Hydrogen Release

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Ruthenium Complexes Carrying Hydride, Dihydrogen, and Phosphine Ligands: Reversible Hydrogen Release**

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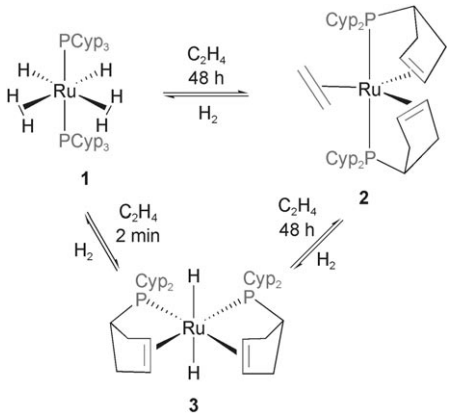
The widespread use of dihydrogen as an energy carrier for on-board applications is an important challenge for economical and environmental issues.[1,2] The lack of efficient hydrogen-storage devices has stimulated the search for new systems.[3,4] During the last decade, inorganic hydrides have been the subject of considerable interest, especially light hydride materials such as alanates, boronates, and metallic alloys.[5] Selective activation and functionalization of alkanes is also a continuing area of interest,[6,7] and efficient production of dihydrogen through catalyzed dehydrogenation of abundant hydrocarbons would be very valuable. An attractive goal is to combine inorganic hydrides and organic compounds as a source of hydrogen materials. Very recently, we reported the synthesis and characterization of a new bis(dihydrogen) complex $[RuH_2(H_2)_2(PCyp_3)_2]$ (**1**; Cyp = cyclopentyl), stabilized by two tricyclopentylphosphine ligands.[8] Complex **1**, which displays six coordinated hydrogen atoms and cycloalkyl substituents on the phosphine ligands, seemed a good model for dehydrogenation studies. We report herein a facile and reversible hydrogen release from **1**. Complex **1** can release up to ten hydrogen atoms, ultimately forming a new zero-valent ruthenium complex. Our study includes a comparison with the analogous complex $[RuH_2(H_2)_2(PCy_3)_2]$ (**A**; Scheme 2) that incorporates tricyclohexylphosphine ligands,[9] and demonstrates that **1** displays unique properties toward intramolecular dehydrogenation.

Treatment of a pentane solution of **1** with ethylene (3 bar) at room temperature leads to the formation of a new Ru^0 complex $[Ru\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2(\eta^2\text{-}C_2H_4)]$ (**2**; Scheme 1). Complex **2** has been fully characterized by NMR spectroscopy and by a single-crystal X-ray diffraction study. The coordination geometry around the ruthenium center is approximately trigonal-bipyramidal with the two phosphorus atoms in the axial positions (Figure 1). One coordinated ethylene ligand and two cyclopentenyl fragments are in the equatorial plane. The dehydrogenation of one cyclopentyl ring on each phosphine ligand, through C–H activation, is confirmed by short C=C bond lengths (C3–C4 1.432(4) Å, C6–C7 1.415(4) Å) together with Ru–C distances typical for olefin coordination (av 2.22 Å). The coordinated ethylene ligand is characterized by a C11–C12 bond length of 1.390(4) Å with Ru–C distances of 2.230(3) Å and 2.234(3) Å. The ^{1}H NMR spectrum of **2** consists of four signals of equal intensity at $\delta = 4.37$ and 3.34 ppm for the cyclopentenyl protons and at $\delta = 3.22$ and 2.55 ppm for the ethylene ligand with a AA′BB′ pattern upon ^{31}P decoupling. Evidence for η^2-C_5H_7 ($\delta = 52.34$, 50.24 ppm) and η^2-C_2H_4 ($\delta =$ 40.47 ppm) ligands is provided by ^{13}C NMR and HSQC experiments.



Scheme 1. Reversible dihydrogen release with tricyclopentylphosphine ligands.

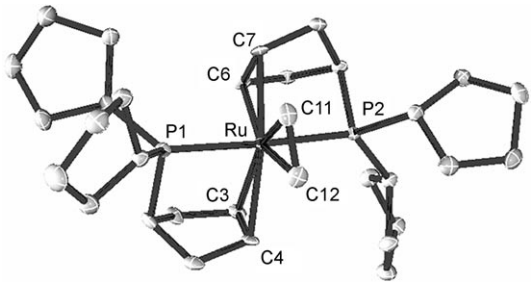


Figure 1. Structure of **2**. Thermal ellipsoids are set at 50% probability.

Formation of **2** contrasts remarkably with the results we have previously obtained by performing a similar experiment with the analogous tricyclohexylphosphine complex $[RuH_2(H_2)_2(PCy_3)_2]$ (**A**; Scheme 2).[9] In that case, only one cyclohexyl ring was partially dehydrogenated, thus leading to a hydrido ethylene complex $[RuH\{PCy_2(\eta^3\text{-}C_6H_8)\}(\eta^2\text{-}C_2H_4)(PCy_3)]$ (**B**) in which the ruthenium center has remained in the formal oxidation state II. It was necessary to use a bulky

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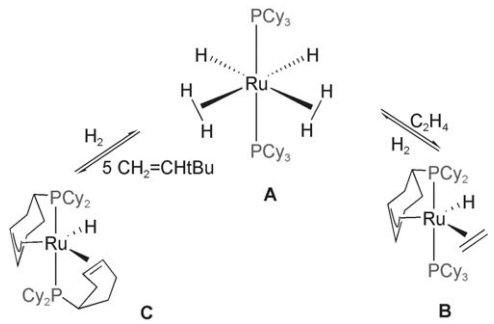


Scheme 2. Comparison with tricyclohexylphosphine ligands.

olefin such as $CH_2{=}CHtBu$ to partially dehydrogenate another cyclohexyl ring, leading ultimately to the formation of $[RuH\{PCy_2(\eta^3\text{-}C_6H_8)\}\{PCy_2(\eta^2\text{-}C_6H_9)\}]$ (**C**).

To trap a putative intermediate during the dehydrogenation process, the reaction of **1** with ethylene was performed under the same conditions as described above, but ethylene pressure was maintained for only 2 min. Ethane was identified in the reaction mixture. After work up, colorless crystals suitable for X-ray diffraction analysis were collected. As for **2**, the molecular structure of $[RuH_2\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2]$ (**3**; Figure 2) shows the dehydrogenation of one cyclopentyl

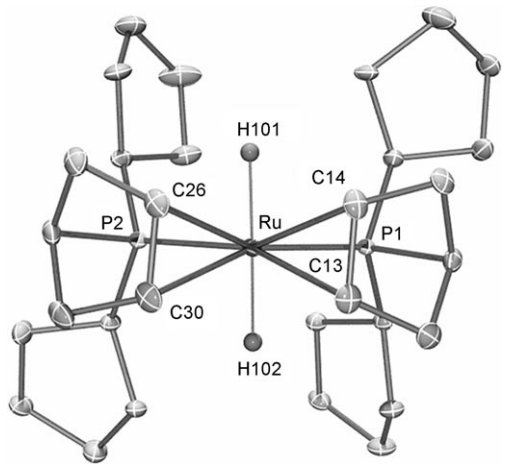
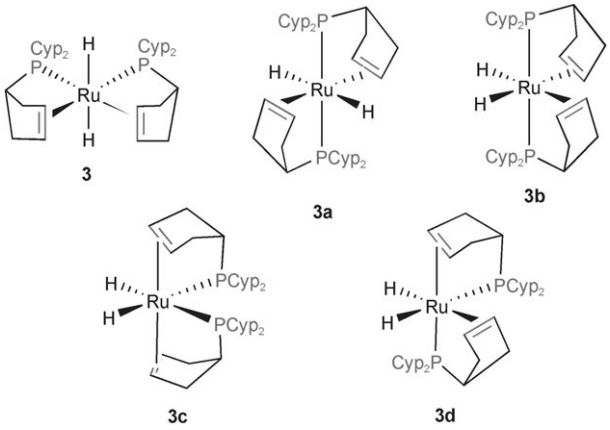


Figure 2. Structure of **3**. Thermal ellipsoids are set at 50% probability.

ring of each phosphine ligand. The two phosphine–olefin ligands are in a *cis* orientation with a P-Ru-P angle of 107.25(2)°. The coordinated C–C double bonds are characterized by short C–C bond lengths (C26–C30 1.410(3) Å, C13–C14 1.416(3) Å). The quality of the data allowed the location of two hydride ligands in a *trans* orientation with a H-Ru-H angle of 151°.

Upon dissolving the crystals of **3** in C_6D_6, the ^1H NMR spectrum (recorded immediately at room temperature) showed two hydride resonances as one triplet at $\delta = -5.27$ ppm ($J_{HP} = 23$ Hz) and one broad signal at $\delta = -9.12$ ppm ($\Delta\nu_{1/2} = 27$ Hz) in an approximately 2:3 ratio. The same spectrum and ratio were obtained from the crude solution in C_6D_6 after the pentane was removed under vacuum. On the basis of NMR data and X-ray crystallography on **3**, the two species are formulated as two isomers of $[RuH_2\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2]$. All our attempts to characterize the second isomer by X-ray diffraction were unsuccessful. The same parameters were obtained for all the crystals we tested randomly. The ^1H NMR chemical shift at about $\delta = -5$ ppm is assigned to **3**, in agreement with a *trans* arrangement of two hydride ligands, as found in other *trans*-dihydride ruthenium complexes.[10,11] The equilibrium was studied as a function of the temperature in the range 293–313 K to prevent thermal decomposition. A van't Hoff plot for the conversion of **3** (see the Supporting Information) yielded an endothermic ΔH value of 6.1 ± 0.4 kJ mol^{-1} and a ΔS value of 27 ± 23 J K^{-1} mol^{-1}. Variable low-temperature ^1H NMR spectra revealed an exchange process. The triplet at $\delta = -5.27$ ppm remained unchanged at all temperatures, but decoalescence was observed at 215 K for the signal at $\delta = -9.12$ ppm, leading at 183 K to two broad signals of equal intensity at $\delta = -6.72$ ppm ($\Delta\nu_{1/2} = 59$ Hz) and $\delta = -11.56$ ppm ($\Delta\nu_{1/2} = 55$ Hz). This process is characterized by a $\Delta G^{\neq}$ value of 36.7 kJ mol^{-1} at 215 K. Five different isomers can be proposed as shown in Scheme 3. The structures with a hydride ligand



Scheme 3. Isomers of $[RuH_2\{PCyp_2(\eta^2\text{-}C_5H_7)\}]$.

trans to phosphorus as in **3c** and **3d** can be ruled out on the basis of the small J_{HP} values. We tentatively propose that the signals at $\delta = -6.72$ and -11.56 ppm correspond to isomers **3a** and **3b**, respectively, in rapid equilibrium at room temperature. Isomerization between *cis* and *trans* dihydrides has been reported in a few cases in ruthenium systems.[10,11] DFT calculations will be performed to gather more information on the isomeric structures and on the exchange process, presumably through successive pseudo rotation steps.

We were then interested in determining the reversibility of the dehydrogenation process. Complete conversion of **2** into the starting complex **1** was achieved within 150 min by exposing a $[D_{12}]$cyclohexane solution of **2** to 1 bar of H_2 at room temperature. It is significant that **3** and its isomers are the only species detected during the reverse process, as monitored by ^1H NMR and ^{31}P NMR spectroscopy.

In summary, we have observed an easy partial dehydrogenation of the phosphine ligands in **1**, leading in a first step to an equilibrium between dihydride complexes. A subsequent dehydrogenation process leads to a new Ru^0 complex. Ten hydrogen atoms have thus been removed from **1**, which represents 1.71% of the weight of the complex. We have demonstrated that the process is fully reversible under very mild conditions. Complex **1** can thus serve as a model for hydrogen storage.[12–14] We are currently studying reversible dehydrogenation processes in the solid state.[15] Moreover, the easy access to the new Ru^0 species opens a new area of chemistry with respect to functionalization of the phosphorus ligands and to catalytic applications. Very recently, Weller and co-workers found a similar dehydrogenative pathway of a $PCyp_3$ ligand in a series of rhodium complexes.[16] Such a reaction thus tends to be rather general and demonstrates that phosphine ligands such as $PCyp_3$ act as versatile ligands.

Experimental Section

All reactions and manipulations were conducted by using standard Schlenk, Fischer–Porter bottle, and dry-box techniques. Solvents were dried by distillation over standard reagents and stored under argon. All NMR solvents were dried and stored in an argon-filled dry box. ^1H, ^{31}P, ^{13}C NMR were recorded on Brucker AV 500 and AV 300 spectrometers. ^1H and ^{13}C NMR chemical shifts are referenced using the chemical shifts of residual proton solvent resonances. The $^{31}P\{^1H\}$ NMR spectra were referenced to external H_3PO_4. $[RuH_2(H_2)_2(PCyp_3)_2]$ was synthesized according to the literature method.[9] $PCyp_3$ was used as received and stored under argon in the dry box.

2: $[RuH_2(H_2)_2(PCyp_3)_2]$ (63.0 mg, 0.108 mmol) was introduced in a Fischer–Porter bottle and pentane (5 mL) was added under argon. The solution was pressurized with 3 bar of ethylene for 48 h. A white solid began to precipitate after a few hours. The pentane volume was reduced to 2 mL and the solution was removed by cannula. The solid was dried rapidly under vacuum. The purity of the resulting solid was verified by NMR. Compound **2** (42.0 mg, 0.070 mmol) was isolated in 65% yield. X-ray diffraction quality crystals of **2** were obtained from a solution of $[RuH_2(H_2)_2(PCyp_3)_2]$ under 3 bar of ethylene, which was kept at low temperature (−34 °C) for 4 days. Full NMR assignment was made with COSY-45$\{^{31}P\}$, HMBC$\{^{31}P\}$, and HSQC$\{^{31}P\}$ NMR measurements. ^1H NMR (500.33 MHz, 263 K, $[D_8]$toluene): $\delta = 4.37$ and 3.34 (br, 4H, CH=CH of η^2-C_5H_7), 3.22 and 2.55 (br, 4H, C_2H_4), 2.40, 2.30, 2.09 and 1.85 (m, 8H, CH_2 of η^2-C_5H_7), 1.50 (m, 2H, CHP of $P(\eta^2$-$C_5H_7)$), 1.70–1.10 ppm (m, 36H, $PCyp_2$); $^{31}P\{^1H\}$ NMR (202.55 MHz, 263 K, $[D_8]$toluene): $\delta = 49.3$ ppm (s); $^{13}C\{^1H\}$ NMR (125.82 MHz, 263 K, $[D_8]$toluene): $\delta = 52.34$ and 50.24 (s, CH=CH of η^2-C_5H_7), 40.47 (s, C_2H_4), 37.8 (t, CH_2 of η^2-C_5H_7, $^3J_{CP} = 5.5$ Hz), 36.9 (t, CH_2 of η^2-C_5H_7, $^3J_{CP} = 4.8$ Hz), 33.2 (t, CH of Cyp, $^2J_{CP} = 6.2$ Hz), 27.7 (t, CH of Cyp, $^2J_{CP} = 5.9$ Hz), 29.6 (t, CH of η^2-C_5H_7, $^2J_{CP} = 10.3$ Hz), 30.2, 29.8, 29.1, 27.5, 26.6, 26.5, 25.6, 24.3 ppm (CH_2 of $PCyp_2$).

$[RuH_2[PCyp_2(\eta^2$-$C_5H_7)]_2]$: In a Fischer–Porter bottle $[RuH_2(H_2)_2$-$(PCyp_3)_2]$ (87 mg, 0.149 mmol) was introduced and pentane (5 mL) was added under argon. The solution was pressurized with 3 bar of ethylene for 2 min. After this period the pentane volume was reduced to 2 mL. After the solution had been cooled to −40 °C, a solid was formed. After filtration, the white solid was dried rapidly under vacuum and was isolated in 64% yield. X-ray diffraction quality crystals were obtained by cooling a saturated pentane solution at −35 °C for a few days. **3**: ^1H NMR (300.13 MHz, 298 K, C_6D_6): $\delta = -5.27$ (t, 2H, RuH, $^2J_{HP} = 23$ Hz), 2.20–1.30 (m, 46H, $PCyp_2(\eta^2$-$C_5H_7)$), 2.55 ppm (s, 4H, CH=CH of η^2-C_5H_7); $^{31}P\{^1H\}$ NMR (121.49 MHz, 298 K, C_6D_6): $\delta = 83.9$ ppm (s); ^1H NMR (500.33 MHz, 183 K, $[D_8]$toluene): $\delta = -5.28$ ppm (t, 2H, RuH, $^2J_{HP} = 22$ Hz); $^{31}P\{^1H\}$ NMR (202.55 MHz, 183 K, $[D_8]$toluene): $\delta = 87.4$ ppm (s). **3a** and **3b**: ^1H NMR (300.13 MHz, 298 K, C_6D_6): $\delta = -9.12$ (t, 2H, RuH, $\Delta\nu_{1/2} = 27$ Hz), 2.20–1.30 (m, 46H, $PCyp_2(\eta^2$-$C_5H_7)$), 3.04 ppm (s, 4H, CH=CH of η^2-C_5H_7); $^{31}P\{^1H\}$ NMR (121.49 MHz, 298 K, C_6D_6): $\delta = 68.6$ ppm (s); ^1H NMR (500.33 MHz, 183 K, $[D_8]$toluene): $\delta = -6.72$ (**3a**, 2H, $\Delta\nu_{1/2} = 59$ Hz), −11.56 ppm (**3b**, 2H, $\Delta\nu_{1/2} = 55$ Hz); $^{31}P\{^1H\}$ NMR (202.55 MHz, 183 K, $[D_8]$toluene): $\delta = 68$ ppm (very broad).

CCDC-633959 (**2**) and CCDC-633960 (**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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