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Photoexcited Hydride Cluster

Bimetallic Activation of 2-Alkanones through Photo-Induced α-Hydrogen Abstraction Mediated by a Dinuclear Ruthenium Tetrahydride Complex**

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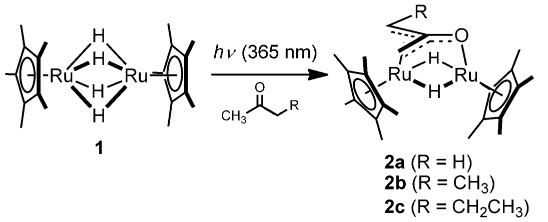
The photochemical behavior of transition-metal complexes has long been a fascinating subject that is related to electron transfer processes, specific organotransformations, photosynthesis, and electrochemical conversion of solar energy. Although there are a vast number of studies on the photochemistry of mononuclear complexes, multimetallic systems remain unexplored.[1]

In general, in cluster complexes with metal–metal bonds, the lowest unoccupied orbital is an antibonding orbital that is delocalized over the metal framework. Whereas mononuclear polyhydride complexes often eliminate hydride ligands as dihydrogen, the elimination of dihydrogen upon photoirradation is hindered in hydride-bridged clusters. As a result, fragmentation of the metal framework of polyhydride-bridged clusters upon photoinduced single electron excitation is suppressed. Therefore, cluster effects, that is, multiple interactions between the substrate and metal sites, are still anticipated, even in the photoexcited state of the polyhydride cluster. These characteristic features of polyhydride-bridged clusters may result in rather exotic photochemical behavior.

We have studied the synthesis of homo- and heterometallic polyhydride cluters and have reported their reaction chemistry under thermal conditions.[2] Some remarkable reactions performed on the reaction sites of these polyhydride clusters were recently highlighted by Lavigne.[3] To extend our research to a new area, we began a project on the photochemistry of a polyhydride cluster which we anticipated to possess increased structural stability.

We report herein an unusual photochemical reaction of a diruthenium tetrahydride complex, $[(\mathrm{Cp^*Ru})(\mu\text{-H})_4(\mathrm{RuCp^*})]$ (**1**) ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$), with 2-alkanones, which produces dinuclear oxatrimethylenemethane (OTMM) complexes.

Upon irradiation with UV light (365 nm) at 10 °C for 48 h under an argon atmosphere, the red suspension of diruthenium tetrahydride (46.1 mg, 96.7 μmol) in acetone (15 mL) became a blue-purple solution. Removal of the solvent under reduced pressure, followed by purification of residual solids by column chromatography on alumina (Merck Aluminium Oxide 90 standardized) with a toluene/tetrahydrofuran (5:1) mixture afforded a dinuclear OTMM complex of ruthenium, $[(\mathrm{Cp^*Ru})\{\mu\text{-}\eta^3\text{:}\eta^1\text{-}(\mathrm{CH_2})_2\mathrm{CO}\}(\mu\text{-H})_2(\mathrm{RuCp^*})]$ (**2a**), in 91 % yield (46.8 mg, 88.2 μmol; Scheme 1).



Scheme 1. Reaction of **1** with 2-alkanones.

The ^{1}H NMR spectrum of **2a** recorded in $[\mathrm{D_6}]$benzene at 25 °C exhibited two singlet signals at $\delta = 1.67$ and 1.80 ppm, which were assignable to the Cp* groups. Two singlet-like signals for the methylene protons of the OTMM ligand appeared at $\delta = 1.22$ (2H, $w_{1/2} = 1.4$ Hz, *anti* to the O atom) and 3.07 ppm (2H, $w_{1/2} = 2.1$ Hz, *syn* to the O atom). A signal corresponding to the chemically equivalent bridging hydride ligands was observed at $\delta = -12.18$ ppm (s, 2H, $w_{1/2} = 13.5$ Hz). A COSY and selective decoupling experiment showed the spin-coupling interactions among the *anti*, *syn*, and Ru-bound protons.[4] The ^{13}C NMR data fully supported the structure of **2a**: the signals for the central carbon atom and the methylene carbons appeared at $\delta = 143.5$ (s) and 51.7 ppm (dd, $J_{\mathrm{CH}} = 151$ and 151 Hz), respectively.

The rate of the reaction largely depends on the solubility of diruthenium tetrahydride: the photochemical reaction of the ethyltetramethylcyclopentadienyl analogue of **1**, $[(\mathrm{C_5Me_4Et})\mathrm{Ru}(\mu\text{-H})_4\mathrm{Ru}(\mathrm{C_5Me_4Et})]$ (**1′**), with acetone was complete within 5 h and was isolated with a yield of 95 % for $[(\mathrm{C_5Me_4Et})\mathrm{Ru}\{\mu\text{-}\eta^3\text{:}\eta^1\text{-}(\mathrm{CH_2})_2\mathrm{CO}\}\mathrm{Ru}(\mathrm{C_5Me_4Et})]$ (**2a′**).[5]

Conclusive evidence for the structure of the dinuclear OTMM complex **2** was obtained from X-ray crystallographic

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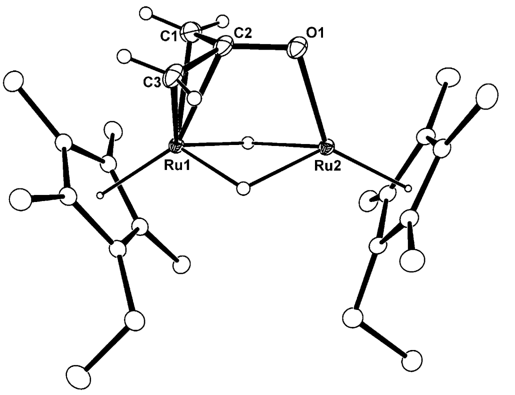


Figure 1. Molecular structure of **2a′** with thermal ellipsoids set at 30%. Relevant bond lengths [Å] and angles [°]: Ru1–Ru2 2.8109(2), Ru2–O1 2.0406(14), Ru1–C1 2.191(2), Ru1–C2 2.186(2), Ru1–C3 2.199(2), C2–O1 1.337(3), C1–C2 1.411(3), C2–C3 1.423(3); O1-C2-C1 121.8(2), O1-C2-C3 121.6(2), C1-C2-C3 115.1(2).

analysis of **2a′**. A single crystal of **2a′** was obtained from cold (−30 °C) pentane solution. The molecule crystallized in space group $P2_1/c$ (#14); the ORTEP drawing of the crystal is shown in Figure 1, along with relevant bond lengths and angles.

The crystal structure clearly reveals that the C_3H_4O ligand bridges the two ruthenium atoms; Ru2 is bonded to the oxygen atom and the C_3 moiety is coordinated to Ru1 atom in a π fashion. The interatomic distances between C2 and O1, C1, and C3 are 1.337(3), 1.411(3), and 1.423(3) Å, respectively; these values are intermediate among those of typical single and double bonds.[6] The sum of the bond angles around C2 is 358.5° and the C1, C2, C3, and O1 atoms are almost coplanar. Because of these structural features, we tentatively characterized the C_3H_4O ligand in **2a** as the OTMM.

The structure of the C_3H_4O moiety in **2a′** is very similar to that in $[Ru_2(CO)_5(\eta^4\text{-C,C,C,O}),\mu\text{-}CH_2C(O)CH_2)(dppm)]$ (dppm = 1,1-bis(diphenylphosphino)methane), which is derived from the reaction of a trinuclear μ-methylene complex, $[Ru_3(CO)_7(\mu_3,\eta^3\text{-}C(O)CH_2)(\mu\text{-}CH_2)(dppm)]$, with CO.[7] Bergman et al. reported the synthesis of a mononuclear OTMM complex, $[Ru(PMe_3)_3(\eta^4\text{-}CH_2C(O)CH_2)]$, using potassium acetone enolate;[8] the OTMM moiety in this complex deviates from planarity and the sum of the bond angles around the central carbon atom of the OTMM ligand, 353.90°, is significantly less than that in **2a′**.

Although there have been many reported examples of catalytic organotransformations in which oxyallyl or OTMM metal species are regarded as key intermediates,[9] there are no successful examples of the isolation and determination of the X-ray crystal structure of the intermediate. Furthermore, the precursors for the oxyallyl or OTMM fragments in most of the reported reactions are substituted or activated ketones, such as dihaloketones, acetoacetic acid derivatives, and enolates. In contrast, acetone was the precursor for the OTMM ligand in our photochemical process. To the best of our knowledge, this is the first example of the production of the OTMM fragment from a simple ketone. This photochemical reaction proceeds through hydrogen abstraction from ketone; no precedents for this type of reaction of ketones under UV irradiation have been reported.

While acetone has no remarkable band around 365 nm, complex **1** has an absorption maximum at 371 nm (ε_{max} = 2200 $M^{-1}cm^{-1}$). Moreover, **1** was quantitatively recovered when it was stirred in acetone in the dark for several days at ambient temperature. Therefore, the photochemical hydrogen abstraction reaction of acetone to yield the OTMM complex is concluded to be a novel type of reaction induced by the photoexcited analogue of **1**. Irradiation of **1** with light (365 nm) for 48 h in tetrahydrofuran instead of acetone resulted in the quantitative recovery of **1**; this is most likely due to the inertness of excited species **1*** towards tetrahydrofuran. Furthermore, neither fluorescence nor phosphorescence were observed upon the photoexcitation of **1** at 365 nm in 2-methyltetrahydrofuran.

The photochemical reaction between **1** and ketones is sensitive to the substituents of the ketones. With methylated ketones, such as 2-butanone and 2-pentanone, the reaction proceeds similarly to afford dinuclear OTMM-type complexes **2b** and **2c**, respectively, although the rate of the reaction is significantly affected by the steric bulk of the substituent on the methylated ketones.[10] Notably, the alkyl substituents on the OTMM ligand in **2b** and **2c** are oriented *syn* to the oxygen atom, as was unequivocally determined by ^1H NMR spectroscopy and X-ray diffraction studies (Figure 2).[11]

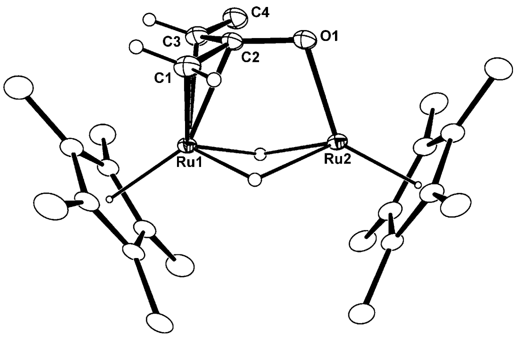
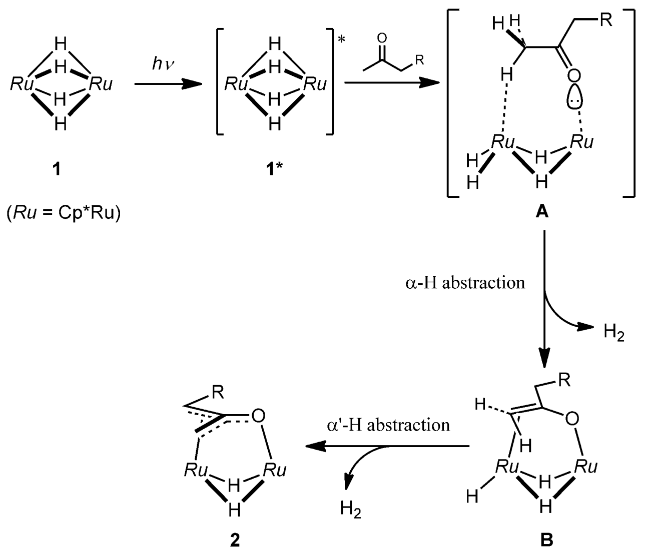


Figure 2. Molecular structure of **2b** with thermal ellipsoids set at 30%. Relevant bond lengths [Å] and angles [°]: Ru1–Ru2 2.8322(3), Ru2–O1 2.0618(18), Ru1–C1 2.173(3), Ru1–C2 2.189(3), Ru1–C3 2.216(3), C2–O1 1.339(3), C1–C2 1.420(4), C2–C3 1.429(4), C3–C4 1.507(4); O1-C2-C1 120.8(3), O1-C2-C3 121.8(3), C1-C2-C3 115.7(3).

Whereas the photoinduced reaction of **1** with 2-alkanones affords the OTMM complex, the photochemical reaction of **1** with ketones containing alkyl substituents longer than a methyl group resulted in the formation of a complicated mixture of unidentified products.

From the characteristic features of this photochemical reaction, we propose the mechanism for the formation of the OTMM complex **2** shown in Scheme 2.

In this mechanism, irradiation (365 nm) of **1** yields the excited species **1***, which would have bonding interaction with 2-alkanone through the lone pair electrons on the oxygen atom to form exciplex [**1***-(2-alkanone)] (**A**) in the initial stage of the reaction. The fact that **1** was quantitatively recovered upon UV-irradiation (at 365 nm) in an inert solvent (tetrahydrofuran) strongly implies the association paths for



Scheme 2. Proposed reaction mechanism for the formation of **2**.

the coordination of ketone. The excited species **1*** would have a somewhat biradical-like character as a result of photo-induced one-electron excitation. Therefore, exciplex **A** undergoes hydrogen abstraction at the methyl group of the coordinated 2-alkanone by the cooperative action of the adjacent ruthenium atom to produce **B**. When both substituents of the ketone are larger than a methyl group, access of the α-methylene group of the ketone to the adjacent ruthenium atom is hindered by the steric repulsion between the substituent and auxiliary C_5Me_5 group. Accordingly, hydrogen abstraction from the α-methylene group is prohibited. Subsequent hydrogen abstraction from the α′-methylene group of ketonyl intermediate **B** leads to the formation of the OTMM complex **2**. During the abstraction of hydrogen at the α′-methylene group, the substituent R is oriented *syn* to the oxygen atom to minimize steric repulsion with the C_5Me_5 group. Thus, conservation of the binuclear cluster core upon photoexcitation is crucial in this reaction and allows bimetallic activation of a substrate, that is, cooperative activation by the adjacent metals.

In summary, we have elucidated the following points through these studies. 1) UV-irradiation (365 nm) of **1** did not result in degradation to a mononuclear species. 2) The irradiation of **1** with UV light (365 nm) in acetone led to the selective formation of a novel dinuclear OTMM complex of ruthenium, $[(\mathrm{Cp^*Ru})(\mu\text{-}\eta^3{:}\eta^1\text{-}(\mathrm{CH_2})_2\mathrm{C{=}O})(\mu\text{-H})_2(\mathrm{RuCp^*})]$ (**2a**), which implies the significant potential of the photochemistry of multimetallic systems connected by hydride ligands. 3) Photoexcited dinuclear species reacted not only with acetone but also with 2-alkanones such as 2-butanone to generate dinuclear OTMM-type complex **2b**, wherein the methyl substituent is oriented *syn* to the carbonyl oxygen. Studies towards the synthetic application of this photochemical system are currently in progress.

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[4] The selective decoupling and H,H-COSY spectra for **2a** and **2b** are given in the Supporting Information.

[5] The C_5Me_4Et analogue of **2a** was identified on the basis of ^1H and ^{13}C NMR spectra. **2a′**: ^1H NMR (400 MHz, $[D_6]$benzene, 23 °C): $\delta = -12{,}19$ (s, 2H, Ru-*H*-Ru), 0.94 (t, $J = 7.6$ Hz, 3H), 1.07 (t, $J = 7.6$ Hz, 3H), 1.24 (s, 2H, *anti*), 1.65 (s, 6H), 1.71 (s, 6H), 1.80 (s, 6H), 1.86 (s, 6H), 2.15 (q, $J = 7.6$ Hz, 2H), 2.33 (q, $J = 7.6$ Hz), 3.08 ppm (s, 2H, *syn*).

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[10] The steric bulk of the substituent on the α′-carbon of the 2-alkanone is crucial for the progress of the photoreaction. Whereas the reaction with 2-butanone afforded **2b** in 57% yield, the yield of the corresponding OTMM-type product was not more than several percent in the reaction with 2-pentanone.

[11] CCDC 902861 (**2a′**) and 902862 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.