Surface Adsorption Models

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Synthesis and Structure of a Triruthenium Complex Containing a Face-Capping Pyridine Ligand**

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The chemistry of organic molecules on a metal surface has been attracting considerable attention with regard to the mechanistic study of heterogeneous catalysis.[1] Polynuclear organometallic molecules have often served as an appropriate model for the adsorbed organic molecules on a metal surface and have made important contributions to surface science. Coordination of an arene on a polynuclear organometallic compound is one of the most intensively studied subjects.[2] Various coordination modes of arenes, such as μ_3-,[3] μ_4-,[4] and μ_5-benzyne complexes[4a,b], as well as trimetallic face-capping arene complexes,[5] have been elucidated by means of diffraction studies, and transformation of a face-capping μ_3-benzene ligand to a μ_3-benzyne ligand as a consequence of double C–H bond activation has also been demonstrated.[5b] These results afford not only information on the structure of the arene species on the metal surface, but also provide information about the reactivity of the absorbed arene.

In contrast to arenes, pyridine has been shown to coordinate to a multimetallic core in quite limited modes. In relation to the hydrodenitrogenation process and poisoning of catalysis, it is important to understand the interaction of pyridine with a polynuclear compound. Since Yin and Deeming synthesized a trimetallic μ-pyridyl complex, $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}C_5H_4N)]$, by the reaction of $[Os_3(CO)_{12}]$ with pyridine,[6a] several trimetallic complexes containing a μ-pyridyl ligand have been prepared.[6] However, a polynuclear complex containing a face-capping μ_3-pyridine ligand has so far never been prepared, although the face-capping mode has been proposed in surface science on the basis of spectroscopic studies.[7] We report herein the first synthesis of a μ_3-η^2:η^2:η^2-pyridine complex and its protonation to yield a μ_3-pyridinium complex.

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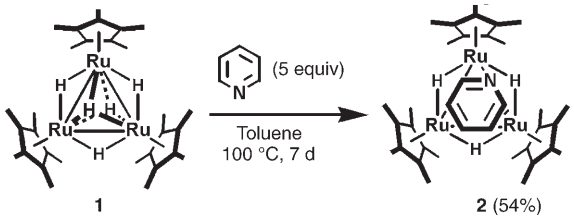
The reaction of the triruthenium pentahydrido complex $[\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2]$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$) with pyridine in toluene at 100 °C afforded the face-capping pyridine complex $[(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_5H_5N)(\mu\text{-}H)_3]$ (**2**) with liberation of H_2 [Eq. (1)].[8] Complex **2** was characterized by ^1H and ^{13}C NMR spectra and elemental analysis, and the structure was determined by means of an X-ray diffraction study.



1 **2** (54%) (1)

The X-ray diffraction study of **2** was performed by using a red single crystal that was obtained from a toluene solution at −30 °C (Figure 1).[9] The structure clearly demonstrates that the pyridine ligand is coordinated to the $\{Ru_3\}$ core in a μ_3-η^2:η^2:η^2 fashion. To the best of our knowledge, complex **2** is the first example of a polynuclear complex with a face-capping pyridine ligand.

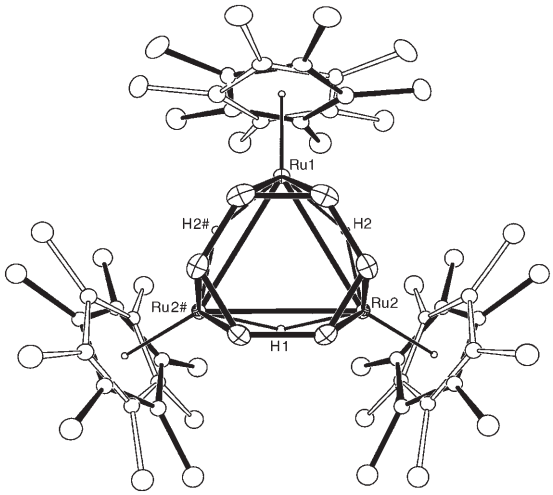


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 30% level of probability. Selected bond lengths [Å] and angles [°]: Ru1-Ru2 3.0346(3), Ru2-Ru2# 3.0298(3); Ru2-Ru1-Ru2# 59.895(6), Ru1-Ru2-Ru2# 60.053(6).

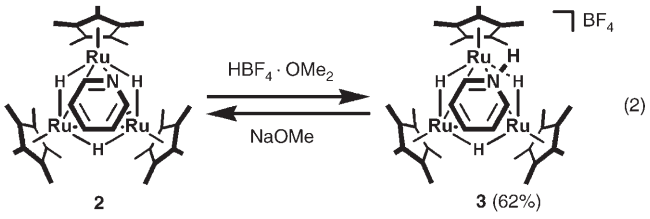
The pyridine ligand in **2** is located parallel to the $\{Ru_3\}$ plane. Although the position of the nitrogen atom was not determined as a result of disorder over the six-membered ring, the average value of the "coordinated" C=C and C=N bond lengths (1.395(6) Å) is shorter than the average of the "uncoordinated" C–C and C–N bond lengths (1.446(5) Å). This difference shows that the pyridine ligand has Kekulé distortion as an azacyclohexatriene-type ring. The Ru–Ru bond lengths (av. 3.0315 Å) correspond to an Ru–Ru single bond.

In the ^{1}H NMR spectrum, measured at room temperature, the five signals stemming from the pyridine ligand appear at $\delta = 2.36$, 2.42, 2.52, 3.47, and 3.60 ppm. These signals resonate in a significantly higher magnetic field in comparison with the free pyridine molecule ($\delta = 7.28$–8.61 ppm). This upfield shift is likely a result of the strong back-donation from the ruthenium centers and the ring-current shielding effect that is caused by the three surrounding Cp* ligands. Signals for the μ_3-benzene ligand of the face-capping benzene complex $[(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)(\mu\text{-}H)_3]$ (**4**) were also observed at higher field ($\delta = 2.43$ ppm).[10] The ^{13}C NMR signals of the pyridine ligand similarly appeared at significantly higher field ($\delta = 34.5$, 35.2, 35.7, 58.5, and 60.3 ppm).

The three sharp signals for the Cp* groups were observed at $\delta = 1.66$, 1.67, and 1.78 ppm. These shifts clearly demonstrate that the μ_3-pyridine ligand of **2** does not rotate on the NMR timescale. This finding is in contrast with the corresponding trimetallic μ_3-η^2:η^2:η^2-arene complex, which is fluxional through the motion of the μ_3-arene ligand.[11]

Heating of **1** in pyridine at 120 °C resulted in quantitative formation of **2** in 48 hours, whereas a face-capping benzene complex **4** was obtained in relatively low yield (32 %) under similar conditions in the analogous reaction of **1** with benzene.[10b] This difference implies that the initial coordination through the lone pair of electrons at the nitrogen atom is a crucial step for the formation of the μ_3-pyridine complex. However, the lone pair of electrons does not participate in the face-capping coordination, as confirmed by the formation of a μ_3-pyridinium complex **3** upon protonation.

Addition of an equimolar amount of $HBF_4{\cdot}OMe_2$ to **2** in diethyl ether immediately afforded a precipitate of the monocationic face-capping pyridinium complex $[(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}(C_5H_5NH)(\mu\text{-}H)_3]BF_4$ (**3**) in 62 % yield [Eq. (2)].[12] In the ^{1}H NMR spectrum of **3** in

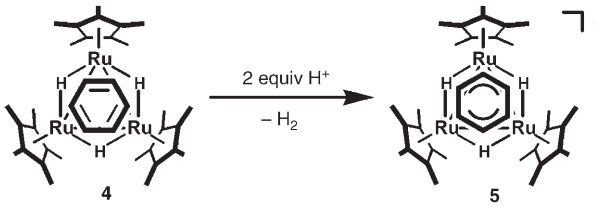


(2)

$[D_2]$dichloromethane, a broad signal from the NH group was observed at $\delta = 5.33$ ppm, which was diminished upon addition of D_2O. A stretching vibration assignable to the N–H bond appeared at 3256 cm^{-1} in the IR spectrum.

Treatment of **3** with a base, such as NaOMe, resulted in complete regeneration of **2**. When the protonation was performed by the use of deuterated tetrafluoroboric acid, a deuterium atom was incorporated only at the NH site. This observation shows that protonation of **2** did not proceed by way of an initial attack at the metal center, but by a direct attack at the nitrogen atom. This fact strongly supports the assertion that the lone pair of electrons was not involved in the bonding with the metal centers. Similar behavior has been observed in the protonation of a perpendicularly coordinated nitrile complex, $[(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}PhCN)(\mu\text{-}H)_2(\mu_3\text{-}H)]$, which resulted in formation of the cationic μ_3-iminoacyl complex $[(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}PhCNH)(\mu\text{-}H)_2(\mu_3\text{-}H)]^+$.[13]

In contrast, protonation of the corresponding μ_3-benzene complex **4** exclusively proceeded at the ruthenium center. A dicationic complex, $[(Cp^*Ru)_3(\mu_3\text{-}\eta^3\text{:}\eta^3\text{-}C_6H_6)(\mu\text{-}H)_3]^{2+}$ (**5**), was formed as a result of liberation of dihydrogen subsequent to protonation [Eq. (3)]. Thus, exclusive formation of the μ_3-



(3)

pyridinium complex is attributed to the presence of the lone pair of electrons at the nitrogen atom, and the cationic μ_3-pyridinium complex does not undergo further protonation at the ruthenium center.

The molecular structure of **3** was determined by an X-ray diffraction study (Figure 2).[9] The position of the nitrogen

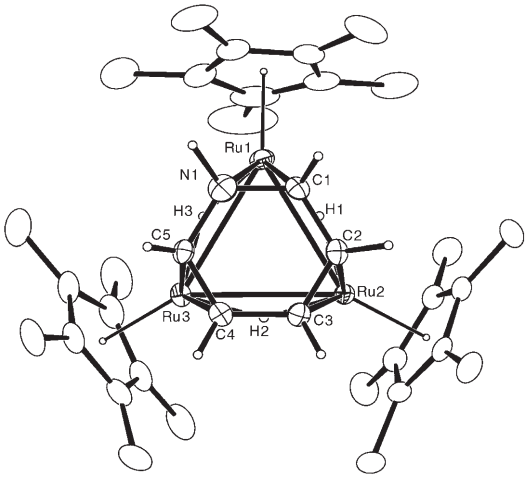


Figure 2. Molecular structure of $\mathbf{3}{\cdot}C_3H_8O$ with thermal ellipsoids at the 30 % level of probability. The BF_4^- ion and 2-propanol are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1-Ru2 3.0321(6), Ru2-Ru3 3.0273(8), Ru1-Ru3 3.0331(6), Ru1-N1 2.131(4), Ru1-C1 2.148(5), Ru2-C2 2.157(4), Ru2-C3 2.165(4), Ru3-C4 2.157(4), Ru3-C5 2.139(4), N1-C1 1.385(6), N1-C5 1.433(6), C1-C2 1.440(7), C2-C3 1.405(6), C3-C4 1.447(6), C4-C5 1.393(6); Ru2-Ru1-Ru3 59.884(17), Ru1-Ru2-Ru3 60.075(13), Ru1-Ru3-Ru2 60.041(14), C1-N1-C5 120.3(4), N1-C1-C2 120.5(4), C1-C2-C3 119.4(4), C2-C3-C4 119.8(4), C3-C4-C5 119.9(4), N1-C5-C4 120.1(4).

atom was determined on the basis of the hydrogen bond between the NH group and one of the fluorine atoms of the BF_4^- ion. The short H···F separation (1.99(5) Å) strongly suggests a hydrogen–fluorine bonding interaction (see the Supporting Information). This hydrogen atom was also observed by NMR spectroscopy. In the ^{19}F{^{1}H} NMR spectrum in $[D_2]$dichloromethane, two signals from the BF_4^- ion appeared at $\delta = -154.02$ and -153.96 ppm with an intensity

ratio of 1:3. All of the ^{1}H NMR signals of **3** become broader in a more polar solvent, such as acetone or methanol. This broadening is probably a result of an equilibrium between the hydrogen-bonded species and the solvent-separated ion pair.

Addition of a proton to the face-capping pyridine ligand did not cause considerable changes in the structure. The average of the "coordinated" C=C and C=N bond lengths (1.394(6) Å) and the average of the "uncoordinated" C–C and C–N bond lengths (1.440(7) Å) are comparable to those of **2**. Although the bond lengths between the ruthenium atoms and the coordinated carbon and nitrogen atoms differ only slightly (shortened by ca. 0.02 Å), a significant upfield shift of the signals of the pyridine ring was observed in the ^{13}C NMR spectrum. The pyridinium carbon atoms were observed at $\delta =$ 24.8, 25.6, 31.7, 39.4, and 44.3 ppm. These values are shifted upfield by about 10–20 ppm in comparison with those of **2**. The ^{1}H NMR signals of the μ_3-pyridinium ligand also exhibited a slight upfield shift ($\delta = 1.78$, 2.47, 2.59, 3.30, and 3.50 ppm) relative to those of **2**.

It is interesting that the ^{13}C NMR signals of the μ_3-pyridinium ligand underwent an upfield shift in spite of the reduction of the electron density. This shift implies that the cationic charge is localized mainly at the nitrogen atom, and the bonding interaction between the triruthenium core and the pyridinium ring would be considerably different from that of the neutral complex.

Density functional theory (DFT) calculations for the adsorbed pyridine ring on an MoS_2 catalyst with 25% hydrogen coverage demonstrated that the pyridinium ion was readily formed by the migration of hydrogen from the neighboring SH group, which interacts with an Mo edge more tightly than pyridine itself.[14] Strong poisoning of the hydrodesulfurization process by pyridine has been ascribed to the formation of a pyridinium ion. Thus, formation of **3** by protonation of **2** must be an appropriate model of an adsorbed pyridine molecule.

In summary, face-capping pyridine complex **2** was formed by the reaction of triruthenium complex **1** with pyridine. Compound **2** is the first example of a pyridine ligand that exhibits μ_3-η^2:η^2:η^2 coordination to a trinuclear complex. The face-capping pyridinium complex **3** was obtained upon protonation of **2**. These results reproduce the behavior of an adsorbed pyridine molecule on a metal surface.

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[8] A 20-mL glass tube equipped with a greaseless valve was charged with **1** (206.1 mg, 0.289 mmol) and toluene (10 mL). Pyridine (0.12 mL, 1.44 mol) was added, and the reaction mixture was heated at 100 °C for seven days. Toluene and the remaining pyridine were removed under reduced pressure. The residual solid was purified by the use of column chromatography on alumina with tetrahydrofuran. The second purple band containing **2** was collected, and the solvent was removed under reduced pressure. Complex **2** was obtained as a purple solid (123.0 mg, 0.155 mmol, 54% yield). ^{1}H NMR (400 MHz, [D$_6$]benzene, 23 °C, TMS): $\delta = -21.50$ (dd, ^2J(H,H) = 3.8, 3.4 Hz, 1H, RuH), −19.68 (dd, ^2J(H,H) = 4.6, 3.8 Hz, 1H, RuH), −19.65 (dd, ^2J(H,H) = 4.6, 3.4 Hz, 1H, RuH), 1.66 (s, 15H, Cp*), 1.67 (s, 15H, Cp*), 1.78 (s, 15H, Cp*), 2.36 (dd, ^3J(H,H) = 6.0, 4.4 Hz, 1H, C$^\beta$H), 2.42 (dd, ^3J(H,H) = 6.0, 4.4 Hz, 1H, C$^\beta$H), 2.52 (dd, ^3J(H,H) = 6.0, 6.0 Hz, 1H, C$^\gamma$H), 3.47 (d, ^3J(H,H) = 4.4 Hz, 1H, C$^\alpha$H), 3.60 ppm (d, ^3J(H,H) = 4.4 Hz, 1H, C$^\alpha$H); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]benzene, 23 °C, TMS): $\delta =$ 10.89 (C$_5$*Me*$_5$), 10.93 (C$_5$*Me*$_5$), 11.2 (C$_5$*Me*$_5$), 34.5 (C$^\beta$ or C$^\gamma$), 35.2 (C$^\beta$ or C$^\gamma$), 35.7 (C$^\beta$ or C$^\gamma$), 58.5 (C$^\alpha$), 60.3 (C$^\alpha$), 89.5 (*C*$_5$Me$_5$), 89.6 (*C*$_5$Me$_5$), 90.5 ppm (*C*$_5$Me$_5$).

[9] X-ray crystallography: All data were collected on a Rigaku R-Axis RAPID imaging plate diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at 153 K. Crystal data for **2**: orthorhombic, space group *Pbcn* (No. 57), $a = 10.8241(16)$, $b = 16.270(3)$, $c = 17.841(3)$ Å, $V = 3141.9(8)$ Å^3, $Z = 4$, $\rho_{calcd} =$

1.672 $Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 1.448\ mm^{-1}$; of the 36407 reflections that were collected, 5092 were unique ($R_{int} = 0.0221$), $R_1 = 0.0357$ [$I > 2\sigma(I)$], $wR_2 = 0.0952$ [$I > 2\sigma(I)$]. Crystal data for **3**·C_3H_8O: monoclinic, space group $P2_1/n$ (No. 14), $a = 16.880(3)$, $b = 14.785(2)$, $c = 17.401(4)$ Å, $\beta = 117.060(8)°$, $V = 3867.5(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.613\ Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 1.206\ mm^{-1}$; of the 44592 reflections that were collected, 11697 were unique ($R_{int} = 0.0740$), $R_1 = 0.0517$ [$I > 2\sigma(I)$], $wR_2 = 0.0998$ [$I > 2\sigma(I)$]. CCDC-617366 (**2**) and CCDC-617367 (**3**) 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.

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[12] A 50-mL Schlenk tube was charged with **2** (20.5 mg, 0.026 mmol) and diethyl ether (20 mL). $HBF_4{\cdot}OMe_2$ (3.2 μL, 0.026 mmol) was added with vigorous stirring at room temperature. A purple precipitate was immediately formed. After 30 min of stirring, the purple precipitate was separated by removing the supernatant and was washed four times with diethyl ether (5 mL). The residual solid was then dried under reduced pressure, and complex **3** was obtained as a purple solid (14.1 mg, 0.016 mmol, 62% yield). ^{1}H NMR (400 MHz, [D$_2$]dichloromethane, 23 °C, TMS): $\delta = -20.69$ (dd, ^2J(H,H) = 4.8, 3.0 Hz, 1H, RuH), −20.15 (dd, ^2J(H,H) = 4.8, 3.4 Hz, 1H, RuH), −19.67 (dd, ^2J(H,H) = 3.4, 3.0 Hz, 1H, RuH), 1.70 (s, 15H, Cp*), 1.71 (s, 15H, Cp*), 1.75 (s, 15H, Cp*), 1.78 (dd, ^3J(H,H) = 6.0, 4.4 Hz, 1H, C$^\beta$H), 2.47 (dd, ^3J(H,H) = 6.4, 4.4 Hz, 1H, C$^\beta$H), 2.59 (dd, ^3J(H,H) = 6.4, 6.0 Hz, 1H, C$^\gamma$H), 3.30 (d, ^3J(H,H) = 4.4 Hz, 1H, C$^\alpha$H), 3.50 (d, ^3J(H,H) = 4.4 Hz, 1H, C$^\alpha$H), 5.33 ppm (br s, $\Delta\nu_{1/2} = 16.4$ Hz, 1H, NH); ^{13}C{^{1}H} NMR (100 MHz, [D$_2$]dichloromethane, 23 °C, TMS): $\delta = 9.8$ (C_5Me_5), 9.9 (C_5Me_5), 10.1(C_5Me_5), 24.8 (C$^\beta$ or C$^\gamma$), 25.6 (C$^\beta$ or C$^\gamma$), 31.7 (C$^\beta$ or C$^\gamma$), 39.4 (C$^\alpha$), 44.3 (C$^\alpha$), 91.3 (C_5Me$_5$), 92.2 (C_5Me$_5$), 95.6 ppm (C_5Me$_5$); ^{19}F{^{1}H} NMR (376 MHz, [D$_2$]dichloromethane, 23 °C, $CFCl_3$): $\delta = -154.02$ (BF_4), −153.96 ppm (BF_4).

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