A Series of Oxorhenium(V) Complexes Containing Tridentate Tris(2-pyridylmethyl)amine Bearing One Free 2-Pyridylmethyl Arm

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Tris(2-pyridylmethyl)amine (tpa) coordinates to oxorhenium(V) with two pyridyl and one amino nitrogen atoms leaving one 2-pyridylmethyl arm uncoordinated, giving a series of complexes, [Re(O)(L)(η^3-tpa)]$^+$ (L is chelating dianion), due to strong trans influence of the oxo ligand.

Tetradentate ligands, tpa[1] and its derivatives, have been widely used to prepare enzyme model complexes where two *cis*-oriented sites are available for further design of the molecules.[2] We have been using these ligands for some heavy-transition metal complexes.[3-6] In these cases, the ligands act almost exclusively as a tetradentate ligand. We have found, however, tpa acts as a tridentate ligand leaving one 2-pyridylmethyl arm uncoordinated when it coordinates to oxorhenium(V) and trioxorhenium(VII) centers. Three η^3-tpa Re(V) complexes **1**, **2**, and **3**, one η^4-tpa Re(V) complex **4**, one Hbpap Re(V) complex **5** and one η^3-tpa Re(VII) complex **6** are reported in this communication.[7]

[Re^V(O)(eg)(η^3-tpa)]$^+$ (**1**), [Re^V(O)(cat)(η^3-tpa)]$^+$ (**2**),
[Re^V(O)(Bu$_2$cat)(η^3-tpa)]$^+$ (**3**),
[Re^V(O)(CH$_3$O)(η^4-tpa)]$^+$ (**4**), [Re^V(O)(eg)(Hbpap)]$^+$ (**5**),
[Re^{VII}(O)$_3$(η^3-tpa)]$^+$ (**6**)

X-ray crystal structures of all these complexes except for **3** have been determined.[8] Figure 1 shows an ORTEP view of the complex cation **1**. Two features are noted; (i) the tertiary amine nitrogen is at the position trans to the oxo ligand with a considerably longer Re-N distance, and (ii) the angle O(oxo)-Re-N(amine) is considerably smaller than 180 °. These features are commonly found in other complexes, **2**, **5**, and **6**, as summarized in Table 1. ^{1}H NMR spectra of **1**, **2**, and **3** in CD$_3$CN show two types of 2-pyridylmethyl signals in a 2:1 ratio, indicating that the solid state structures are retained in solution and the exchange of coordinated and free 2-pyridylmethyl groups are slow with respect to the NMR time scale.

Table 1. Structural and electrochemical data of the complexes

com-plex	Re-O(oxo) (Å)	Re-N-(amine) (Å)	O(oxo)-Re-N(amine) (°)	$E_{1/2}$ V^a (III/IV)	(IV/V)
1	1.699(5)	2.326(5)	154.1(2)	-1.90	-1.29
2	1.729(8)	2.332(8)	156.9(4)	-1.80	-0.88
3	---------	----------	-----------	-1.83	-0.95
4	1.644(10)	1.86(1)	166.9(5)	b	-0.41^c
5	1.674(6)	2.157(7)	156.7(3)	b	d
6	1.69(1)	2.27(1)	155.2(6)	--------	--------

^{a} vs Ag/AgCl, ^{b} not observed. ^{c} Value for the η^3-tpa complex (see text). ^{d} E_p^{red}, -1.26 and -1.32; E_p^{ox}, -1.20 and -1.06.

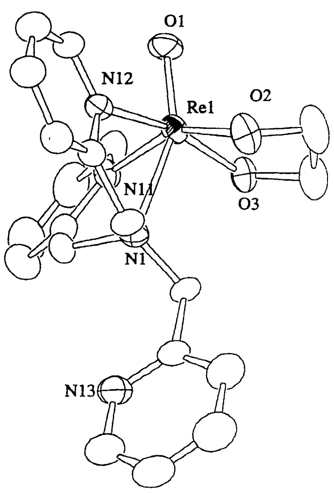

Figure 1. Molecular structure of the complex cation **1**.

The compound **4** which has η^4-tpa, shows significantly different structural characteristics (Figure 2). In CD$_3$CN solution, this complex shows three kinds of 2-pyridylmethyl methylene protons in a 1:1:1 integrated intensity ratio, indicating the replacement of one of the pyridyl arms by a solvent molecule. This fact indicates that the η^4 coordination of tpa in **4** is a highly stressed one and that tpa tends to take η^3 coordination in oxorhenium(V) complexes. Complex **5** has a tripodal ligand in which one of the 2-pyridylmethyl arms of tpa is replaced by a 2-hydroxy-benzil group. The 2-hydroxy-benzil group remains uncoordinated to oxorhenium(V).[9] Complex **6** is a trioxorhenium(VII) complex. Since there is a dioxorhenium(VII) complex,[10] the rhenium(VII) center could form a dioxo complex if the η^4 coordination of tpa is favorable.[11] It appears that η^3 coordination of tpa is not unusual when strongly trans influencing ligands such as oxide ion coexists in the coordination sphere.

Complex **2** is the first structurally characterized mono(catecholato) rhenium complex. There are some di- and tri(catecholato) complexes; [Re^V(O)(OPPh$_3$)(Cl$_4$cat)$_2$]$^-$,[12] [Re^V(O)(CH$_3$OH)(Cl$_4$cat)$_2$]$^-$,[12] Re^{VI}(Bu$_2$cat)$_3$,[13] and [Re^{VII}(O)$_2$(cat)$_2$]$^-$.[10] The redcution potentials of the rhenium(V) complexes are summarized in Table 1. The potentials for the (IV)/(V) process of **1** - **3** show that it becomes more negative with

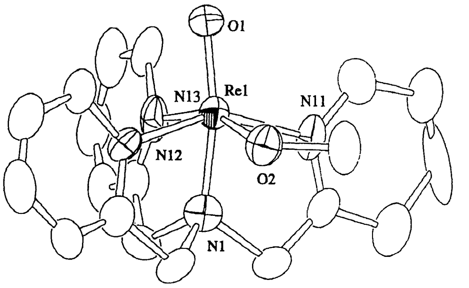

Figure 2. Molecular structure of the complex cation **4**.

an increase in pK_a of the chelating ligands.

Attempts to coordinate the free pyridylmethyl arm to some metal centers such as $Fe(CN)_5^{3-}$ and $Rh_2(CH_3COO)_4$ were not successful, probably because of steric reasons. Replacement of one of the 2-pyridylmethyl arms in tpa by a 4-pyridylmethyl group gives a new ligand, which coordinates to oxorhenium(V) with an uncoordinated 4-pyridyl group. As expected, this complex shows higher coordinating ability to form for example the bis adduct of tetraacetatodirhodium.[14]

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References and Notes

1 Abbreviations of ligands: tpa, tris(2-pyridylmethyl)amine; eg, ethyleneglycolate(2-); cat, *o*-catecholate(2-); Hbpap, bis(2-pyridylmethyl)(phenol-2-yl)amine; Bu_2cat, 3,5-di-*tert*-butyl-1,2-catecholate(2-); Cl_4cat, 3,4,5,6-tetrachloro-1,2-catecholate(2-).

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7 Preparation of [**1**](PF_6): $ReOCl_3(PPh_3)_2$ (0.3 g, 0.36 mmol) was added to a solution of ethyleneglycol (0.05 g, 0.72 mmol), triethylamine (0.15 g, 1.44 mmol) and tpa (0.11 g, 0.36 mmol) in methanol (50 mL). The suspension was stirred for 4 d to give a purple solution. A methanolic solution (5 mL) of NH_4PF_6 (0.16 g, 1 mmol) was added to the solution. Purple block crystals were filtered off after several days, washed with cold ethanol, and air dried. Yield 0.12 g (48%). Preparation of the other complexes: The complexes [**2**](PF_6) and [**3**](PF_6) were prepared by similar methods by using catechol and 3,5-di-*tert*-butyl catechol, respectively, in place of ethylenegycol and triethylamine. [**5**](PF_6) was prepared by a similar method to that of [**1**](PF_6) by using Hbpap instead of tpa. Preparation of [**4**]$(PF_6)_2$: A yellow suspension of $ReOCl_3(PPh_3)_2$ (0.3 g, 0.36 mmol), NH_4PF_6 (0.33 g, 2.0 mmol), and tpa (0.11 g, 0.36 mmol) in methanol (100 mL) was stirred for about 2 weeks at room temperature to give a clear red-brown solution, which was then concentrated to 40 mL under reduced pressure. Red microcrystalline powder was filtered off, washed with ether and air dried. Recrystallization from acetonitrile gave red crystals. Yield 0.2 g (68%). Preparation of [**6**](PF_6): An acetonitrile solution of **4** was kept at room temperature for several days, during which time light orange crystals deposited slowly. These were filtered off, washed with ether and air dried. Elemental analysis (C, H, and N for **1** - **6**) gave satisfactory results.

8 Crystal structure analyses: Intensity data of [**1**](PF_6), [**2**](PF_6), [**4**]$(PF_6)_2$ and [**6**](PF_6) and those of [**5**](PF_6) were collected with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71059$ Å) on a Rigaku AFC5R diffractometer and on a MacScience MXC18 diffractometer, respectively, at 293 K corrected for Lorentz polarization effect and absorption (ψ scans). Crystal data for [**1**](PF_6) ($C_{20}H_{22}N_4O_3F_6PRe$): monoclinic, space group $P2_1/n$ (no. 14), $a = 9.257(6)$, $b = 22.238(2)$, $c = 11.905(4)$ Å, $\beta = 108.25(3)$ °, $V = 2327(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.99$ g cm^{-3}. $R = 0.038$ and $R_W = 0.048$ against 4753 observed reflections [$F > 5\sigma(F_O)$]. Crystal data for [**2**](PF_6) ($C_{24}H_{22}N_4O_3F_6PRe$): triclinic, space group $P\overline{1}$ (no. 2), $a = 10.711(2)$, $b = 13.275(5)$, $c = 10.344(5)$ Å, $\alpha = 103.54(3)$, $\beta = 91.57(2)$, $\gamma = 99.92(2)$ °, $V = 1412.9(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.75$ g cm^{-3}. $R = 0.068$ and $R_W = 0.075$ against 5869 observed reflections [$F > 5\sigma(F_O)$]. Crystal data for [**4**]$(PF_6)_2$ ($C_{19}H_{21}N_4O_2F_{12}P_2Re$): orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 13.472(3)$, $b = 15.478(3)$, $c = 12.723(3)$ Å, $V = 2653.0(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.04$ g cm^{-3}. $R = 0.060$ and $R_W = 0.068$ against 3272 observed reflections. Crystal data for [**5**](PF_6) ($C_{19}H_{23}N_3O_4F_6PRe$): triclinic, space group $P\overline{1}$ (no. 2), $a = 8.627(2)$, $b = 12.142(3)$, $c = 12.888(3)$ Å, $\alpha = 104.01(1)$, $\beta = 113.84(2)$, $\gamma = 98.70(1)$ °, $V = 1182.9(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.95$ g cm^{-3}. $R = 0.040$ and $R_W = 0.047$ against 5701 observed reflections [$I > 2.5\sigma(I_O)$]. Crystal data for [**6**](PF_6) ($C_{36}H_{36}N_8O_6F_{12}P_2Re_2$): orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 12.423(4)$, $b = 29.425(3)$, $c = 11.729(3)$ Å, $V = 4287(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.07$ g cm^{-3}. $R = 0.061$ and $R_W = 0.062$ against 4827 observed reflections [$F > 3\sigma(F_O)$]. The structures were solved by standard direct methods (DIR92) and Fourier syntheses, and were further refined with full-matrix least-square techniques. Computational works for [**1**](PF_6), [**2**](PF_6), [**4**]$(PF_6)_2$, and [**6**](PF_6), were carried out by using standard programs in TEXSAN Program System, while those for [**5**](PF_6) in Crystan Program System.

9 Similar complexes with chelating ligands, cat and Bu_2cat, have not been isolated, nor an η^4 complex with CH_3O^-.

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