

The First Structurally Determined Ruthenium Nitrate Complex of Chelating Diphosphine Ligand

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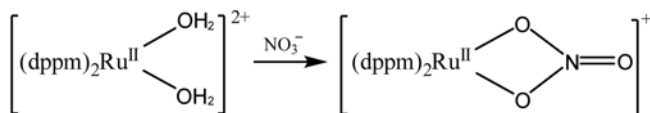
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Among the reported functionalized complexes, oxo and nitrido ruthenium or osmium complexes containing multi-dentate nitrogen-based ligands have proven to be especially valuable in mechanistic and oxidative catalytic studies.¹ During the last decade the chemistry of inorganic and organometallic complexes with phosphine ligands has been well developed to apply them to catalysts.² Therefore it is of interest to combine these two characteristics to prepare oxo complexes surrounded by the phosphine ligands.

A general way to synthesize Ru-oxo complexes can be started from the related Ru-chloro species *via* the corresponding Ru-aquo complexes. Oxidation of the Ru-aquo complexes by a powerful one-electron oxidant like (NH₄)₂Ce(NO₃) (CAN) can lead to the formation of the final products.¹ Accordingly we prepared and characterized ruthenium di-chloro complexes, [Ru(dppm)₂Cl₂] and [Ru(dppe)₂Cl₂], by using the reaction of [Ru(PPh₃)₂Cl₂] with the dppm or dppe ligand (PPh₃: triphenylphosphine, dppm: 1,1-bis(diphenylphosphino)methane, dppe: 1,2-bis(diphenylphosphino)ethane).³ A ruthenium di-aquo complex, [Ru(dppm)₂(H₂O)₂](PF₆)₂, can be obtained by adding AgClO₄ to the [Ru(dppm)₂Cl₂] complex followed by precipitating with saturated NH₄PF₆ solution.⁴ CAN in HClO₄ was added into the di-aquo complex and the residue was put into the refrigerator. The crystals obtained by diffusion method from acetone/water show the formation of an unexpected complex rather than the desired ruthenium di-oxo species.

In organic chemistry CAN has been known to catalyze the ring opening reaction of different epoxides through the formation of nitrate compound in aprotic solvent, which is a key intermediate in the stereoselective syntheses and is useful for a variety of oxidative transformations.⁵ The photochemical reaction of CAN with olefins also produced 1,2-nitrate adduct *via* the initial formation of nitrate radical.⁶ It is quite interesting to show that CAN can be used to prepare the nitrate complexes in coordination chemistry.

Here we found out that the reaction of CAN in perchloric acid with the di-aquo complex gave the unusual nitrate complex rather than the di-oxo complex.⁷ In the reaction it is presumed that the more labile aquo group in the di-aquo complex can be quickly substituted by the nitrate anion in a bi-dentate fashion, which is more favorable in entropy.



The structure of the nitrate complex, which turned out to be [Ru^{II}(dppm)₂(O₂NO)] [ClO₄], has been determined from X-ray diffraction. The perspective view with the numbering scheme of the atoms is shown in Figure 1.

The complex consists of discrete [Ru^{II}(dppm)₂(O₂NO)]⁺ and ClO₄⁻, which contains a ruthenium atom surrounded by two chelating diphosphine ligands and the nitrate ligand. The presence of the nitrate ligand coordinated to the ruthenium metal was confirmed by a singlet resonance at 13.8 ppm in the ¹⁴N NMR spectrum and that of the perchlorate anion by a sharp singlet peak at 1.01 ppm in the ³⁵Cl NMR spectrum. The magnitude of the splitting of peaks at 1435 and 1232 cm⁻¹ observed in the FT IR spectrum re-confirmed that the nitrate ligand coordinated to the metal in a bi-dentate way.⁸

The coordination polyhedron around the ruthenium metal is described as a severely distorted octahedron. Selected bond distances and angles listed in Table 1 are comparable with other structurally characterized complexes containing the dppm ligand.⁹

The Ru-P bond distances range from 2.277(1) to 2.393(1) Å. The phosphorous atoms coordinated to ruthenium metal deviate strongly from a square planar arrangement as noted by the P1-Ru-P2 and P3-Ru-P4 bond angles of less than 90° (70.76(3)° and 70.35(3)°, respectively) for two phosphorous atoms bonded to the ruthenium metal *cis* to one another and by the P1-Ru-P4 and P2-Ru-P3 angles of less than 180° (103.8(1)° and 102.7(1)°, respectively) for those in the opposite position.

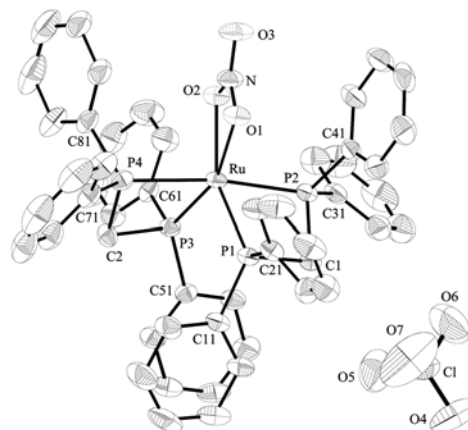


Figure 1. Molecular structure of [Ru(dppm)₂(O₂NO)] [ClO₄] in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected bond distances and angles

Ru-P1	2.284(1)	Ru-P2	2.354(1)	Ru-P3	2.277(1)
Ru-P4	2.393(1)	Ru-O1	2.188(2)	Ru-O2	2.184(2)
P1-C1	1.837(3)	P1-C11	1.807(3)	P1-C21	1.828(3)
P2-C1	1.815(3)	P2-C31	1.812(3)	P2-C41	1.815(3)
P3-C2	1.840(3)	P3-C51	1.804(3)	P3-C61	1.823(3)
P4-C2	1.818(4)	P4-C71	1.816(3)	P4-C81	1.813(4)
N-O1	1.272(3)	N-O2	1.282(3)	N-O3	1.216(4)
P1-Ru-P2	70.76(3)	P3-Ru-P4	70.35(3)	P1-Ru-P4	103.8(1)
P2-Ru-P3	102.7(1)	O1-Ru-O2	58.9(1)	O1-Ru-P1	104.6(1)
O2-Ru-P3	107.2(1)	O2-Ru-P4	94.1(1)	Ru-P4-C2	93.2(1)
Ru-P3-C2	96.5(1)	Ru-P1-C1	96.6(1)	Ru-P2-C1	94.8(1)
Ru-O1-N	93.3(2)	Ru-O2-N	93.1(2)	P3-C2-P4	94.8(2)
P1-C1-P2	94.7(2)	O1-N-O2	114.7(3)	O2-N-O3	122.8(3)
O1-N-O3	122.5(3)	C71-P4-C81	105.2(2)	C51-P3-C61	102.4(1)
C11-P1-C21	101.6(1)	C31-P2-C41	105.2(2)		

The O-Ru-O bite angle of the nitrate ligand containing N at the apical position is 58.9(1)^o with Ru-O distances of 2.188(2) and 2.184(2) Å. The N-O3 distance to the uncoordinated oxygen atom in the nitrate ligand is 1.216(4) Å. The bonding parameters in the [Ru^{II}(dppm)₂(O₂NO)][ClO₄] complex are comparable with those of other mono-nitrate complexes, which show Ru-O distances in the range of 2.151–2.391 Å and O-Ru-O angles in the range of 50.3–59.9^o.¹⁰ However the averaged M-O distances for oxygen atoms of the nitrate ligand attached to the Group III metals fall in a range of 2.255–2.646 Å for bis-nitrate complexes.¹¹ For lanthanide tris-nitrate complexes, the averaged distance reveals 2.151–2.391 Å and the averaged O-M-O (M = Eu or Cd) bond angles of 48.5–56.5^o.¹²

Generally the O-M-O bond angles decrease as the number of the nitrate ligands increase. The averaged bond distance of two oxygen atoms of the coordinated nitrate group in the complex is comparatively short. The nitrate anion can also act as a uni-dentate coordinating ligand with only one of two oxygen atoms to the metal; in this case, however, the distance is getting longer.¹³ Even if reports on the preparation of mono-nitrate complexes are not uncommon, nevertheless most of them are related to uni-dentative nitrate complexes.^{10,14} Although products of [Ru^{II}(dppe)₂(NO₃)] [ClO₄] were obtainable, we have been unable to characterize and grow crystals suitable for X-ray analysis.

X-ray Crystallography

Crystal data: C₅₀H₄₄ClNO₇P₄Ru, monoclinic, space group *P*2₁/*c* (No. 14), *a* = 11.048(2), *b* = 24.527(5), *c* = 17.569(4) Å, β = 100.08(3)^o, *V* = 4687.1(16) Å³, *R*_{int} = 0.0905, *Z* = 4, *T* = 200 K, *d*_{calc} = 1.462 g/cm³. A STOE IPDS instrument equipped with an image plate area detector and employing graphite monochromated MoKα radiation (λ = 0.71073 Å) was used for data collection. A total of 40457 (11043 independent) reflections were collected, which yielded 5969 reflections observed for [*I* > 2σ(*I*)]. The structure was solved by direct methods and subjected to a full-matrix least-squares refinement procedure for all non-hydrogen atoms. The final agreement factors were *R*₁ = 0.0975 (all data), *R*₁ = 0.0403 for [*I* > 2σ(*I*)], *wR*₂ = 0.0696 and *wR*₂ = 0.0607 for [*I* > 2σ(*I*)] (753 parameters, 0 restraints). Crystallographic data

in CIF format have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 299067.

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Supplementary Information Available: Experimental procedures for the complexes in references 3, 4 and 7 studied here are available via the internet at <http://www.kcsnet.or.kr/bkcs>.

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- [Ru(dppm)₂(H₂O)₂](PF₆)₂, Anal. Calc. for C₅₀H₄₈F₁₂O₂P₆Ru: C, 50.22; H, 4.05; P, 15.54. Found: C, 50.89; H, 4.18; P, 14.92. [Ru(dppe)₂(H₂O)₂](PF₆)₂, Anal. Calc. for C₅₂H₅₂F₁₂O₂P₆Ru: C, 51.03; H, 4.28; P, 15.18. Found: C, 52.02; H, 4.43; P, 14.76.
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