berube, C. D.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2002**, *21*, 1240.

(12) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

(13) DuBois, M. R.; Vasquez, L. D.; Peslherbe, L.; Noll, B. C. *Organometallics* **1999**, *18*, 2230.

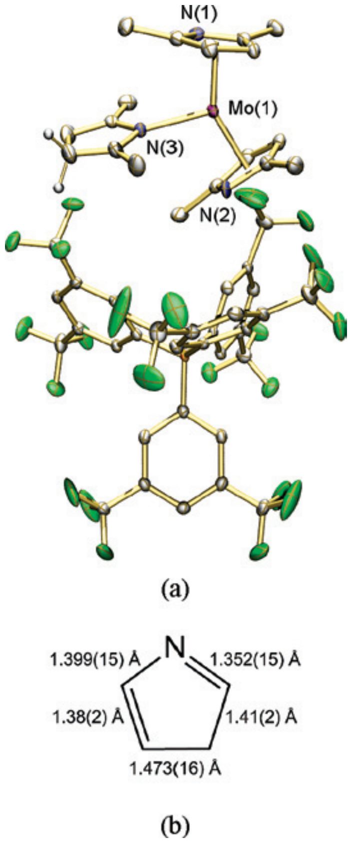

Figure 3. (a) Thermal ellipsoids of **3** displayed at the 50% probability level. Hydrogen atoms are omitted, except the two on the β-carbon with respect to N(3). (b) Distances within the 3*H*-pyrrole ring in one disordered position in **3**.

RR′)$_3$ species,[14] Molybdenum tris(2,6-dimesitylphenylthiolate),[15] in which one of the mesityl rings is π-bonded to the molybdenum, and paramagnetic, and likely monomeric, Mo[OSi(t-Bu)$_3$]$_3$,[16] for which no crystals suitable for an X-ray study have been obtained. Mo[N(i-Pr)$_2$]$_3$ and Mo[N(SiMe$_3$)$_2$]$_3$ have been reported, but they were not isolated in pure form and their monometallic nature was not established.[17] No tungsten(III) or chromium(III) analogues or variations of **1** are known.[18] A relevant account has been published recently that reviews highlights from the development and use of bulky monodentate ligands in general.[19] The synthesis of analogues of **1** that contain unsubstituted pyrrolide or pyrrolides such as 2,5-Ph$_2$Pyr or 2,3,4,5-Me$_4$Pyr has not yet been successful, and all attempts so far to remove one or more pyrrolides through protonolysis (e.g., with alcohols or phenols) or through nucleophilic displacement (e.g., with neopentyllithium) have failed.

Acknowledgment. R.R.S. thanks the National Science Foundation (Grant CHE-0554734) for supporting this research.

Supporting Information Available: Complete experimental procedures for all compounds, a variable-temperature ^{1}H NMR spectrum of **1**, CV and electron spin resonance spectra for **1** and **3**, and crystallographic information files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic data for **1** (08045), **2** (08065), and **3** (08072) are also available to the public at http://reciprocal.mit.edu.

IC801695J

---

(14) Cummins, C. C. *Prog. Inorg. Chem.* **1998**, *47*, 685.

(15) Buyuktas, B. S.; Power, P. P. *Chem. Commun.* **1998**, 1689.

(16) Kuiper, D. S.; Wolczanski, P. T.; Lobkovsky, P. T.; Cundari, T. R. *J. Am. Chem. Soc.* **2008**, *130*, 12931.

(17) (a) Chisholm, M. H. *Acc. Chem. Res.* **1990**, *23*, 419. (b) Chisholm, M. H.; Reichert, W. *Adv. Chem. Ser.* **1976**, *150*, 273. (c) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273.

(18) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; van Bolhuis, F.; Speck, A. L.; Smeets, W. J. J. *Inorg. Chem.* **1990**, *29*, 2147.

(19) Power, P. P. *J. Organomet. Chem.* **2004**, *689*, 3904.