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Oxidative C(sp³)–C(sp³) bond cleavage reaction of an isopropyl group to give an acetyl group upon O_2-treatment of a labile cationic ruthenium species, $[Tp^{iPr}Ru(dppene)(OH_2)]^+$†

Yoshiaki Takahashi, Shiro Hikichi, Munetaka Akita* and Yoshihiko Moro-oka*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. E-mail: makita@res.titech.ac.jp

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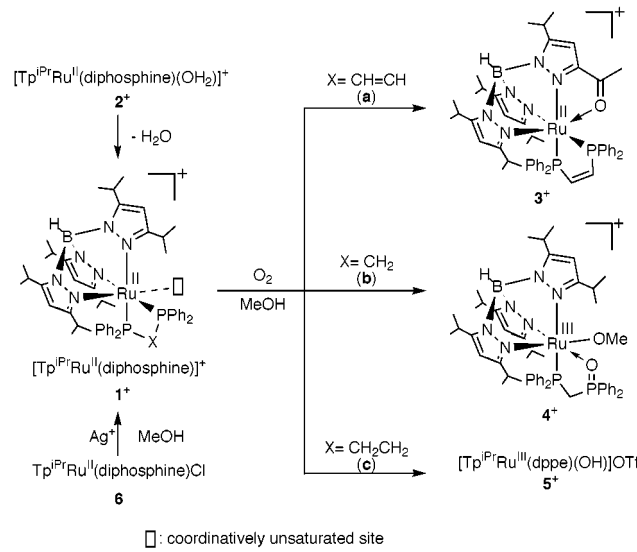
Exposure of a cationic aquoruthenium(II) complex, $[Tp^{iPr}Ru(dppene)(OH_2)]^+$ [Tp^{iPr} = hydrotris(3,5-diisopropylpyrazolyl)borato; dppene = 1,2-bis(diphenylphosphino)ethene], to O_2 at ambient temperature results in oxidative cleavage of the C(sp³)–C(sp³) bond in an isopropyl group in the Tp^{iPr} ligand to give an acetyl functional group.

Oxygenation reactions mediated by a transition metal species are involved as key steps in organic synthesis and metabolic reactions, and selective aerobic oxygenation of hydrocarbyl functional groups has long been a challenging research target.[1] Transition metal–O_2 adducts have been studied extensively as pivotal intermediates of oxygenation reactions but the adducts may be too reactive to be isolated and they frequently oxidize external or internal functional groups including hydrocarbyl substrates. In contrast to a considerable number of C–H and C(sp²)=C(sp²) bond oxygenation reactions induced by O_2-treatment of a transition metal complex,[2] oxygenation of saturated C(sp³)–C(sp³) bond has few precedent examples.[3] During the course of our systematic synthetic study on dioxygen complexes coordinated by hydrotris(pyrazolyl)borato ligands (Tp^R),[4] we observed an oxidative cleavage reaction of a C(sp³)–C(sp³) bond in a ruthenium complex.

We attempted the synthesis of a ruthenium–dioxygen complex bearing the Tp^{iPr} ligand [Tp^{iPr} = hydrotris(3,5-diisopropylpyrazolyl)borato] by O_2-treatment of a coordinatively unsaturated cationic ruthenium(II) species, $[Tp^{iPr}Ru(diphosphine)]^+$ **1**$^+$ [diphosphine = Ph_2P–X–PPh_2: X = CH=CH (**a**: dppene), CH_2 (**b**: dppm), CH_2CH_2 (**c**: dppe)], which should be formed from labile cationic aquo complexes, $[Tp^{iPr}Ru(diphosphine)(OH_2)]^+$ **2**$^+$.[5,6] Exposure of the aquo complexes **2**$^+$ to O_2, however, did not afford the desired product but instead resulted in three different types of oxygenation reactions giving complexes **3**–**5** depending on the structure of the diphosphine ligand (Scheme 1).[7]

Stirring a methanol solution of the dppene complex **2a**OTf[5] (OTf = trifluoromethansulfonate) under an O_2 atmosphere (1 atm) at room temperature gave a mixture containing the red–brown diamagnetic complex **3**OTf (20 % isolated yield) as a major product. The three inequivalent 4-pz-H signals (^{1}H NMR)‡ indicated an unsymmetrical structure but **3**OTf could not be identified by the spectroscopic data alone. In addition, single crystals suitable for X-ray crystallography were not obtained. The coordinatively unsaturated species **1**$^+$ may be generated by an alternative method, *i.e.* dechlorination of the corresponding chloro complex **6** by the action of a Ag salt. Treatment of **6a** with $AgBF_4$ under O_2 atmosphere afforded **3**BF_4 showing spectroscopic properties† similar to those of the OTf salt and its molecular structure was determined by X-ray crystallography [Fig. 1(a)].‡ The most striking structural feature was formation of the acetyl group (C15–C14–O1) resulting from oxygenation of an isopropyl group in the Tp^{iPr} ligand proximal to the metal center, and coordination of the acetyl oxygen atom to the metal center leads to a distorted octahedral coordination geometry [N11–Ru1–N21 93.0(2)°, N11–Ru1–N21 77.8(2)°, N21–Ru1–Ru31 85.2(2)°, Ru1–P1 2.271(2) Å, Ru1–P2 2.297(2) Å, Ru1–O1 2.118(5) Å, Ru1–N11 2.051(5) Å, Ru1–N21 2.123(5) Å, Ru1–N31 2.180(7) Å]. In accord with the structure, a singlet signal at δ_H 1.66 (3H) assignable to the coordinated acetyl group was observed. The acetyl oxygen atom came from O_2 molecule as revealed by a labeling experiment using $^{18}O_2$. When the reaction was carried out in propan-2-ol, formation of methanol was detected by GLC analysis of the solution phase and, therefore, the removed methyl group should be converted to methanol. Thus interaction of the coordinatively unsaturated species **1a**$^+$ with O_2 resulted in unprecedented oxidative cleavage of the C(sp³)–C(sp³) bond in an isopropyl substituent under mild reaction conditions.



Scheme 1

In order to examine the generality of the oxygenation reaction, related diphosphine complexes **1b** and **1c**$^+$ were exposed to O_2. Although oxygenation of a hydrocarbyl group

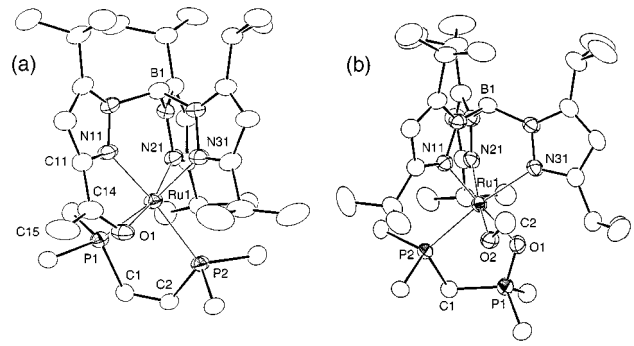


Fig. 1 Structures of the cationic parts of the oxygenated products, **3**BF_4 (a) and **4**PF_6 (b), drawn at the 30% probability level. For the phenyl groups only *ipso* carbons are shown for clarity and the acetyl part in **3**$^+$ is shaded.

did not occur, other types of oxygenation reactions were observed. Dechlorination of **6b** with $AgPF_6$ in MeOH under an O_2 atmosphere produced the red–brown paramagnetic complex **4**$^+$,† and its FD-MS data [*m/z* 998: Tp^{iPr}Ru(dppm)(OMe)(O)] suggested occurrence of oxygenation. X-Ray crystallography [Fig. 1(b)]‡ revealed that complex **4**$^+$ was a cationic ruthenium(III) complex with a 5-oxa-2,4-diphospharuthenacyclopentane structure resulting from oxygenation of one of the two phosphorus atoms in the dppm ligand, and the sixth coordination site was occupied by the methoxo ligand coming from the reaction solvent. In this case, an active oxidizing species bonded to the metal center should be trapped by the neighboring phosphorus atom to release strain of the four membered Ru–P–C–P ring in **2b**$^+$. Finally, treatment of the dppe complex **2c**PF_6 with O_2 resulted in one-electron oxidation of the ruthenium center coupled with deprotonation of the aquo ligand to give a hydroxo–Ru(III) complex **5**PF_6,† which was characterized by X-ray crystallography,‡ but no ligand oxygenation was observed. Complex cation **5**$^+$ is octahedral with a η^1-hydroxo ligand and it should be noted that the Ru–O distance [2.158(5) Å] is comparable to that in the cationic aquoruthenium(II) complex **2c** [2.148(8) Å] [5] but significantly longer than that in the Ru(II) analogue, Tp^{iPr}Ru(dppe)(OH) [2.067(4) Å].[8]

Thus O_2-treatment of the labile aquo–Ru(II) complexes **2**$^+$ resulted in oxidative C–C bond cleavage (dppene: **3**$^+$) or P-oxidation (dppm: **4**$^+$) or oxidation of the metal center (dppe: **5**$^+$) depending on the nature of the diphosphine ligands. The present oxygenation reactions should consist of complex multi-step reaction sequences, and several plausible mechanisms involving a combination of O–O homolysis, Ru–O homolysis, H-abstraction, ·OH-addition, epoxidation, *etc*. can be depicted. Although no other species could be isolated and further study is needed for clarification of the mechanisms, we propose a Ru(III)–η^1-superoxo species, [Tp^{iPr}Ru^{III}(dppe)(η^1-O_2^-)]$^+$, as a likely intermediate on the basis of the following consideration. In **1**$^+$, the chelating κ^3-Tp^{iPr} and κ^2-diphosphine ligands are tightly bound to the Ru center and the sixth coordination site originally occupied by the aquo ligand in **2**$^+$ is the only accessible coordination site. Coordination of an O_2 molecule, therefore, is feasible only in η^1-fashion (η^1-superoxo species). Because the oxygenation was observed only in alcohols, subsequent hydrogen abstraction from the solvent may lead to a hydroperoxo intermediate, which should induce oxidative C–C cleavage. In addition, the alcohol should also act as a reducing agent to regenerate a Ru(II) species like **3**$^+$. The Ru(II) system is in sharp contrast to the Rh(I) system, which undergoes oxidative addition of an O_2 molecule (two-electron oxidation process), and many (η^2-O_2)Rh(III) complexes were prepared by this method.[9] For elucidation of the mechanism of the O-atom transfer step, further experiments are now under way.

In summary, we reported oxidative C(sp^3)–C(sp^3) bond cleavage reaction induced by O_2-treatment of the coordinatively unsaturated Ru(II) species **1**$^+$. The present study revealed that such a highly active oxidizing species can be generated by simple exposure of a precursor **1**$^+$ to O_2 at ambient temperature. It is also notable that the reaction pathway is dependent on the electronic and structural features of the diphosphine ligand (*e.g.* strain of the diphosphametallacyclic structure and electron-donating ability of the diphosphine ligand).[10]

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Notes and references

† *Selected spectroscopic data*: for **3**BF_4: δ_H($CDCl_3$) 5.76, 5.65, 5.45 (1H × 3, s, 4-pz^{iPr} in Tp^{iPr}), 1.66 (3H, s, $COCH_3$). IR (KBr) ν_{BH} 2542 cm^{-1}. For **4**PF_6: ν_{BH} 2561 cm^{-1}. For **5**PF_6: ν_{OH} 3547 (sh), 3433, ν_{BH} 2552 cm^{-1}.

‡ X-Ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å).

Crystal data: **3**BF_4·OEt_2: $C_{56}H_{74}B_2N_6O_2F_4P_2Ru$, M = 1123.84, T = −60 °C, triclinic, space group $P\bar{1}$, a = 14.960(4), b = 17.991(5), c = 12.659(3) Å, α = 104.15(2), β = 113.902(15), γ = 67.30(2)°, V = 2858.0(12) Å^3, Z = 2, D_c = 1.31 g cm^{-3}, μ = 3.9 cm^{-1}, $R1$ = 0.0878 for the 8133 unique data with $F > 4\sigma(F)$ ($wR2$ = 0.2484, for all 9085 data) and 671 parameters.

4PF_6: $C_{53}H_{71}BN_6O_2F_6P_3Ru$, M = 1142.95, T = −60 °C, monoclinic, space group $P2_1/n$, a = 13.076(2), b = 15.096(2), c = 29.955(5) Å, β = 101.324(3)°, V = 5798.3(14) Å^3, Z = 4, D_c = 1.31 g cm^{-3}, μ = 4.2 cm^{-1}, $R1$ = 0.0651 for the 8886 unique data with $F > 4\sigma(F)$ ($wR2$ = 0.1812 for all 10184 data) and 662 parameters.

5PF_6·THF: $C_{57}H_{79}BF_6N_6O_2P_3Ru$, M = 1199.05, T = −60 °C, triclinic, space group $P\bar{1}$, a = 13.452(5), b = 21.594(9), c = 11.612(3) Å, α = 102.06(2), β = 110.21(2), γ = 94.22(2)°, V = 3056.0(19) Å^3, Z = 2, D_c = 1.30 g cm^{-3}, μ = 4.0 cm^{-1}, $R1$ = 0.0890 for the 10023 unique data with $F > 4\sigma(F)$ ($wR2$ = 0.2426 for all 10667 data) and 755 parameters. CCDC 182/1300.

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