processed by using SCALEPACK. The structure was solved using the teXsan system and refined by full-matrix least-squares. (The programs DENZO and SCALEPACK are available from Mac Science Co., Z. Otwinowski, University of Texas, Southwestern Medical Center. The program teXsan is available from Rigaku Co.) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-141764, -141765, and -141766. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Diels–Alder Type Addition of 1,3-Dienes to a Disulfide Bridging Ligand in Diruthenium Complexes**

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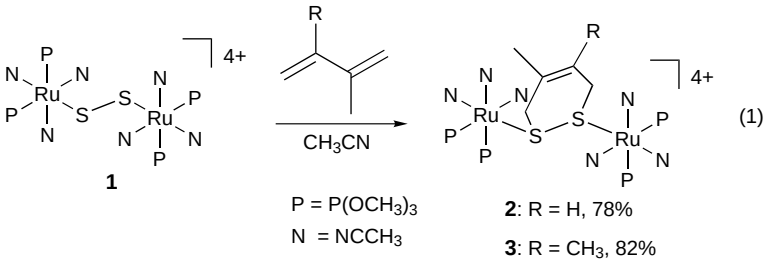
Carbon–sulfur bond formation and C–S bond cleavage reactions have been the focus of research for several years because of their relevance to the biologically related metallo-sulfide proteins, the industrially important hydrodesulfurization (HDS) process, and the organic synthesis of sulfur-containing compounds.[1] Reactions of transition metal sulfides with unsaturated organic substrates, such as alkynes, alkenes, and nitriles, have been reported, in which [2+3] cycloadditions occur between $M(S)_2$ and C–X double or triple bonds (X = C or N) to give metalacycles.[2] The addition of olefins to a bridging sulfide ligand in the dimolybdenum complex has also been reported.[3] Nevertheless, to the best of our knowledge, the reaction of transition metal sulfides with dienes has not been reported. It is well known that in the HDS process thiophene is converted into butadiene and hydrogen sulfide.[3d, 4] As a reverse reaction of the HDS process, the treatment of dienes with sulfur is especially noteworthy on transition metal centers. In our recent studies on the Ru_2S_2 core chemistry in the disulfide-bridged diruthenium complexes,[5] we found that $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2(\mu\text{-}S_2)]^{4+}$ (**1**, as CF_3SO_3 salt) reacts with unsaturated organic molecules, such as ketones and terminal olefins, to form C–S bonds on the disulfide ligand via the C–H bond activation reaction.[6] These are very rare processes and only one analogous C–S bond formation reaction can be found in the literature: The reaction of acetone with a terminal sulfide ligand,[7] which, however, seems to have been found by chance and no systematic study was carried out. Through our recent study of new reactions, we have found that the S_2 ligand in the electron-deficient Ru^{III} complex **1** and its analogues is activated to achieve C–H bond splitting both through electronic and steric effects. In our previous reports, we suggested that the addition of a C–H bond to the S=S double bond is the key step in the C–H bond activation process of acetone and monoolefins.[6b,c] In the present report, we demonstrate directly the double bond character of the S=S bond between the two Ru centers by isolating the [2+4] cycloaddition products from the reaction of **1** with dienes.

Treatment of **1** with a conjugated diene, such as isoprene or 2,3-dimethylbutadiene in CH_3CN at room temperature, resulted in the formation of a pale yellow solution, from which $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2\{\mu\text{-}SCH_2C(R)=C(CH_3)\text{-}CH_2S\}]^{4+}$ (**2**, as CF_3SO_3 salt, R = H, 78%; **3**, as CF_3SO_3 salt, $R = CH_3$, 82%) was obtained after standard work-up [Eq. (1)]. When the complex **1** was treated with 1,3-pentadiene, a similar color change was observed, however, the product was a mixture according to the ^1H NMR spectrum. Separation of these products was not successful. Furthermore, the reaction of **1** with 2,4-hexadiene was also examined but no sign of the C–S bond formation was observed: Only $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2(\mu\text{-}S_2)](CF_3SO_3)_3$[5a] was recovered. Therefore, it seems that the C–S bond formation reaction of **1** needs at least one of the two double bonds at the terminal position. The structure of **3** was determined by X-ray diffraction, as shown in Figure 1.[8, 10]



Analogously, the reaction of the dicationic complex $[\{Ru[P(OCH_3)_3]_2(CH_3CN)\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]^{2+}$ (**4**, as CF_3SO_3 salt) with 2,3-dimethylbutadiene gave $[\{Ru[P(OCH_3)_3]_2(CH_3CN)\}_2\text{-}\{\mu\text{-}SCH_2C(CH_3)=C(CH_3)CH_2S\}(\mu\text{-}Cl)_2]^{2+}$ (**5**, as CF_3SO_3 salt)

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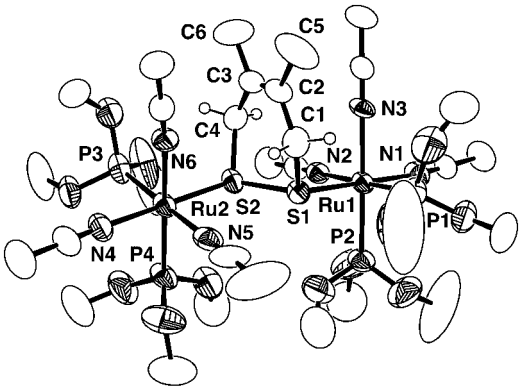
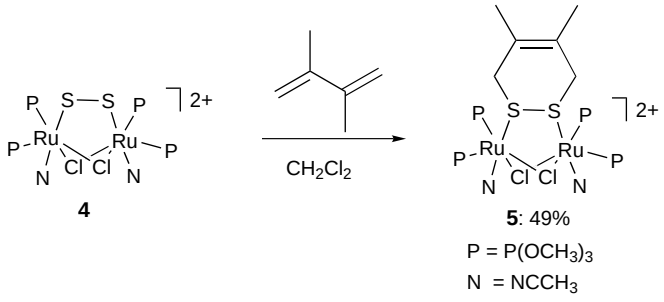


Figure 1. Structure of the cation **3** drawn at a 50% probability level. Methyl H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1-S1 2.3629(18), Ru2-S2 2.3707(18), Ru1-P1 2.257(2), Ru1-P2 2.256(2), Ru2-P3 2.275(3), Ru2-P4 2.277(2), S1-S2 2.099(3), S1-C1 1.827(8), S2-C4 1.808(8), C1-C2 1.517(14), C2-C3 1.295(14), C3-C4 1.518(13), C2-C5 1.511(15), C3-C6 1.520(15); Ru1-S1-S2 112.77(9), Ru2-S2-S1 111.18(9), Ru1-S1-C1 111.8(3), Ru2-S2-C4 113.1(3), S1-C1-C2 121.0(6), S2-C4-C3 121.4(6), C1-C2-C3 126.3(8), C1-C2-C5 108.9(10), C5-C2-C3 124.7(11), C2-C3-C4 126.1(8), C4-C3-C6 107.9(10), C2-C3-C6 125.9(10).

as yellow crystals in 49% yield [Eq. (2)]. The structure of **5** was also determined by X-ray diffraction, as shown in Figure 2.[9, 10]



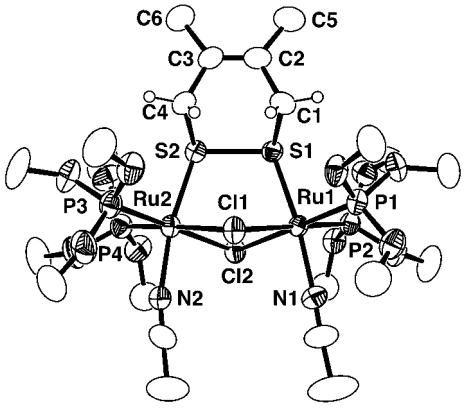


Figure 2. Structure of the cation **5** drawn at a 50% probability level. Methyl H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1-S1 2.317(2), Ru2-S2 2.316(2), Ru1-P1 2.230(2), Ru1-P2 2.233(2), Ru2-P3 2.236(2), Ru2-P4 2.231(2), Ru1-Cl1 2.468(2), Ru1-Cl2 2.472(2), Ru2-Cl1 2.484(2), Ru2-Cl2 2.480(2), S1-S2 2.176(3), S1-C1 1.821(8), S2-C4 1.825(8), C1-C2 1.519(11), C2-C3 1.304(12), C3-C4 1.527(12), C2-C5 1.507(12), C3-C6 1.508(11); Ru1-S1-S2 108.12(10), Ru2-S2-S1 107.27(10), Ru1-S1-C1 114.4(3), Ru2-S2-C4 114.6(3), S1-C1-C2 110.3(6), S2-C4-C3 110.4(6), C1-C2-C3 117.6(8), C1-C2-C5 116.0(8), C5-C2-C3 126.4(9), C2-C3-C4 118.4(8), C4-C3-C6 116.3(8), C2-C3-C6 125.3(9).

According to the structures of **3** and **5**, the C2–C3 bond distances (1.295(14) (**3**) and 1.304(12) Å (**5**)) fall in the range of C=C double bond distances, whereas the C1–C2 and C3–C4 distances (1.517(14) – 1.527(12) Å) are comparable to a C–C single bond. Through the C–S bond formation process, the bond multiplicities in the diene moiety are changed. The S1–S2 bond distances (2.099(3) (**3**) and 2.176(3) Å (**5**)) are considerably longer than the corresponding ones in their respective starting complexes (1.933(11) (**1**) and 1.973(7) Å (**4**)). The C–S bond distances (1.808(8) – 1.827(8) Å) are comparable to those known.[6a, 11] A significant difference is observed between **3** and **5** in the conformations of the C_4S_2 six-membered ring (chair for **3**, boat for **5**) and the bridging mode of the S_2 ligand between the two Ru centers (*trans* for **3** and *cis* for **5**). The C1-S1-S2-C4 torsion angles (48.3(4)° (**3**) and 0.4(4)° (**5**)) also reflect the conformation differences. It is noteworthy that **3** crystallizes in the noncentrosymmetric space group *Pn*. This is due to the existence of the two chiral sulfur atoms, whose *R*/*R* and *S*/*S* configurations alone are in the single crystal lattice. As the diasteromers of *R*/*S* (or *S*/*R*) were not found in the NMR spectrum of **3**, the ring formation reaction is diastereospecific.

We reported previously that 1-pentene reacts with **1** and forms a C_3S_2 five-membered ring through the C–H bond activation reaction.[6c] We also extended the reaction of terminal olefins to **4**, however, no reaction took place. Therefore, terminal olefins react only with the RuSSRu core of the open structure, such as in **1**, to form the five-membered C_3S_2 ring via a C–H activation reaction and do not react with **4**, which has a closed RuSSRu core. In contrast, dienes can readily react with both **1** and **4** to form two C–S bonds of the C_4S_2 ring. The mechanism of these reactions involves no C–H bond activation reaction but rather another reaction type, as explained later. (2)

The chemistry of a multiple bond between heteroatoms has been extensively studied.[12] In one of the typical reactions, the unstable heteroatomic multiple bond is trapped by an appropriate conjugated diene.[13] The reaction is regarded as of the Diels – Alder type [2+4] cycloaddition, in which the X=Y bond (X, Y = heteroatoms) acts as a dienophile. Neutral S_2 is a known but, as yet, uncharacterized species.[12] Several precursors types and preparative methods for disulfur have been reported, as well as its reactions with dienes. On the other hand, the S_2 units in **1** or **4** are stabilized by the two Ru moieties but they still exhibit reactivity towards dienes to give the [2+4] cycloadduct and the reaction suggests the double bond character of the S_2 ligand. With regard to the electronic structure of the $RuSSRu^{4+}$ core, three types of formulation have been suggested in the literature, namely a) two Ru^{III} centers bridged by a disulfide S_2^{2-}, b) two Ru^{II} centers bridged by a singlet disulfur S_2^0, or c) an Ru^{II} center and an Ru^{III} center bridged by a $S_2^{-\bullet}$ (supersulfide). Our cycloaddition reaction suggests that the type (b) contribution is significantly involved. In contrast, the structural analyses and an electrochemical study show that the major contribution of $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$ [14, 15] is type (c). The electronic structure would be dependent on the electron densities on

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the Ru centers, which are determined by the ligands. Similar reactions of 2,3-dimethylbutadiene with $[Cp(Ph_3P)RuSSRu(PPh_3)Cp]^{2+}$,[16] and the PMe_3 analogues of **1** and **4**[17] did not take place under the similar condition. Only the disulfur in **1** and **4** are sufficiently activated to react with dienes. The stabilization and activation of S_2 seem to depend on the donating abilities of the ligands on the Ru centers. The steric effect of the bond angles within the RuSSRu core with respect to the S_2 may be small, since both **1** (*trans* type) and **4** (*cis* type) can react with dienes. In the reactions, it may seem possible that the C=C bond coordinates to the Ru center by replacing CH_3CN, as suggested previously in the monoolefin reactions.[6c] However, even if such diene substitution with CH_3CN occurs in **4**, the diene molecule is located away from the S_2 and the following reaction would be impossible. Therefore, the mechanism involving coordination of the C=C double bond to the Ru atom can be ruled out and a Diels–Alder-type mechanism is supported.

We can successfully show that the stable disulfide ligands in **1** and **4** can react with dienes via a Diels–Alder reaction. The reaction shows that the S_2 bond has a double bond character, which is noteworthy, since only in situ prepared unstable S_2 was used in all the previous Diels–Alder reactions of S_2 with dienes.

Experimental Section

All experiments were carried out under a dry atmosphere of nitrogen, using standard Schlenk techniques or in a dry N_2 box. Dry solvents were purchased from Kanto chemical. CD_3CN was dried over CaH_2 and then trap-to-trap distilled prior to use. The NMR spectra were recorded on a Lambda 270 spectrometer (JEOL) operating at 270 MHz for ^{1}H, 109 MHz for ^{31}P, and 68 MHz for ^{13}C. The chemical shifts are reported in δ units (ppm) downfield from Me_4Si for ^{1}H and ^{13}C, and H_3PO_4 (85%, external reference) for ^{31}P. Elemental analyses were carried out on a PE 2400II Elemental Analyzer (Perkin–Elmer).

2 and **3**: **2** and **3** were prepared similarly, thus only the synthesis of **2** is described here. Isoprene (1 mL) was added to a CH_3CN (2 mL) solution of $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2(\mu\text{-}S_2)]^{4+}$ (**1**, as CF_3SO_3 salt; 33.9 mg, 0.021 mmol). The immediate color change from dark blue to pale yellow was observed and the solution was stirred for 1 h at room temperature. Addition of Et_2O (8 mL) resulted in the formation of a pale yellow precipitate and the supernatant solution was removed via syringe. The residue was again dissolved in CH_3CN (0.5 mL) and slow addition of DME (ca. 3 mL) gave the pale yellow crystals of $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2\{\mu\text{-}SCH_2C(CH_3)=CHCH_2S\}]^{4+}$ (**2**, as CF_3SO_3 salt; 27.5 mg, 0.016 mmol, 78%). Elemental analysis for $Ru_2S_6P_4C_{33}H_{62}N_6O_{24}F_{12}$: calcd: C 23.69, H 3.73, N 5.02; found: C 23.69, H 3.61, N 4.94. ^{1}H NMR (270 MHz, CD_3CN): $\delta = 1.9$ (s, 3H; $SCH_2C(CH_3)$), 2.48 (s, 6H; CH_3CN *trans* to S), 3.15 (d, $^2J(H,H) = 17.6$ Hz, 1H; eq $SCH_2C(CH_3)$), 3.40 (m, 1H; eq SCH_2CH), 3.85 (m, 36H; $P(OCH_3)_3$), 3.99 (d, 1H; ax $SCH_2C(CH_3)$), 4.11 (m, 1H; ax SCH_2CH), 5.99 (m, 1H; SCH_2CH). ^{13}C{^{1}H} NMR (68 MHz, CD_3CN): $\delta = 4.5$ (CH_3CN trans to S), 25.8 ($SCH_2C(CH_3)$), 34.9 (SCH_2CH), 36.2 ($SCH_2C(CH_3)$), 55.8 (m; $P(OCH_3)_3$), 117.5 (SCH_2CH), 130.3 ($SCH_2C(CH_3)$). ^{31}P{^{1}H} NMR (109 MHz, CD_3CN): $\delta = 124.8$ (d, $^2J(P,P) = 78$ Hz, 1P), 125.6 (d, 1P), 124.9 (br. s, 2P).

$[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2\{\mu\text{-}SCH_2C(CH_3)=C(CH_3)CH_2S\}]^{4+}$ (**3**, as CF_3SO_3 salt) was prepared from treatment of **1** (124 mg, 0.077 mmol) with 2,3-dimethylbutadiene (0.1 mL). Yield: 107 mg, 0.063 mmol, 82%. Elemental analysis for $C_{34}H_{64}F_{12}N_6O_{24}P_4Ru_2S_6$: calcd: C 24.20, H 3.82, N 4.98; found: C 24.23, H 3.80, N 4.95. ^{1}H NMR (270 MHz, CD_3CN, 40 °C): $\delta = 1.92$ (s, 6H; $SCH_2C(CH_3)$), 2.50 (s, 6H; CH_3CN trans to S), 3.20 (d, $^2J(H,H) = 16.5$ Hz, 2H; eq SCH_2), 3.87 (d, $^3J(P,H) = 10.8$ Hz, 36H; $P(OCH_3)_3$), 4.12 (d, 2H; ax SCH_2). ^{13}C{^{1}H} NMR (68 MHz, CD_3CN, RT): $\delta = 4.5$ (CH_3CN trans to S), 20.9 ($SCH_2C(CH_3)$), 37.8 (SCH_2), 55.8 (m; $P(OCH_3)_3$), 128.6 ($SCH_2C(CH_3)$). ^{31}P{^{1}H} NMR (109 MHz, CD_3CN): $\delta = 124.7$, 125.6 (d, $^2J(P,P) = 75$ Hz)

5: To a CH_3CN (3 mL) solution of $[\{Ru(P(OCH_3)_3)_2Cl\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$ (90 mg, 0.1 mmol), $AgCF_3SO_3$ (54 mg, 0.2 mmol) was added and the solution was stirred for 3 h at room temperature. The resulted green solution was centrifuged to remove the AgCl and evaporated to dryness. The residue was washed with Et_2O (8 mL) and dried under reduced pressure to give the crude product of $[\{Ru[P(OCH_3)_3]_2(CH_3CN)\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]^{2+}$ (**4**, as CF_3SO_3 salt; 111 mg, 0.091 mmol, 91%). This material was again dissolved in CH_2Cl_2 (1 mL) and 2,3-dimethylbutadiene (0.5 mL) was added. An immediate color change from green to yellow was observed. To the reaction mixture, Et_2O (16 mL) was added to give a gummy solid after 3 h with stirring. The supernatant was removed and dried. The residue was recrystallized from CH_2Cl_2/DME to give yellow needles of $[\{Ru[P(OCH_3)_3]_2(CH_3CN)\}_2\{\mu\text{-}SCH_2C(CH_3)=C(CH_3)CH_2S\}(\mu\text{-}Cl)_2]^{2+}$ (**5**, as CF_3SO_3 salt; 53 mg, 0.045 mmol, 49% yield based on **4**). Elemental analysis for $C_{24}H_{52}N_2Cl_2F_6O_{18}P_4Ru_2S_4$: calcd: C 22.24, H 4.04, N 2.16; found: C 22.41, H 4.09, N 2.12. ^{1}H NMR (270 MHz, CD_3CN, −30 °C): $\delta =$ 1.88 (s, 6H; $SCH_2C(CH_3)$), 2.46 (s, 6H; CH_3CN trans to S), 3.44 (d, $^2J(H,H) = 14.0$ Hz, 2H; SCH_2), 3.74 (dd, $J(P,H) = 8.9$ Hz, 10.2 Hz, 36H; $P(OCH_3)_3$), 4.01 (d, 2H; SCH_2). ^{31}P{^{1}H} NMR (109 MHz, CD_3CN): $\delta =$ 130.1, 131.6 (d, $^2J(P,P) = 75$ Hz).

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[8] Crystal data for **3**: $C_{34}H_{64}F_{12}N_6O_{24}P_4Ru_2S_6$, $F_w = 1687.29$, pale yellow plates, monoclinic, space group *Pn*, $a = 12.7169(11)$, $b = 14.4751(13)$, $c = 18.3891(16)$ Å, $\beta = 96.001(2)°$, $V = 3366.5(5)$ Å^3, $Z = 2$, $\rho_{calc} = 1.665$ g cm^{-1}, $R1 = 0.0642$; $wR2 = 0.1558$ for 9187 reflections ($F_0^2 > 2\sigma(F_0^2)$), $R1 = 0.0830$; $wR2 = 0.1690$ for all 12361 reflections.

[9] Crystal data for **5**: $C_{24}H_{52}Cl_2F_6N_2O_{18}P_4Ru_2S_4$, $F_w = 1295.84$, yellow needles, monoclinic, space group $P2_1/c$, $a = 9.1280(4)$, $b = 22.4015(10)$, $c = 24.6537(11)$ Å, $\beta = 96.2770(10)°$, $V = 5011.0(4)$ Å^3, $Z = 4$, $\rho_{calc} = 1.718$ g cm^{-1}, $R1 = 0.0584$; $wR2 = 0.1484$ for 5456 reflections ($F_0^2 > 2\sigma(F_0^2)$), $R1 = 0.1436$; $wR2 = 0.1991$ for all 11514 reflections.

[10] Diffraction data of complexes **3** and **5** were collected on a SMART 1000 CCD diffractometer (Bruker) using $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). All the intensity data were processed with the SAINT plus program package. Absorption corrections were applied

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to the integrated intensity with a SADABS program. The structure solution was performed on a SHELXTL software package. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142966 and -142967. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] The C–S bond distances of structurally characterized complexes in our laboratory are varied from 1.81 to 1.89 Å.

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Regiospecific Hydride Transfer from *cis*-[Ru(bpy)$_2$(CO)(CHO)]$^+$ to NAD$^+$ Model Compounds: A Model for Enzymatic Reactions by Aldehyde Dehydrogenases**

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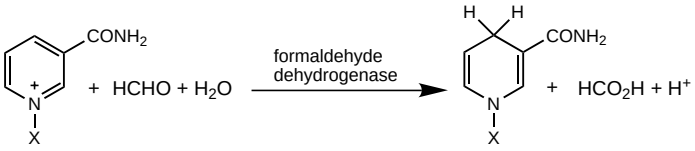
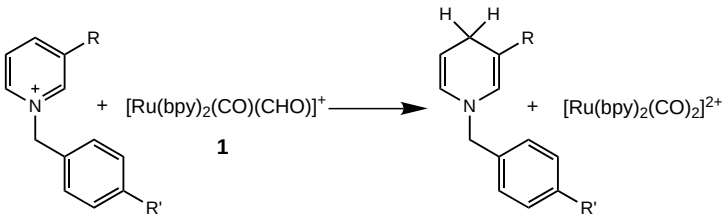
The nicotinamide adenine dinucleotide coenzyme NAD$^+$ is required for the clearance of potentially toxic aldehydes by the enzymes of the aldehyde dehydrogenase (ALDH) family.[1, 2] For example, the oxidation of formaldehyde by NAD$^+$ occurs in the presence of the formaldehyde dehydrogenase (EC 1.2.1.46.) to give formic acid and 1,4-NADH (Scheme 1).[3] A crucial point of this reaction is the direct and



Scheme 1. The oxidation of formaldehyde by NAD$^+$ in the presence of formaldehyde dehydrogenase. For clarity, only the pyridine ring of NAD$^+$ and the 1,4-dihydropyridine ring of NADH are shown; the remainder of the molecule in each case is represented by X.

regiospecific hydrogen transfer from the carbonyl carbon of the aldehyde to the 4-position of the pyridinium ring of NAD$^+$.[4] In nonbiological systems, however, only a few nonenzymatic models for this important biological reaction have been reported so far.[5] Herein we report the regiospecific reduction of NAD$^+$ model compounds **2a–e** by a ruthenium formyl complex *cis*-[Ru(bpy)$_2$(CO)(CHO)]PF$_6$ (**1**; bpy = 2,2′-bipyridine) which acts as a mimic of the formaldehyde dehydrogenase reaction.

In a typical run, the reaction of **1** (7.6 mmol) with **2a** (11.4 mmol) was carried out in CD_3CN (0.75 mL) at 0 °C under an argon atmosphere in dim light, and the progress of the reaction was monitored by ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopy. Within a few minutes, 1-benzyl-1,4-dihydronicotinamide (**3a**) and an equimolecular amount of *cis*-[Ru(bpy)$_2$(CO)$_2$]$^{2+}$ were produced in a quantitative yield based on the quantity of **1** used in the reaction (Scheme 2). The other isomers of dihydronicotinamide, that is, the 1,2-dihydro and 1,6-dihydro forms, were not detected at all.



Scheme 2. The reduction of NAD$^+$ models **2a–e** by the ruthenium complex **1**. For respective R and R′ groups, see Table 1. For reaction conditions, see text.

Other NAD$^+$ models with various electron-withdrawing groups at the 3-position were also regioselectively reduced by **1** to give the corresponding 1,4-dihydro forms (Scheme 2). Table 1 contains a summary of the results of the reactions, together with the reduction potentials of **2a–e**. The reductions of **2a–d** were completed within 15 min along with the quantitative formation of the corresponding 1,4-dihydro forms. In the case of **2e**, the reaction was negligible at 0 °C but occurred significantly at 25 °C to result in selective formation of **3e**, albeit in lower yield than was obtained from the other NAD$^+$ models.

In order to identify the hydrogen origin for the selective reduction of **2a–e**, isotope experiments were carried out by two methods. The reduction of **2a** with *cis*-

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