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An Axial Phosphine Diadduct of Diruthenium(II,III) Tetraacetate

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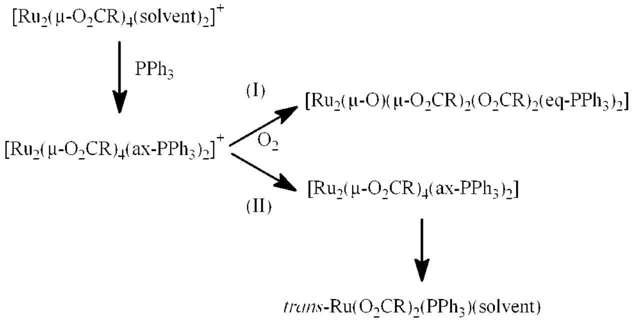
The reaction of $Ru_2(\mu\text{-}O_2CR)_4Cl$ (R = alkyl or aryl) with PPh_3 has been studied extensively in a variety of solvents in an attempt to isolate the $[Ru_2(\mu\text{-}O_2CR)_4(PPh_3)_2]^+$ species. However, contrary to the ease with which diadducts of the form $[Ru_2(\mu\text{-}O_2CR)_4L_2]^+$ are formed with L = various O and N donors,[1] no axial diadduct with triphenylphosphine (or any other phosphine) has been isolated to date. When the reaction is carried out in refluxing methanol or ethanol, the initial products are characterized as oxo-bridged dimers or trimers.[2] A violet μ-oxo dimer, $Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(O_2CCH_3)_2(PPh_3)_2$, where the phosphines have assumed equatorial positions, has been isolated and structurally characterized from THF solution.[3] An apparent parallel pathway leads to cleavage of the Ru−Ru bond and the formation of various mononuclear complexes whose structure is dependent on the nature of solvent.[2−4] Barral et al.[3] have proposed that the rapidly formed $[Ru_2(\mu\text{-}O_2CR)_4(PPh_3)_2]^+$ species undergoes an aerobic disproportionation reaction (Scheme 1), the reductant in pathway II possibly being the phosphine itself.

Some of these phosphine complexes are known to act as useful hydrogenation catalysts;[2a,d] others undergo unusual solvent abstraction reactions.[4] More recently the reaction between PPh_3 and various arenecarboxylates, $Ru_2(\mu\text{-}O_2CAr)_4Cl$, in $MeCN/H_2O$ (1:2) was undertaken by Chakravarty and co-workers,[5] and they were able to isolate and structurally characterize a trapped mixed-valent diruthenium(II,III) compound, $Ru_2(\mu\text{-}OH_2)(O_2CAr)_4(MeCN)(PPh_3)_2Cl$, in which two of the carboxylates are still bridging the two rutheniums but the other two are essentially monodentate with their free oxygens H-bonded to the bridging water. This intermediate may precede the oxo-bridged dimer characterized by Barral et al.[3] since two of the carboxylates are not yet bidentate to each ruthenium, but the axial to equatorial migration of the phosphines has already taken place. Here we report on the first structurally characterized axial phosphine diadduct of a diruthenium(II,III) tetracarboxylate, $[Ru_2(\mu\text{-}O_2CCH_3)_4(PCy_3)_2](PF_6)$ (PCy_3 = tris(cyclohexyl)phosphine), and the interesting properties it displays.

Scheme 1



To synthesize what presumably would be a rapidly forming intermediate, we shortened our reaction time by employing $[Ru_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]^+$ as our starting material, which has more labile axial sites than the polymeric chloride and slowed down any axial to equatorial phosphine migration by increasing the steric bulk of the phosphine, hence the choice of PCy_3. We also employed 2-propanol as our reaction solvent, which we have used in the past to elicit rapid precipitation of axial diadducts involving nitrogen heterocycles[6] which also undergo axial−equatorial migration, albeit much slower. Thus, a 2-fold excess of the PCy_3 (0.240 mmol) was added to a solution of $[Ru_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2](PF_6)$ (0.120 mmol in 25 mL of 2-propanol) and allowed to react for 5 min. A red-brown precipitate formed and could be isolated (yield = 82%).

The product, formulated as $[Ru_2(\mu\text{-}O_2CCH_3)_4(PCy_3)_2](PF_6)$ **(1)**,[7] *does not* undergo conversion to a violet μ-oxo dimer, in either donor (acetone) or nondonor (chlorinated hydrocarbon) solvents, but converts slowly to what appears to be a yellow mononuclear species (pathway II in Scheme 1) over a period of about 2 days. Crystals of **1** could be grown from dichloromethane, and Figure 1 shows an ORTEP confirming the diadduct structure.[8] The Ru−Ru bond length of 2.427(1) Å is the longest reported for a diruthenium tetracarboxylate (the previous record of 2.29 Å was seen in a number of adducts).[1,6] The Ru−P axial bond length is short at 2.369(2) Å and is similar to many Ru−O and Ru−N axial bond lengths,[1] indicating a strong axial interaction. This bond is shorter than Rh−P bonds in $Rh_2(\mu\text{-}O_2CR)_4(PR_3)_2$ complexes, which range from 2.42 to 2.49 Å.[9] A third structural feature to be noted is the acute Ru−Ru−P bond angle of 160.40(5)°, which deviates significantly from the normal 175−180° for these complexes.

Cyclic voltammetry measurements[10] on **1** in 1,2-dichloroethane (Figure 2) reveal an accessible $Ru_2^{5+/6+}$ oxidation at $E_{1/2}$ = 522

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(7) For **1**: Anal. Calcd for $C_{44}H_{78}O_8P_3F_6Ru_2$: C, 46.19; H, 6.87; P, 8.12. Found: C, 45.84; H, 6.55; P, 8.08.

(8) Crystal data for $\mathbf{1}\cdot CH_2Cl_2$: $C_{45}H_{80}O_8F_6P_3Cl_2Ru_2$, M = 1229.08, triclinic, space group $P\bar{1}$, a = 11.616(3) Å, b = 12.793(2) Å, c = 10.536(5) Å, α = 111.10(2)°, β = 108.77(3)°, γ = 77.29(2)°, V = 1373.4(9) Å^3, Z = 1. Final R indices ($I > 3\sigma(I)$): R = 0.048, R_w = 0.052.

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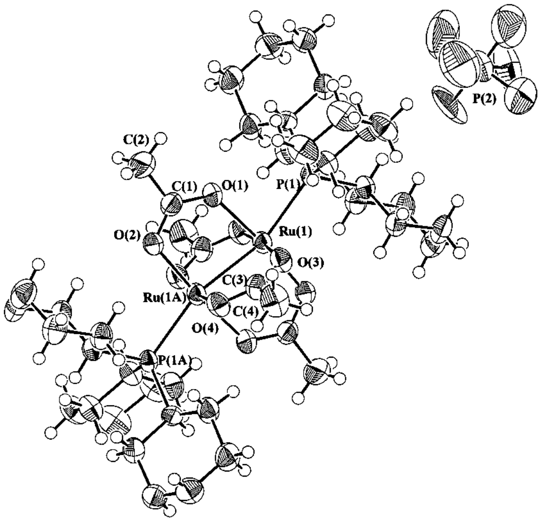

Figure 1. ORTEP diagram of **1**.

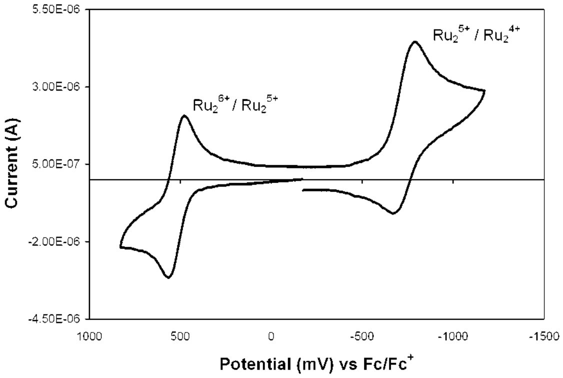

Figure 2. Cyclic voltammogram of **1** in 1,2-dichloroethane.

mV (vs Fc/Fc$^+$ at 100 mV s^{-1}), which is unprecedented for a tetra*carboxylate*. Until now the only diruthenium tetrabridged species with access to the Ru_2^{6+} oxidation state have been the formamidinato and pyrimidinato complexes studied by Bear[11] and Cotton.[12] The anodic to cathodic peak separation for the $Ru_2^{5+/6+}$ couple is slightly scan rate dependent, but the current ratio ($i_{p,c}/i_{p,a}$) is close to 1 over the scan rate range used (50−500 mV s^{-1}), making the process chemically reversible. A scan rate dependent one-electron reduction is also seen with $E_{1/2} = -730$ mV (vs Fc/Fc$^+$ at 100 mV s^{-1}), corresponding to the $Ru_2^{5+/4+}$ couple. This is the lowest value observed for any diruthenium tetracarboxylate diadduct. It is consistent with the increased difficulty of reduction observed as the Lewis basicity of the axial ligand increases. An earlier study using N and O donor ligands made this clear.[6] Since a phosphine is the strongest Lewis base that has been coordinated, the $E_{1/2}$ for reduction should be the lowest. The cathodic to anodic current ratio deviates from 1 ($i_{p,c}/i_{p,a} \approx 1.5$) since reduction of $[Ru_2(\mu\text{-}O_2CR)_4(PCy_3)_2]^+$ leads to further weakening of the already extended Ru−Ru bond, resulting in bond rupture (pathway II) and some chemical irreversibility. $\Delta E_{1/2}$ (1252 mV) yields a comproportionation constant of 1.4×10^{21} for the Ru_2(II,III) species.

As Scheme 1 outlines, the formation of an initial axial phosphine diadduct (kinetic product) is clear. The mechanism of conversion to the μ-oxo dimer (pathway I) or mononuclear species (pathway II) (thermodynamic products) still needs to be determined, but the former may be driven by the phosphine's apparent preference for equatorial (versus axial) coordination. There is greater π electron density at the dimetal core available for back-bonding to the strong π-acid phosphine equatorially rather than axially.[13] Other moderate π-acid ligands, such as 1-methylimidazole, have also shown preference for equatorial coordination.[14] In our case the PCy_3 may prefer to go equatorially (Ru−Ru−P angle = 160°) but, due to its steric bulk (cone angle = 170°),[15] cannot. PPh_3 has a smaller cone angle (145°) and converts quickly to the violet μ-oxo dimer as does $PPhEt_2$ (cone angle = 136°). The degree to which pathway I occurs appears to be controllable by the steric bulk of the phosphine with pathway II driven by its σ-donor strength, increasing the antibonding electron density between the metals and weakening the Ru−Ru bond. The effect of varying the σ-basicity/π-acidity of the phosphine while keeping the steric bulk constant is currently being studied.

In conclusion, we have isolated the first axial phosphine diadduct of a diruthenium(II,III) tetracarboxylate by employing a sterically bulky phosphine, PCy_3, thereby trapping this kinetic product. Complex **1** shows the longest Ru−Ru bond length and most acute Ru−Ru−axial bond angle (in a diadduct) to date as well as providing access to the $Ru_2^{5+/6+}$ redox couple.

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Supporting Information Available: X-ray crystallographic data in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Cyclic voltammetry was carried out on a BAS CV-50 voltammetric analyzer using a Pt button working electrode, a Pt wire auxiliary, and a Ag wire quasi-reference electrode. Ferrocene was used as an internal reference and appeared at 372 mV vs Ag wire (at 100 mV s^{-1} with ΔE_p = 81 mV). Tetrabutylammonium hexafluorophosphate (TBAH) (0.100 M) was used as the supporting electrolyte, and all runs were carried out at 25 °C under Ar.

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