Syntheses, Structures, and Fluxional Behavior of Tricarbonylmolybdenum(0) and Trioxomolybdenum(VI) Complexes of Tris(2-pyridylmethyl)amine with One Free Arm

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The Mo(0) and Mo(VI) complexes of tris(2-pyridylmethyl)amine (tpa), $Mo(CO)_3(tpa)$ and $Mo(O)_3(tpa)\cdot H_2O$, were synthesized. Structural analyses revealed tridentate coordination of tpa in both compounds. The fluxional behavior of both species was investigated by variable-temperature ^1H NMR spectroscopy.

Tris(2-pyridylmethyl)amine (tpa) and its derivatives have been widely used as a tripodal tetradentate ligand to design a variety of metalloenzyme model and related complexes.[1-3] In these complexes, tpa acts almost exclusively as a tetradentate ligand.[1-3] Recently, a series of Re(V or VII) compounds containing tridentate tpa were reported.[4] Complexes containing tridentate tpa are of special interest from kinetic point of view since chemical exchange between the coordinated and free pyridyl rings is anticipated. However, such exchange behavior was not observed in tridentate rhenium(V or VII) complexes such as $[Re(O)_3(tpa)]^+$ and $[Re(O)(OCH_2CH_2O)(tpa)]^+$ up to room temperature. We report here on the first molybdenum complexes of tpa with two extreme oxidation states, $Mo^0(CO)_3(tpa)$ (**1**) and $Mo^{VI}(O)_3(tpa)\cdot H_2O$ (**2**) in which tpa acts as a tridentate ligand with the free pyridyl arm undergoing rapid exchange with the coordinated pyridyl rings at room temperature.

Compound **1** was prepared in about 50% yield by heating a mixture of $Mo(CO)_6$ and tpa in ethanol under reflux in argon. Elemental analysis of the resulting red-orange crystalline product gave the formulation of $Mo(CO)_3(tpa)$ (**1**).[5] **1** is stable as crystalline solid. In CH_3CN, it was oxidized in air to produce the Mo(VI) complex $Mo(O)_3(tpa)\cdot H_2O$ (**2**) almost quantitatively.[5] The UV-vis spectrum initially showed two d-π^* transitions at 420 (1204 $M^{-1}cm^{-1}$) and 340 nm (1420 $M^{-1}cm^{-1}$) at room temperature, which disappeared within 2 h, indicating that the air oxidation is rapid. Both compounds have been characterized by X-ray crystallography.[6] Compound **1** contains two independent $Mo(CO)_3(tpa)$ molecules one of which is shown in Figure 1. The Mo(0) atom has a distorted octahedral coordination geometry with two faces being occupied by three carbonyl ligands and three nitrogen atoms from the amine and two pyridyl rings. The third pyridylmethyl arm is clearly uncoordinated. The fact that tpa appears as a tridentate rather than tetradentate ligand may be explained as follows: (1) the CO stretching frequencies were observed at 1900 and 1759 cm^{-1}, similar to those of $Mo(CO)_3$(1,4,7-triisopropyl-1,4,7-triazacyclononane) (1872, 1741, 1720 cm^{-1}),[7a] but much lower than those of $Mo(CO)_6$ (2115, 1893 cm^{-1}),[7b] indicating poor π-acceptor capability of tpa. The tetradentate $Mo(CO)_2(tpa)$ is thus believed to be thermodynamically unstable if formed; (2) the Mo-CO bonds in **1** (av. 1.932(8) Å) are remarkably shorter than in $Mo(CO)_6$ (2.06(2) Å), leading to difficulty in further substitution of the carbonyl groups. The structure of **2** (Figure 2) shows tridentate coordination of tpa bearing an uncoordinated pyridyl arm. Strong repulsion between the terminal oxo groups leads to more distorted octahedral coordination geometry around the Mo(VI) center than the Mo(0) center (O-Mo-O, av. 106.6(2)° in **2** vs 87.0(2)° (C-Mo-C) in **1**, N-Mo-N, 72.3(3)° in **2** vs. 76.0(2) in **1**). The Mo-N distances are longer by ca. 0.06 Å than in **1** despite of the stronger *trans* influence of the terminal oxo groups. The structural features are similar to those of oxorhenium(VII) complex, $[Re(O)_3(tpa)]^+$.[4]

Chemical exchange between the coordinated and free pyridyl rings in **1** was examined in non-donor solvent CD_2Cl_2.

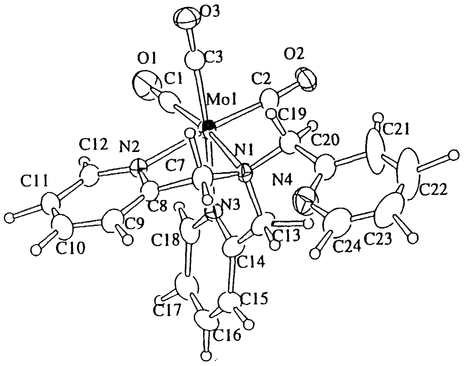

Figure 1. ORTEP drawing of $Mo(CO)_3(tpa)$ (**1**) with 30% probability ellipsoid. Selected bond lengths (Å) and angles (deg): Mol-N1, 2.333(5); Mol-N2, 2.253(5); Mol-N3, 2.255(5); Mol-C1, 1.915(8); Mol-C2, 1.930(7); Mol-C3, 1.950(7); N1-Mol-N2, 75.1(2); N1-Mol-N3, 75.6(2); N2-Mol-N3, 77.5(2); C1-Mol-C2, 85.7(3); C1-Mol-C3, 86.2(3); C2-Mol-C3, 88.2(3).

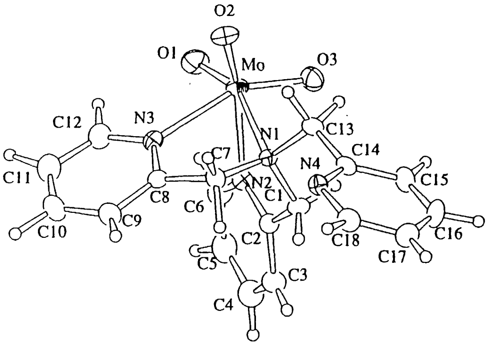

Figure 2. ORTEP drawing of $Mo(O)_3(tpa)$ (**2**) with 30% probability ellipsoid. Selected bond lengths (Å) and angles (deg): Mo-N1, 2.397(4); Mo-N2, 2.320(4); Mo-N3, 2.302(4); Mo-O1, 1.726(3); Mo-O2, 1.735(3); Mo-O3, 1.748(3); N1-Mo-N2, 71.6(1); N1-Mo-N3, 72.0(1); N2-Mo-N3, 72.9(1); O1-Mo-O2, 106.5(2); O1-Mo-O3, 106.8(2); O2-Mo-O3, 106.4(3).

The temperature-dependent NMR spectra of **1** is illustrated in Figure 3. At low temperature (-90 °C), the exchange is slow and the proton signals from coordinated and free pyridyl rings are well separated. Two sets of doublet centered at 8.86 ppm and 8.75 ppm in the intensity ratio of 2:1 are attributed to the *ortho*-protons on the coordinated and free pyridyl groups, respectively. Two sets of triplets centered at 7.82 and 7.45 ppm are assigned to the *para*-protons from the free and coordinated pyridyl rings, respectively, the latter being overlapped with the *meta*-proton signals from the free pyridyl arm. The methylene protons from the free pyridyl arm resonate at 4.92(s) ppm and those from the coordinated ones at 4.73(d) and 3.99(d) ppm in the intensity ratio of 1:1:1. As the temperature is raised to -40 °C, the *ortho*-proton signals merge into a singlet. At room temperature (25 °C), one can see a quite sharp doublet for the *ortho*-protons (8.15 ppm), a triplet for the *para*-protons (7.56 ppm) centered at the weighted frequencies, respectively. The exchange rate constant (k) were estimated at -40, -35, -29, and -20 °C as 66, 113, 220, and 552 s^{-1}, respectively, which give $\Delta H^{\ddagger} = 50(\pm 5)$ kJ mol^{-1} and $\Delta S^{\ddagger} = 8(\pm 2)$ J $mol^{-1}K^{-1}$. The value of $\Delta H^{\ddagger}$ is considerably smaller than that in $Mo(CO)_3$(*N*,*N'*-dimethyl-2,11-diaza[3,3](2,6)pyridinophane) for which the exchange behavior is claimed to be dominated by the breakage of the Mo-N (tertiary amine) bond.[8]

Similar chemical exchange was observed for **2** in CD_3OD. At -55 °C, the *ortho*-proton signals from the coordinated and free pyridyl rings appear at 8.87(d) and 8.75(d) ppm, respectively, that are close to those of **1**. The signals merge into a broad singlet at ca. 5 °C with the rate constant $k = 72$ s^{-1}, indicating that the exchange is much smaller than in **1** which shows a quite sharp doublet at 5 °C in CD_3OD. It is interesting to note that the Mo-N bonds are longer but the exchange rate is slower for **2**. Also Mo(0) has a typical substitution inert electronic configuration (low spin d^6), while Mo(VI) has labile d^0 one. Generally, higher oxidation states tend to show smaller substitution rate constant at a given electronic configuration. Significant difference in the oxidation states of **1** and **2** overwhelms other factors in determining the exchange rate. Slower exchange of $[Re(O)_3(tpa)]^+$ is consistent with this view.

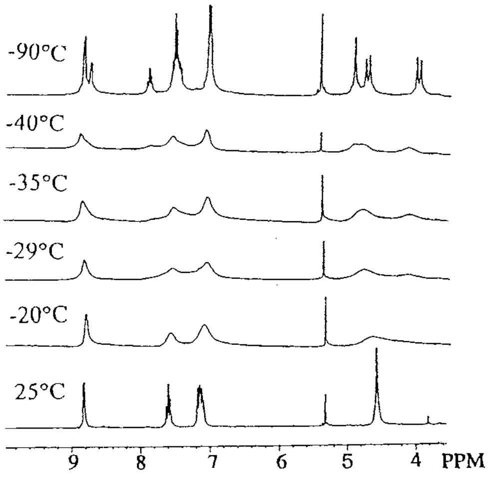

Figure 3. 270 MHz temperature-dependent ^1H NMR spectra of **1** in CD_2Cl_2.

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References and Notes

1 Recent examples of 3d metal complexes. a) Z. Tyeklár, R. R. Jacobson, N. Wei, N. N. Murthy, J. Zubieta, and K. D. Karlin, *J. Am. Chem. Soc.*, **115**, 2677 (1993). b) Y. Zang, J. Kim, Y. Dong, E. C. Wilkinson, E. H. Appleton, and L. Que, Jr., *J. Am. Chem. Soc.*, **119**, 4197 (1995). c) K. Kanamori, E. Kameda, T. Kabetani, K. Suemoto, and S. Kaizaki, *Bull. Chem. Soc. Jpn.*, **68**, 2581 (1995). d) A. Ghosh, J. Almlof, and L. Que, Jr., *Angew. Chem. Int. Ed. Engl.*, **35**, 770 (1996).

2 4d metal complexes. a) T. Kojima, *Chem. Lett.*, **1996**, 121. b) M. Yamaguchi, H. Kousaka, and T. Yamagishi, *Chem. Lett.*, **1997**, 769. c) T. Kojima, T. Amano, Y. Ishii, M. Ohba, Y. Okaue, and Y. Matsuda, *Inorg. Chem.*, **37**, 4076 (1998).

3 Examples from the author's group. a) T. Takahira, K. Umakoshi, and Y. Sasaki, *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.*, **C50**, 1870 (1994). b) H. Sugimoto, K. Kamei, K. Umakoshi, M. Yamasaki, Y. Sasaki, and M. Suzuki, *Inorg. Chem.*, **32**, 7082 (1996). c) C. Koshi, K. Umakoshi, and Y. Sasaki, *Chem. Lett.*, **1997**, 1155. d) K. Umakoshi, Y. Tsuruma, C.-H. Oh, A. Takasawa, H. Yasukawa, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, in press.

4 a) H. Sugimoto and Y. Sasaki, *Chem. Lett.*, **1997**, 541. b) H. Sugimoto and Y. Sasaki, *Chem. Lett.*, **1998**, 197.

5 **1**. Found: C, 53.10; H, 3.99; N, 11.70%. Calcd for $C_{21}H_{18}N_4O_3Mo$: C, 53.63; H, 3.86; N, 11.91%.
2. Found: C, 47.33; H, 4.76; N, 12.33%. Calcd for $C_{18}H_{20}N_4O_4Mo$: C, 47.80; H, 4.46; N, 12.39%.

6 Crystallographic data for **1**: $P\bar{1}$, $a = 13.108(4)$, $b = 14.105(4)$, $c = 11.620(3)$ Å, $\alpha = 99.01(2)$, $\beta = 104.43(3)$, $\gamma = 78.24(2)$°, $V = 2024(1)$ $Å^3$, $Z = 2$, fw = 470.34, Dc = 1.543 g/cm^3, $R = 0.041$ for 3879 reflections. For **2**: Pbca, $a = 16.471(4)$, $b = 13.856(4)$, $c = 18.846(6)$ Å, $V = 4301(1)$ $Å^3$, $Z = 8$, fw = 506.37, Dc = 1.560 g/cm^3, $R = 0.037$ for 2744 reflections.

7 a) G. Haselhorst, S. Stoetzel, A. Strassburger, W. Walz, K. Wieghardt, and B. Nuber, *J. Chem. Soc., Dalton Trans.*, **1993**, 83. b) A. Beachn and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5713 (1968).

8 H. Kelm and H.-J. Krugwe, *Eur. J. Inorg. Chem.*, **1998**, 1381.