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Synthesis of the monohydride complexes $HRu_2(X)(CO)_5(^iPr\text{-}N{=}CHCH{=}N\text{-}^iPr)$ (X = Cl, I); hydrogenation of the central C–C bond of the coordinated α-diimine ligands. X-ray single crystal structure of $HRu_2(Cl)(CO)_5(^iPr\text{-}N{=}CHCH{=}N\text{-}^iPr)$

Marco J. A. Kraakman, Cornelis J. Elsevier, Vincent W. de Haar, Kees Vrieze*

Anorganisch Chemisch Laboratorium, J. H. van't Hoff Instituut, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (Netherlands)

and Anthony L. Spek

Bijvoet Centre for Biomolecular Research, Vakgroep Kristal- en Structuurchemie, RijksUniversiteit Utrecht, Padualaan 8, 3584 CH Utrecht (Netherlands)

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Abstract

Reaction of $H_2Ru_2(CO)_5(^iPr\text{-}DAB\{H,R\})$ (R = H (**1a**); R = Me (**1b**)), which contains one terminal and one bridging hydride, with CX_4 (X = Cl; X = I) afforded $HRu_2(X)(CO)_5(^iPr\text{-}DAB\{H,R\})$ (X = Cl, R = H (**3a**); X = Cl, R = Me (**3b**); X = I, R = H (**3c**)). As confirmed by a single crystal X-ray structure determination, complex **3a** contains a bimetallic unit bridged by a hydride and a 6e σ-N,μ_2-N',η^2-C=N' bonded DAB ligand, whereas the chloride is terminally bonded. Crystals of **3a** are monoclinic, space group $P2_1/c$, $a = 12.421(2)$, $b = 12.003(2)$, $c = 13.227(1)$ Å, $\beta = 90.22(1)°$, $Z = 4$. The structure was refined to $R = 0.043$ for 2947 observed reflections. Reaction of **3a** with D_2 at 70 °C afforded $DRu_2(Cl)(CO)_5(^iPr\text{-}DAB)$ (**3a'**), whereas **3a'** could be reconverted to **3a** by reaction with H_2. To rationalize these results it is suggested that in the first step of the reaction, e.g. of **3a** with D_2, the D_2 molecule attacks the empty position created by rupture of the Ru-η^2-C=N' bond. Exchange of H by D may occur via an intermediate containing a HD_2 species coordinated to the bimetallic moiety. Raising the reaction temperature to 90 °C leads subsequently to the reduction of the coordinated DAB ligand, whereby **3a** and **3c** are converted to $HRu_2(X)(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (X = Cl (**4a**); X = I (**4c**), together with small amounts of the side product $Ru_2(CO)_6(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**5a**). The latter was formed from **4a**, as established by refluxing complexes **4** in toluene which yielded **5a**. However, in contrast to **3a** and **3c**, reaction of **3b** with hydrogen at 90 °C afforded only $Ru_2(CO)_6(^iPr\text{-}N\text{-}C(H)(Me)CH_2\text{-}N\text{-}^iPr)$ (**5b**). Complexes **4** could also be prepared by reacting $H_2Ru_2(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**2a**) with CX_4. Interestingly, for example, reaction of $DRu_2(Cl)(CO)_5(^iPr\text{-}DAB\{H,R\})$ with D_2 at 90 °C showed in the final product the presence of D at all sites of the reduced central C–C bond of R-DAB with an average varying between 0.5 and 1 proton on this moiety, indicating the occurrence of intramolecular C–H/C–D bond making and bond breaking steps during the hydrogenation process. Reaction of **3a** with AgOTF yielded $[OTF][HRu_2(CO)_5(^iPr\text{-}DAB)]$ (**6**), which subsequently could be converted to $[OTF][HRu_2(CO)_5(L)(^iPr\text{-}DAB)]$ (L = CO (**8**); L = ^{t}Bu-NC (**9**)) and to $[HRu_2(X)(CO)_5(^iPr\text{-}DAB)]$ (X = $Co(CO)_4$ (**3d**); X = $Mn(CO)_5$ (**3e**); X = CN (**3f**)). Whereas the DAB ligand of **6** could be reduced, complexes **3d–f**, **8** and **9** could not be hydrogenated.

Introduction**

Recently our interest has focussed on the rather unusual reduction of coordinated α-diimines with hydrogen [1–4], which in the case of $FeRu(CO)_5(L)(^iPr\text{-}DAB)$ (L = CO, PPh_3) led to the formation of $FeRu(CO)_5(L)(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ [1, 4], whereas use of D_2 afforded $FeRu(CO)_5(L)(^iPr\text{-}N\text{-}CHDCHD\text{-}N\text{-}^iPr)$, in which the two D atoms are exclusively *trans* to each other. A proposed mechanism for these reactions has recently been reported (Scheme 1) [1, 4].

However, in the case of $Ru_2(CO)_6(^iPr\text{-}DAB)$ reaction with H_2 first $H_2Ru_2(CO)_5(^iPr\text{-}DAB)$ (**1a**) was formed at 90 °C [5], which subsequently could be converted to $H_2Ru_2(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**2a**) and the side

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*Author to whom correspondence should be addressed.

**R-DAB{X,Y} = 1,4-diaza-1,3-butadiene; R-N=C(X)C(Y)=N-R. In this paper ^{i}Pr-N=C(H)C(H)=N-^{i}Pr and ^{i}Pr-N=C(H)C(Me)=N-^{i}Pr are used. ^{i}Pr-DAB{H,H} will be abbreviated as ^{i}Pr-DAB.

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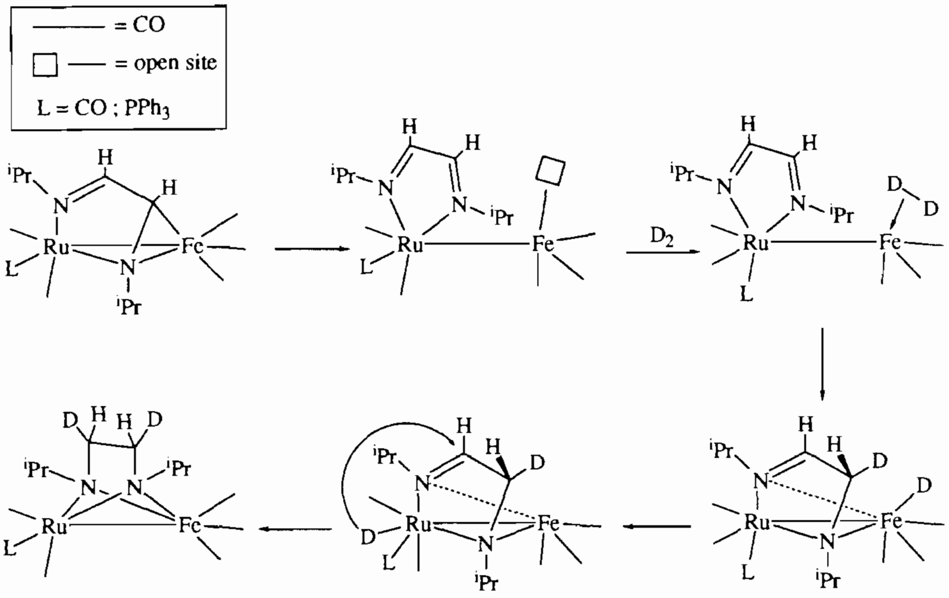
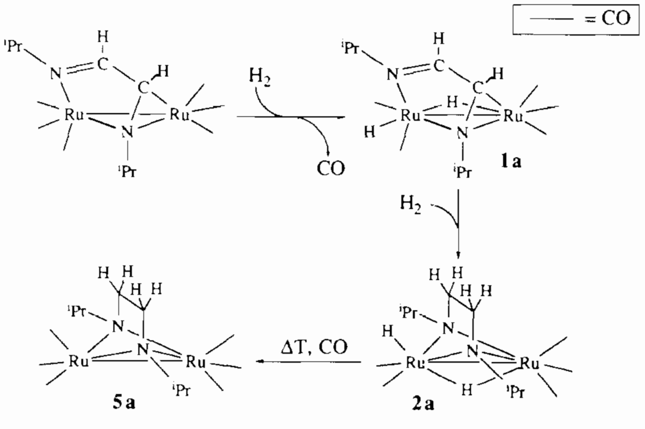


Scheme 1. Proposed mechanism for the hydrogenation of $FeRu(CO)_5(L)(^iPr\text{-}DAB)$ [1, 4].

product $Ru_2(CO)_6(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**5a**) [3]. The hexacarbonyl compound **5a** could also be formed directly from **2a** (Scheme 2).

In contrast to the FeRu system it turned out that, for example, $D_2Ru_2(CO)_5(^iPr\text{-}DAB)$ (**1a′**), having one terminal and one bridging deuteride, reacted with D_2 to give products in which the proton intensity that was observed on the central C–C moiety was less than one proton, whereas D had been substituted randomly on all four positions of the C_2 unit [3]. Furthermore substantial proton intensity was present on the position of the bridging deuteride, whereas virtually no H was observed on the terminal deuteride position. These observations could only be explained by the occurrence of C–H/C–D and Ru–H/Ru–D bond making and breaking processes in key stages of the reduction process [3].



Scheme 2. Observed reaction sequence for treatment of $Ru_2(CO)_6(^iPr\text{-}DAB)$ with molecular hydrogen [3, 5].

It should be realized that although kinetic information could be obtained for the FeRu system [1], it turned out to be impossible to perform kinetic measurements for the Ru_2 systems, because of the above mentioned side reaction and due to decomposition. Therefore we attempted to prepare more stable compounds that could be used for our hydrogenation studies. In this article we report the results on diruthenium monohydride systems, which might further give information about the intimate steps of the hydrogenation processes.

Experimental

Materials and apparatus

^1H and ^{13}C NMR spectra were recorded on Bruker AC-100 and AMX-300 spectrometers. IR spectra (ν(CO); 2200–1600 cm^{-1}) were measured on a Perkin-Elmer 283 spectrometer. Elemental analyses were carried out by the section elemental analyses of the Institute of Applied Chemistry TNO, Zeist, The Netherlands. All preparations were carried out under an atmosphere of purified nitrogen, using carefully dried solvents. Column chromatography was performed using silica gel (Kieselgel 60, Merck, 70–230 Mesh ASTM, dried and activated before use) as the stationary phase. CI_4 (Janssen Chimica) was washed with hexane several times before use to remove I_2 impurities. Silver trifluorosulfonate (Janssen), hydrogen (Hoekloos, Netherlands), deuterium (Air Products), carbon monoxide (Mattheson) and ^{t}Bu-isocyanide (Aldrich) were used as commercially obtained. Complexes $H_2Ru_2(CO)_5(^iPr\text{-}DAB\{H,R\})$ (**1a, b**) [3, 5], $H_2Ru_2(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}$

N-^{i}Pr) (**2a**) [3], [$Mn(CO)_5^-$] [6], and [$Co(CO)_4^-$] [6] were prepared by published procedures.

Preparation of $HRu_2(X)(CO)_5$(^{i}Pr-DAB{H,R}) (X = Cl, R = H (3a); X = Cl, R = Me (3b); X = I, R = H (3c))

A heptane solution of **1a, b** was prepared *in situ*, by reaction of $Ru_2(CO)_6$(^{i}Pr-DAB{H,R}) with hydrogen at 90 °C [3, 5]. For ^{i}Pr-DAB an amount of 300 mg $Ru_2(CO)_6$(^{i}Pr-DAB) [7] was used as starting material. For ^{i}Pr-DAB{H,Me} the $Ru_2(CO)_6$(^{i}Pr-DAB{H,Me}) was prepared *in situ* starting from 430 mg of $Ru_3(CO)_{12}$ and 215 mg of ^{i}Pr-DAB{H,Me} [3]. Subsequently the reaction mixture was cooled to room temperature and treated with 1.5 ml CCl_4 (**a, b**) or with 0.5 g CI_4 in 10 ml CH_2Cl_2 (**c**)*. IR spectroscopy indicated an instantaneous conversion to **3a–c**. The reaction mixture was then evaporated to dryness, the product was extracted with CH_2Cl_2 and purified by means of column chromatography. The product was eluted as a yellow–orange fraction with ligroin/CH_2Cl_2 (1/3). Evaporation of the solvent afforded $HRu_2(X)(CO)_5$(^{i}Pr-DAB{H,R} (X = Cl, R = H (**3a**); X = Cl, R = Me (**3b**); X = I, R = H (**3c**)) in yields of about 70% for **3a** (based on the amount of $Ru_2(CO)_6$(^{i}Pr-DAB) used), 35% for **3b** (based on the amount of $Ru_3(CO)_{12}$ used) and 50% for **3c** (based on the amount of $Ru_2(CO)_6$(^{i}Pr-DAB) used). Finally, elution with CH_2Cl_2/CH_3CN (8/2) afforded an orange fraction, containing traces of $Ru(X)_2(CO)_2$(R-DAB) together with $[Ru(CO)_3(X)_2]_2$.

Reaction of $DRu_2(Cl)(CO)_5$(^{i}Pr-DAB) (3a′) with H_2 to $HRu_2(Cl)(CO)_5$(^{i}Pr-DAB) (3a) and vice versa

An amount of 300 mg of $Ru_2(CO)_6$(^{i}Pr-DAB) [7] was converted to $DRu_2(Cl)(CO)_5$(^{i}Pr-DAB) (**3a′**) by treatment with D_2 at 90 °C [3] and subsequent reaction with CCl_4. After purification by means of column chromatography the product was dissolved in benzene (40 ml) and stirred under H_2 at 70 °C while samples were taken hourly and analyzed by means of ^1H NMR spectroscopy. The NMR data indicated that an H/D exchange reaction took place converting $DRu_2(Cl)(CO)_5$(^{i}Pr-DAB) (**3a′**) to $HRu_2(Cl)(CO)_5$(^{i}Pr-DAB) (**3a**). The reverse reaction could also be performed in about 5 h by changing the H_2 atmosphere for D_2.

Reaction of $HRu_2(X)(CO)_5$(^{i}Pr-DAB) (3a/3c) with H_2 and of $DRu_2(X)(CO)_5$(^{i}Pr-DAB) (3a′/3c′) with D_2 at 90 °C

An amount of 200 mg of complex **3a** or **3c** was dissolved in 35 ml of benzene and stirred under an atmosphere of hydrogen (1.5 bar) at a temperature of about 90 °C. The hydrogen atmosphere was refreshed regularly and the reaction was monitored by means of IR spectroscopy. After 5 h IR spectroscopy indicated that the starting complex was no longer present, after which the reaction mixture was evaporated to dryness. Subsequently the residue was dissolved in a minimum amount of CH_2Cl_2 and purified by means of column chromatography. Elution with ligroin afforded a pale yellow fraction, containing $Ru_2(CO)_6$(^{i}Pr-N-CH_2CH_2-N-^{i}Pr) (**5a**) in a yield of about 20% (**a**) or 10% (**c**). Elution with ligroin/CH_2Cl_2 (4/6) gave a yellow–orange fraction, which after evaporation of the solvent yielded $HRu_2(X)(CO)_5$(^{i}Pr-N-CH_2CH_2-N-^{i}Pr) (X = Cl (**4a**); X = I (**4c**)) in a yield of 65% (**a**) or 70% (**c**). The same procedure was applied for the reaction of $DRu_2(X)(CO)_5$(^{i}Pr-DAB) (**3a′**/**3c′**) with D_2 at 90 °C, leading to the isolation of the deuterated products **4a′**/**4c′** and **5a′**.

Reaction of $HRu_2(Cl)(CO)_5$(^{i}Pr-DAB{H,Me}) (3b) with H_2 and of $DRu_2(Cl)(CO)_5$(^{i}Pr-DAB{H,Me}) (3b′) with D_2 at 90 °C

For this reaction the same procedure was applied as described for the hydrogenation of **3a** and **3c**. However, in this case only $Ru_2(CO)_6$(^{i}Pr-N-C(H)(Me)CH_2-N-^{i}Pr) (**5b**) was isolated in about 50% yield. The complex $HRu_2(Cl)(CO)_5$(^{i}Pr-N-C(H)(Me)CH_2-N-^{i}Pr) was not isolated at all, and was also not detected in solution. The reaction of **3b′** with D_2 in this case also resulted in the isolation of the hexacarbonyl complex **5b′** exclusively.

Preparation of $HRu_2(X)(CO)_5$(^{i}Pr-N-CH_2CH_2-N-^{i}Pr) (X = Cl (4a); X = I (4c)) starting from $H_2Ru_2(CO)_5$(^{i}Pr-N-CH_2CH_2-N-^{i}Pr) (2a)

An amount of 200 mg of $H_2Ru_2(CO)_5$(^{i}Pr-N-CH_2CH_2-N-^{i}Pr) (**2a**) [3] was dissolved in 40 ml of hexane and treated with 1 ml CCl_4 or with 0.4 g CI_4 in 10 ml CH_2Cl_2. IR spectroscopy showed a rapid conversion to **4a** and **4c**, respectively. The reaction mixture was stirred for an additional 15 min and subsequently evaporated to dryness. The residue was then dissolved in a minimum of CH_2Cl_2 and purified by column chromatography as described above. This route yielded **4a** or **4c** in more than 80% yield.

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*For the preparation of **3c** it proved to be preferable to evaporate the obtained $H_2Ru_2(CO)_5$(^{i}Pr-DAB) (**1a**) to dryness, dissolve the residue in CH_2Cl_2 and treat this solution with small portions of the CI_4 solution until IR spectroscopy indicated the conversion to **3c** had completed.

Thermal conversion of $HRu_2(X)(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ ($X=Cl$ (4a); $X=I$ (4c)) to $Ru_2(CO)_6(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (5a)

An amount of 200 mg of $HRu_2(X)(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (X = Cl (**4a**); X = I (**4c**)) was dissolved in 40 ml of toluene and refluxed while the reaction was monitored by means of IR spectroscopy. During the reaction a conversion to $Ru_2(CO)_6(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**5a**) was observed, reaching completion in about 6 (**4a**) and 8 (**4c**) h, respectively. Evaporation of the solvent and purification by means of column chromatography resulted in the isolation of **5a** in about 70% yield.

Hydrogenation reactions with and without carbon monoxide

An amount of 200 mg of $HRu_2(Cl)(CO)_5(^iPr\text{-}DAB)$ (**3a**) was dissolved in 20 ml of toluene and stirred at 100 °C. A stream of hydrogen and a stream of carbon monoxide were bubbled through a reverse-flow bubbler with approximately equal velocity and led into a mixing chamber. The gas mixture was then bubbled through the toluene solution of **3a** while the reaction was monitored by means of IR spectroscopy. After 4 h IR spectroscopy indicated that only a small amount of **3a** had converted to $Ru_2(CO)_6(^iPr\text{-}DAB)$ [7], but no evidence was found for the presence of complexes containing a hydrogenated DAB ligand. Subsequently the stream of carbon monoxide was stopped and only hydrogen was bubbled through the reaction mixture, resulting in a complete conversion of **3a** to $HRu_2(Cl)(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**4a**) together with small amounts of the side product $Ru_2(CO)_6(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**5a**) within 1.5 h.

Attempted H/D exchange for $HRu_2(Cl)(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (4a)

An amount of 150 mg of $HRu_2(Cl)(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**4a**) was dissolved in 40 ml of toluene and stirred under an atmosphere of deuterium. The reaction mixture was analyzed by means of ^1H NMR after 3 and 6 h at 100 °C. The NMR spectra showed no changes in the proton intensities of the hydride ligand and the hydrogenated DAB ligand and only a partial conversion to $Ru_2(CO)_6(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**5a**) was observed.

Synthesis of $[OTF][HRu_2(CO)_5(^iPr\text{-}DAB)]$ (6)

An amount of 300 mg of $HRu_2(Cl)(CO)_5(^iPr\text{-}DAB)$ (**3a**) (0.58 mmol) was dissolved in 30 ml of CH_2Cl_2 and subsequently 300 mg of AgOTF (1.17 mmol, 2 equiv.) was added to the reaction mixture. IR spectroscopy indicated a complete conversion to $[OTF][HRu_2(CO)_5(^iPr\text{-}DAB)]$ (**6**), reaching completion within a few minutes. The reaction mixture was then filtered over celite and either used directly for further experiments or evaporated to dryness and stored at −20 °C.

Hydrogenation of $[OTF][HRu_2(CO)_5(^iPr\text{-}DAB)]$ (6)

An amount of 200 mg of $[OTF][HRu_2(CO)_5(^iPr\text{-}DAB)$ (**6**) was dissolved in 40 ml of toluene and stirred at 90 °C under an atmosphere of hydrogen (about 1.5 bar), while the reaction was monitored by means of IR spectroscopy. After 3 h IR spectroscopy indicated that the absorptions of starting complex **6** were completely replaced by those belonging to $[OTF][HRu_2(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)]$ (**7**) and the reaction mixture was evaporated to dryness. The residue was then dissolved in 50 ml of methanol, 500 mg of $[NH_4][Cl]$ was added and the mixture was stirred at 30 °C for about 2 h. Subsequently the reaction mixture was evaporated to dryness, the residue was dissolved in a minimum of CH_2Cl_2 and purified by means of column chromatography. Elution with ligroin afforded a pale yellow fraction, which after evaporation of the solvent yielded $Ru_2(CO)_6(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**5a**) in about 30% yield. Elution with ligroin/CH_2Cl_2 (4/6) gave a yellow fraction, containing $HRu_2(Cl)(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**4a**) in about 55% yield. Elution with CH_2Cl_2/CH_3CN (8/2) afforded an orange fraction, containing $Ru(Cl)_2(CO)_2(^iPr\text{-}DAB)$ in small amounts (<5%). Finally, **4a** obtained this way was re-converted to $[OTF][HRu_2(CO)_5(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)]$ (**7**) by treatment with AgOTF in CH_2Cl_2. The same procedure was applied for the corresponding deuteration of **6** using D_2 instead of H_2. This resulted in the isolation of the deuterated species **7′** and **5a′**.

Reaction of $[OTF][HRu_2(CO)_5(^iPr\text{-}DAB)]$ (6) with carbon monoxide to give $[OTF][HRu_2(CO)_6(^iPr\text{-}DAB)]$ (8)

An amount of 100 mg $[OTF][HRu_2(CO)_5(^iPr\text{-}DAB)]$ (**6**) (0.16 mmol) was dissolved in 15 ml of CH_2Cl_2 and stirred under an atmosphere of carbon monoxide, while the conversion was monitored by means of IR spectroscopy. After 8 h the reaction mixture was evaporated to dryness and the residue was extracted with 15 ml of hexane/CH_2Cl_2 (2/1). Subsequently the extract was filtered over celite and evaporated to dryness, giving 60 mg of $[OTF][HRu_2(CO)_6(^iPr\text{-}DAB)]$ (**8**) (55%).

Synthesis of $[OTF][HRu_2(CO)_5(^tBu\text{-}NC)(^iPr\text{-}DAB)]$ (9)

An amount of 100 mg $[OTF][HRu_2(CO)_5(^iPr\text{-}DAB)]$ (**6**) (0.16 mmol) was dissolved in 15 ml of CH_2Cl_2 and 45 μl ^{t}Bu-isocyanide (0.40 mmol, 2.5 equiv.) was added. The reaction mixture was stirred for an additional 15 min and then evaporated to dryness. The residue was washed with hexane (10 ml) three times and dried *in vacuo*, leaving $[OTF][HRu_2(CO)_5(^tBu\text{-}NC)(^iPr\text{-}DAB)]$ (**9**) behind in 85% yield.

Preparation of [$HRu_2(X)(CO)_5(^iPr$-DAB)] ($X=Co(CO)_4^-$ (3d); $Mn(CO)_5^-$ (3e); CN^- (3f))

$Co(CO)_4^-$. A solution of 150 mg of [OTF]-[$HRu_2(CO)_5(^iPr$-DAB)] (**6**) (0.24 mmol) in 25 ml CH_2Cl_2 was cooled to −60 °C by means of an CO_2/ethanol bath. Subsequently about 1.5 equiv. of $Co(CO)_4^-$ was added as a THF solution. The reaction mixture was then stirred at this temperature for 30 min and subsequently the CO_2/ethanol bath was removed, after which the reaction mixture was allowed to reach room temperature slowly. The reaction mixture was evaporated to dryness, extracted with hexane (30 ml) and placed overnight at −30 °C. The resulting red–brown crystals were collected and dried *in vacuo*, resulting in the isolation of $HRu_2(Co(CO)_4)(CO)_5(^iPr$-DAB) (**3d**) in about 45% yield. Further crystallization from the mother liquor, which beside **3d** also contained traces of $Co_2(CO)_8$, led to a total yield of **3d** of about 80%.

$Mn(CO)_5^-$. The same procedure as described for $Co(CO)_4^-$ was used, except that the purification was not performed by means of fractional crystallization, but by means of column chromatography. Upon elution with ligroin two fractions were obtained. The first yellow fraction contained $Mn_2(CO)_{10}$, while the second orange colored fraction yielded $HRu_2(Mn(CO)_5)(CO)_5(^iPr$-DAB) (**3e**) in about 55% yield.

CN^-. A solution of 150 mg of [OTF][$HRu_2(CO)_5(^iPr$-DAB)] (**6**) (0.24 mmol) in 25 ml CH_2Cl_2 was cooled to −60 °C by means of an CO_2/ethanol bath. Two equivalents of KCN (31 mg, 0.48 mmol) were dissolved in 12 ml of methanol and added to the reaction mixture, which was kept at −60 °C for an additional one hour. Subsequently the reaction mixture was allowed to reach room temperature, concentrated to a few ml, and purified by means of column chromatography. Elution with ligroin/CH_2Cl_2 afforded a bright yellow fraction, which after evaporation of the solvent yielded $HRu_2(CN)(CO)_5(^iPr$-DAB) (**3f**) in about 65% yield.

X-ray structure determination of $HRu_2(Cl)(CO)_5(^iPr$-DAB) (3a)

X-ray data were collected on an Enraf-Nonius CAD4 diffractometer for a brownish crystal mounted on top of a glass fiber. Crystal data and numerical details of the structure determination are given in Table 1. Unit cell parameters and their standard deviations were derived from the SET4 setting angles of 25 reflections in the range $14 < \theta < 18°$. The space group was derived from the observed systematic absences. Data were corrected for a small decay of 2% as indicated by three reference reflections, Lorentz and polarization effects and absorption with DIFABS [8] (corrections in the range 0.81–1.36). The structure was solved with the PATT-option of SHELXS86 [9] and refined on F by full matrix least-squares with SHELX76 [10]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced on calculated positions, except those on C4 and C5 and the bridging hydride atoms that were located from a difference Fourier map and their positions refined.

TABLE 1. Crystallographic data for $HRu_2(Cl)(CO)_5(^iPr$-DAB{H,H}) (**3a**)

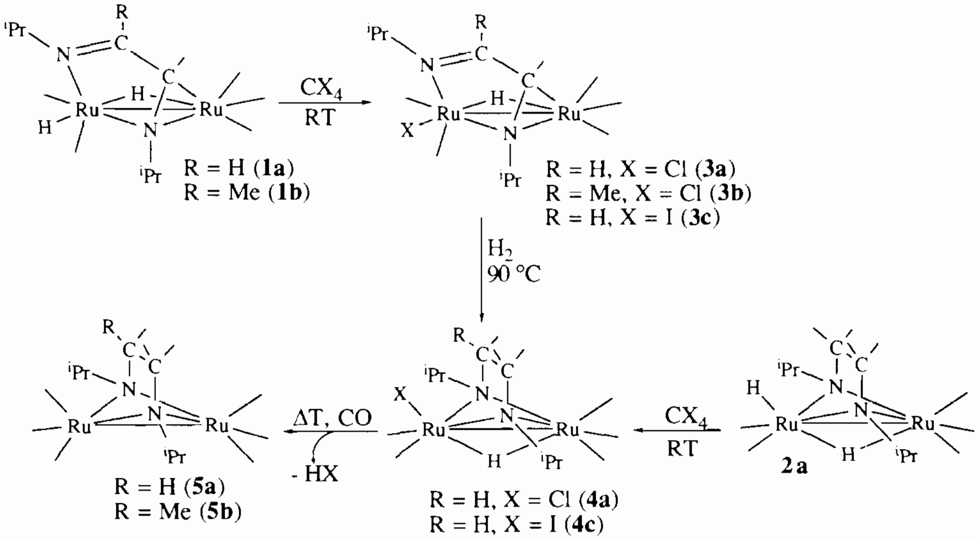
Crystal data	
Formula	$C_{13}H_{17}ClN_2O_5Ru_2$
Molecular weight	518.88
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	12.421(2)
b (Å)	12.003(2)
c (Å)	13.227(1)
β (°)	90.22(1)
V (Å^3)	1972.0(5)
D_{calc}	1.748
Z	4
$F(000)$	1016
μ (cm^{-1})	16.6
Crystal size (mm)	0.40×0.40×0.40
Data collection	
Temperature (K)	295
Radiation (Å)	Mo Kα (Zr-filtered) 0.71073
$\theta_{min}/\theta_{max}$ (°)	1.54, 28.47
Scan type	$\omega/2\theta$
$\Delta\omega$ (°)	$1.40 + 0.35 \tan(\theta)$
Horizontal and vertical aperture (mm)	3.00, 4.00
Reference reflections	0 −2 4, 2 −2 0, 4 0 4
Data set	−16:16, −15:0, 0:17
Total data	4832
Unique data	4598
Observed data ($I > 2.5\sigma(I)$)	2948
Refinement	
Refined parameters	232
R, R_w, S	0.043, 0.037, 1.69
Weighting scheme	$1/\sigma^2(F)$
Max. and av. shift/error	0.03, 0.68
Max./min. residual density (e Å^{-3})	−0.62, 0.84

Neutral scattering factors were obtained from Cromer and Mann [11] and corrected for anomalous dispersion [12]. The programs PLATON and PLUTON of the EUCLID package [13] were used for the geometrical calculations and molecular graphics. All calculations were done on a micro-VAX cluster. See also 'Supplementary material'.

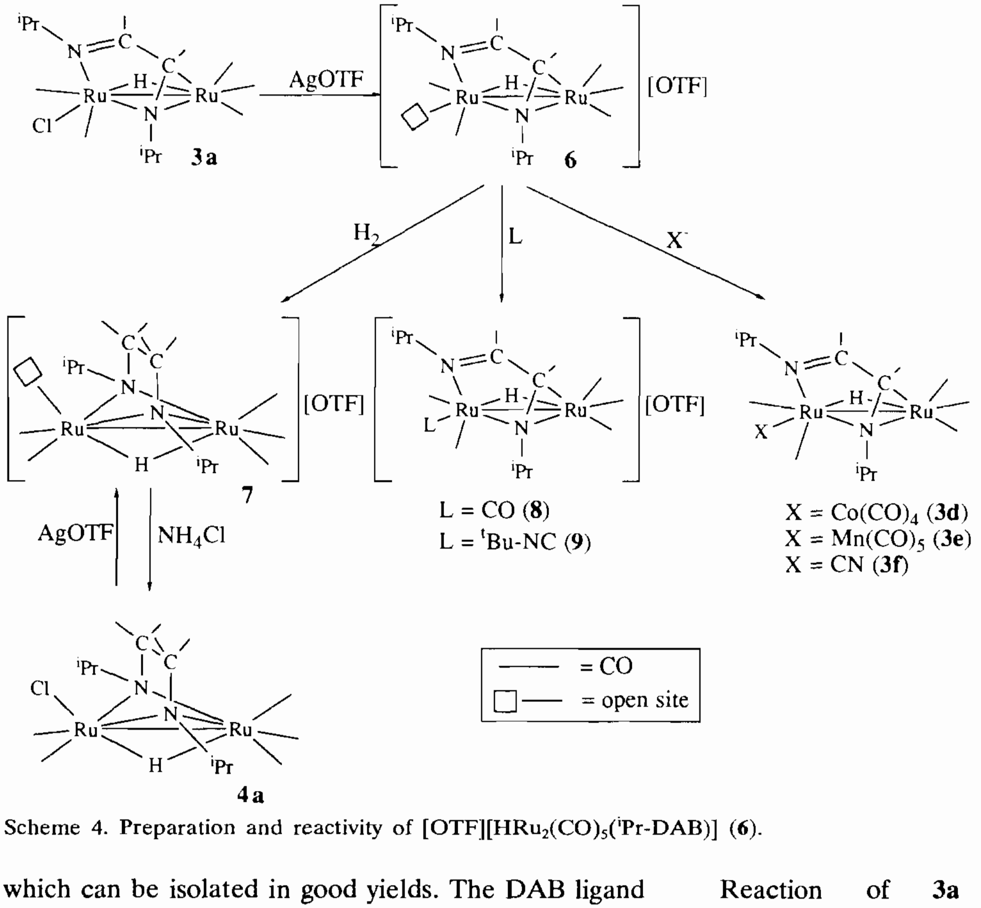
Results and discussion

Synthesis and structures of the new complexes

Reaction of the dihydride complex $H_2Ru_2(CO)_5(^iPr$-DAB{H,R}) (**1a, b**) with CX_4 resulted in a rapid conversion to $HRu_2(X)(CO)_5(^iPr$-DAB{H,R}) ($X=Cl$, $R=H$ (**3a**); $X=Cl$, $R=Me$ (**3b**); $X=I$, $R=H$ (**3c**))



Scheme 3. Preparation and structures of complexes **3a–c**, **4a**, **4c** and **5a**, **b**.



Scheme 4. Preparation and reactivity of [OTF][$HRu_2(CO)_5$(^iPr-DAB)] (**6**).

which can be isolated in good yields. The DAB ligand in complexes **3a–c** could be hydrogenated, which resulted in the formation of $HRu_2(X)(CO)_5$(^iPr-N-CH_2CH_2-N-^iPr) (X = Cl (**4a**); X = I (**4c**)) and $Ru_2(CO)_6$(^iPr-N-C(H)(R)CH_2-N-^iPr) (R = H (**5a**); R = Me (**5b**)) (Scheme 3). Alternatively complexes **4a** and **4c** could be obtained by reaction of $H_2Ru_2(CO)_5$(^iPr-N-CH_2CH_2-N-^iPr) (**2a**) with CX_4 (Scheme 3).

Reaction of **3a** with AgOTF afforded [OTF][$HRu_2(CO)_5$(^iPr-DAB)] (**6**), which with H_2 gave hydrogenation of the DAB ligand, yielding [OTF][$HRu_2(CO)_5$(^iPr-N-CH_2CH_2-N-^iPr)] (**7**) (Scheme 4). Treatment of **6** with CO, ^{t}Bu-NC and various anionic substrates gave the new complexes [OTF]-[$HRu_2(CO)_5$(L)(^iPr-DAB)] (L = CO (**8**); L = ^{t}Bu-NC (**9**)) and [$HRu_2(X)(CO)_5$(^iPr-DAB)] (X = $Co(CO)_4^-$

(**3d**). X = Mn(CO)$_5^-$ (**3e**); X = CN$^-$ (**3f**)). In the following we will first discuss the structural and spectroscopic aspects of the relevant compounds and subsequently deal with the aspects of the reduction reactions.

Molecular structure of HRu$_2$(Cl)(CO)$_5$(^{i}Pr-DAB) (3a)

A view of the molecular structure of **3a** is shown in Fig. 1 together with the atomic numbering. Tables 2, 3 and 4 contain the fractional coordinates, the bond lengths and the bond angles of the non-hydrogen atoms of **3a**, respectively.

The molecular structure of the complex consists of a Ru(CO)$_3$ fragment and a Ru(CO)$_2$(Cl) fragment that are bridged by a DAB ligand and a hydride. The molecule possesses an Ru–Ru bond with a bond length of 2.8293(8) Å, which is normal for an Ru–Ru bond [14–16].

The ^{i}Pr-DAB ligand is coordinated to Ru(2) via both N atoms and to Ru(1) via η^2-coordination of the C(4)=N(1) imine bond. Coordination to the metal elongates the C(4)=N(1) imine bond length significantly (1.405(7) Å) as compared to for instance the value of 1.258(3) Å in the case of uncoordinated ^{c}Hex-DAB [17], or compared to the value of the uncoordinated imine moiety N(2)–C(5) (1.272(9) Å). This lengthening of the imine bond is caused by donation of electron density from the metal into the antibonding π^*-orbitals of the imine moiety [18, 19].

The hydride is located in a bridging position with comparable distances to both metal centres (Ru(2)–H(1) = 1.70(4) Å, Ru(1)–H(1) = 1.81(4) Å). This bridging position agrees with the ^{1}H NMR data of the complex in solution (*vide infra*). An interesting aspect is the C–H···Cl bridge interaction between the chloride atom and the H atom H(10) on C(5) of a second molecule (H···Cl = 2.45(6) Å) in the solid state. This results in a lengthening of the C(5)–H(10) bond length (1.06(6) Å) compared to for instance the value of C(4)–H(9) (0.85(5) Å). Finally, C(7) exhibits high thermal motion and/or disorder, resulting in an artificial short C(6)–C(7) distance of 1.318(14) Å.

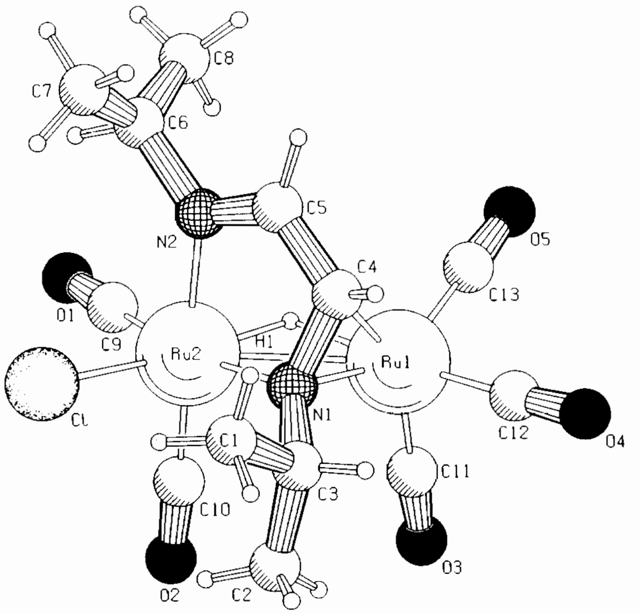


Fig. 1. Molecular structure of HRu$_2$(Cl)(CO)$_5$(^{i}Pr-DAB) (**3a**).

TABLE 2. Fractional coordinates and equivalent isotropic thermal parameters of the non hydrogen atoms of HRu$_2$(Cl)(CO)$_5$(^{i}Pr-DAB) (**3a**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	U_{eq} (Å^2)^a
Ru(1)	0.76230(4)	0.58008(4)	0.34895(3)	0.0521(2)
Ru(2)	0.71279(3)	0.46228(4)	0.16942(3)	0.0434(2)
Cl	0.79022(17)	0.36122(18)	0.03253(13)	0.1017(9)
O(1)	0.4888(4)	0.4202(5)	0.0926(4)	0.105(2)
O(2)	0.7141(4)	0.6705(5)	0.0438(4)	0.108(2)
O(3)	0.7127(4)	0.8122(5)	0.2690(5)	0.118(3)
O(4)	0.9328(5)	0.6671(5)	0.4919(4)	0.125(3)
O(5)	0.5931(5)	0.5785(6)	0.5162(5)	0.159(3)
N(1)	0.8567(3)	0.4897(3)	0.2504(3)	0.0433(16)
N(2)	0.7157(4)	0.3180(4)	0.2568(4)	0.0580(17)
C(1)	1.0242(6)	0.4210(7)	0.1797(7)	0.108(4)
C(2)	0.9662(6)	0.6140(6)	0.1453(6)	0.090(3)
C(3)	0.9686(4)	0.5202(5)	0.2184(5)	0.063(2)
C(4)	0.8467(5)	0.4248(6)	0.3383(4)	0.056(2)
C(5)	0.7817(6)	0.3264(5)	0.3302(5)	0.066(3)
C(6)	0.6472(6)	0.2173(6)	0.2485(8)	0.101(4)
C(7)	0.6938(11)	0.1230(9)	0.2223(10)	0.248(9)
C(8)	0.5535(6)	0.2268(8)	0.3166(7)	0.127(4)
C(9)	0.5731(5)	0.4371(5)	0.1209(4)	0.066(3)
C(10)	0.7145(5)	0.5937(6)	0.0922(4)	0.067(3)
C(11)	0.7297(5)	0.7245(6)	0.2987(6)	0.075(3)
C(12)	0.8679(6)	0.6368(6)	0.4375(5)	0.080(3)
C(13)	0.6528(6)	0.5808(7)	0.4541(5)	0.096(3)

$^a U_{eq}$ = 1/3 of the trace of the orthogonalized *U*.

TABLE 3. Bond distances (Å) of the hydride atom and the non-hydrogen atoms of HRu$_2$(Cl)(CO)$_5$(^{i}Pr-DAB) (**3a**) with e.s.d.s in parentheses

Ru1–Ru2	2.8293(8)	Ru1–N1	2.065(4)	Ru1–C4	2.143(7)
Ru1–C11	1.900(7)	Ru1–C12	1.883(7)	Ru1–C13	1.949(7)
Ru2–CL	2.385(2)	Ru2–N1	2.106(4)	Ru2–N2	2.082(5)
Ru2–C9	1.872(6)	Ru2–C10	1.879(7)	O1–C9	1.129(8)
O2–C10	1.122(9)	O3–C11	1.143(9)	O4–C12	1.137(9)
O5–C13	1.109(10)	N1–C3	1.500(6)	N1–C4	1.405(7)
N2–C5	1.272(9)	N2–C6	1.482(9)	C1–C3	1.47(1)
C2–C3	1.484(10)	C4–C5	1.434(9)	C6–C7	1.318(14)
C6–C8	1.479(10)	Ru1–H1	1.81(4)	Ru2–H1	1.70(4)

IR spectroscopy and analyses

The IR spectroscopic data have been collected in Table 5 together with the results of the elemental analyses.

All complexes contain only terminal coordinated carbonyl ligands, except the trimetallic Ru$_2$Co complex

TABLE 4. Bond angles (°) of the hydride atom and the non-hydrogen atoms of $HRu_2(Cl)(CO)_5$(^{i}Pr-DAB) (**3a**) with e.s.d.s in parentheses

Ru2–Ru1–N1	47.91(11)	N1–C4–C5	116.5(5)	Ru1–Ru2–C10	91.94(18)
Ru2–Ru1–C11	96.7(3)	N2–C6–C7	117.9(8)	N1–Ru2–C9	169.47(20)
Ru2–Ru1–C13	116.8(2)	C7–C6–C8	125.0(9)	N2–Ru2–C9	94.0(2)
N1–Ru1–C11	112.3(2)	Ru2–C10–O2	177.9(6)	C9–Ru2–C10	87.8(3)
N1–Ru1–C13	148.5(3)	Ru1–C12–O4	177.4(6)	Ru1–N1–C3	125.4(3)
C4–Ru1–C12	90.9(3)	Ru2–Ru1–H1	35.0(12)	Ru2–N1–C3	132.9(3)
C11–Ru1–C12	92.0(3)	C4–Ru1–H1	89.6(12)	C3–N1–C4	117.0(4)
C12–Ru1–C13	92.3(3)	H1–Ru1–C12	175.8(12)	Ru2–N2–C6	128.9(5)
CL–Ru2–N1	96.99(12)	CL–Ru2–H1	174.8(12)	N1–C3–C1	109.7(5)
CL–Ru2–C9	91.92(18)	N1–Ru2–H1	83.5(13)	C1–C3–C2	113.3(6)
Ru1–Ru2–N1	46.67(10)	C9–Ru2–H1	87.1(13)	Ru1–C4–C5	116.5(5)
Ru1–Ru2–C9	124.51(17)	Ru2–Ru1–C4	67.36(15)	N2–C5–C4	118.9(6)
N1–Ru2–N2	80.49(17)	Ru2–Ru1–C12	148.4(2)	N2–C6–C8	110.2(7)
N1–Ru2–C10	97.7(2)	N1–Ru1–C4	38.97(18)	Ru2–C9–O1	178.8(6)
N2–Ru2–C10	178.2(2)	N1–Ru1–C12	100.8(2)	Ru1–C11–O3	178.3(6)
Ru1–N1–Ru2	85.43(14)	C4–Ru1–C11	150.9(3)	Ru1–C13–O5	177.2(7)
Ru1–N1–C4	73.5(3)	C4–Ru1–C13	113.2(3)	N1–Ru1–H1	82.20(12)
Ru2–N1–C4	104.9(3)	C11–Ru1–C13	95.6(3)	H1–Ru1–C11	89.60(12)
Ru2–N2–C5	111.6(4)	CL–Ru2–Ru1	143.55(5)	H1–Ru1–C13	83.60(12)
C5–N2–C6	119.3(6)	CL–Ru2–N2	89.55(15)	Ru1–Ru2–H1	37.60(13)
N1–C3–C2	110.7(5)	CL–Ru2–C10	90.51(19)	N2–Ru2–H1	85.40(13)
Ru1–C4–N1	67.5(3)	Ru1–Ru2–N2	86.93(14)	C10–Ru2–H1	94.60(13)

TABLE 5. IR spectroscopic data of the complexes **3a–f**, **4a**, **4c**, **6**, **7**, **8** and **9**

Complex	IR (cm^{-1}) $\nu(C{\equiv}O)$	Elemental analysis: obs. (calc.) (%)		
		C	H	N
3a^a	2088(s), 2053(vs), 2018(vs), 2010(s), 1996(m)	29.91	3.36	5.13
3a^b	2087(s), 2052(vs), 2016(vs, br) 1991(m)	(30.09)	(3.30)	(5.40)
3b^b	2081(s), 2044(vs), 2008(vs, br), 1984(m)	31.44 (31.55)	3.57 (3.59)	5.01 (5.26)
3c^a	2079(s), 2046(vs), 2011(vs), 2006(sh), 1994(m)	25.50 (25.58)	2.85 (2.81)	4.40 (4.59)
3d^c	2082(s), 2056(s), 2025(s), 2011(s), 1990(s), 1950(w), 1855(w)	31.07 (31.20)	2.66 (2.62)	4.32 (4.28)
3e^c	2084(w), 2060(s), 2047(w), 2012(s), 2006(m), 1998(sh), 1981(vs), 1969(m), 1961(w)	32.23 (31.87)	2.67 (2.53)	3.91 (4.13)
3f^c	2131(w), 2087(vs), 2058(vs), 2016(vs)	not analyzed		
4a^c	2100(s), 2053(m), 2038(vs, br), 1977(m, br)	29.90 (29.98)	3.77 (3.68)	5.39 (5.38)
4c^a	2097(s), 2039(vs), 2029(m), 2025(sh), 1984(m, br)	25.67 (25.50)	2.96 (3.12)	4.43 (4.57)
6^b	2092(s), 2061(s), 2024(s), 2009(sh)	27.04 (26.59)	2.81 (2.71)	4.36 (4.43)
7^b	2105(s), 2049(vs), 2038(m), 2028(sh), 1992(m)	26.84 (26.50)	3.18 (3.02)	4.30 (4.41)
8^b	2128(m), 2093(vs), 2067(s), 2031(s)	not analyzed		
9^b	2205(m), 2097(s), 2071(s), 2030(s)	31.79 (31.89)	3.73 (3.66)	5.77 (5.87)

^{a}Hexane/CH_2Cl_2 solution (9/1). ^{b}CH_2Cl_2 solution. ^{c}Hexane solution.

3d. The absorption at 1855 cm^{-1} suggests the presence of a bridging CO. The signal at 2131 cm^{-1} of **3f** has been attributed to an absorption of the coordinated cyano group. The shift to higher wavenumber as compared to uncoordinated CN^- (2080 cm^{-1}) is normal for coordinated cyano groups and has been explained by assuming that the character of the M–CN bond is primarily σ-donor instead of a π-acceptor interaction [20]. The absorption of the ^{t}Bu-isocyanide ligand in **9** (2205 cm^{-1}) has shifted towards a higher wavenumber as compared to the uncoordinated ligand (2130 cm^{-1}) [21]. It is known that CN frequencies of isocyanide ligands may shift both to lower and to higher wavenumber upon coordination [22]. The value observed here is well within the limits reported [21, 23].

NMR spectroscopy

The ^{1}H NMR and ^{13}C NMR spectroscopic data have been summarized in Tables 6 and 7, respectively. The ^{1}H NMR spectra of DAB ligands in a 6e donating σ-N,μ_2-N$'$,η^2-C=N$'$ coordination mode usually show signals in the 7–9 and 3–4 ppm regions, arising from the σ-N coordinated imine moiety and the η^2-C=N coordinated imine moiety, respectively [7, 18, 24]. The corresponding carbon atoms have been observed in the 170–190 and 60–70 ppm regions, respectively. Similar shifts have been observed for the complexes **3a–f**, **6**, **8** and **9**, indicating that these complexes all contain a DAB ligand in the 6e donating σ-N,μ_2-N$'$,η^2-C=N$'$ coordination mode. The ^{1}H NMR spectrum of **3b** shows that the N=C(Me) moiety is σ-N coordinated while the N=C(H) moiety is μ_2-N,η^2-C=N bonded. This agrees with earlier reports and with the fact that the N=C(Me) moiety is known to be a weaker π-acceptor as compared to the N=C(H) moiety [7, 25].

Complex **3a** was also analyzed with high-resolution ^{1}H NMR, which revealed the presence of a small coupling (about 0.5 Hz) between the hydride ligand

TABLE 6. ^{1}H NMR data of the complexes **3a–f**, **4a**, **4c**, **6**, **7**, **8** and **9**

3a^a	7.20 (1H, d, 1 Hz, σ-N=CH); 3.45/3.02 (1H/1H, sept/sept, 6.5 Hz, ^{i}Pr-CH); 3.09 (1H, dd, 0.5 Hz/1 Hz, η^2-N=CH); 1.58/1.48/0.99/0.85 (4×3H, 4×d, 6.5 Hz, ^{i}Pr-CH$_3$); −19.0 (1H, d, 0.5 Hz, Ru–H)
3b^a	3.12 (2H, sept, 6.5 Hz, ^{i}Pr-CH); 3.02 (1H, s, η^2-N=CH); 1.61/1.52/1.42/0.71 (4×3H, 4×d, 6.5 Hz, ^{i}Pr-CH$_3$); 1.12 (3H, s, N=C(CH)$_3$; −18.89 (1H, s, Ru–H)
3c^a	6.81 (1H, d, 0.7 Hz, σ-N=CH); 3.60/3.05 (1H/1H, sept/sept, 6.5 Hz, ^{i}Pr-CH); 2.97 (1H, d, 0.7 Hz, η^2-N=CH); 1.61/1.37/0.84.0.73 (4×3H, 4×d, 6.5 Hz, ^{i}Pr-CH$_3$); −16.31 (1H, s, Ru–H)
3d^b	7.89 (1H, s, σ-N=CH); 3.66 (1H, s br, η^2-N=CH); 3.56 (2H, sept, 6.5 Hz, ^{i}Pr-CH); 1.41/1.29/1.10 (3H/3H/6H, 3×d, 6.5 Hz, ^{i}Pr-CH$_3$); −15.10 (1H, s, Ru–H)
3e^b	7.80 (1H, s, σ-N=CH); 3.83/3.68 (1H/1H, sept/sept, 6.5 Hz, ^{i}Pr-CH); 3.78 (1H, s, η^2-N=CH); 1.39/1.03/0.78/0.72 (4×3H, 4×d, 6.5 Hz, ^{i}Pr-CH$_3$); −13.53 (1H, s, Ru–H)
3f^c	7.93 (1H, d, 1 Hz, σ-N=CH); 3.64/3.01 (1H/1H, sept/sept, 6.5 Hz, ^{i}Pr-CH); 3.48 (1H, d, 1 Hz, η^2-N=CH); 1.64/1.55/1.23/1.13 (4×3H, 4×d, 6.5 Hz, ^{i}Pr-CH$_3$); −15.50 (1H, s, Ru–H)
4a^a	3.55 (2H, dd br, 10.1 Hz/3.8 Hz, N-CH$_2$CH$_2$-N); 2.74 (2H, sept, 6 Hz, ^{i}Pr-CH); 2.43 (2H, dd br, 10.1 Hz/3.8 Hz, N-CH$_2$CH$_2$-N); 1.29/0.80 (6H/6H, d/d, 6Hz, ^{i}Pr-CH$_3$); −15.06 (1H, s, Ru–H)
4c^a	3.66 (2H, dd br, 10.5 Hz/3.8 Hz, N-CH$_2$CH$_2$-N); 2.79–2.50 (4H, m, ^{i}Pr-CH+N-CH$_2$CH$_2$-N); 1.33/0.78 (6H/6H, d/d, 6 Hz, ^{i}Pr-CH$_3$); −12.79 (1H, s, Ru–H)
6^b	8.13 (1H, d, 0.9 Hz, σ-N=CH); 3.73/3.30 (1H/1H, sept/sept, 6.5 Hz, ^{i}Pr-CH); 3.70 (1H, d, 0.9 Hz, η^2-N=CH); 1.59/1.47/1.16/1.12 (4×3H, 4×d, 6.5 Hz, ^{i}Pr-CH$_3$); −23.23 (1H, s, Ru–H)
6^a	7.39 (1H, d, 0.9 Hz, σ-N=CH); 3.39/2.93 (1H/1H, sept/sept, 6.5 Hz, ^{i}Pr-CH); 3.07 (1H, d, 0.9 Hz, η^2-N=CH); 1.43/1.37/0.96/0.84 (4×3H, 4×d, 6.5 Hz, ^{i}Pr-CH$_3$); −23.14 (1H, s, Ru–H)
7^c	3.40 (2H, dd br, 11.1 Hz/4.1 Hz, N-CH$_2$CH$_2$-N); 3.22–3.06 (4H, m, ^{i}Pr-CH+N-CH$_2$CH$_2$-N); 1.42–1.29 (12H, m, ^{i}Pr-CH$_3$); −18.99 (1H, s, Ru–H)
8^b	8.37 (1H, s, σ-N=CH); 3.85 (1H, s, η^2-N=CH); 3.63/3.18 (1H/1H, sept/sept, 6 Hz, ^{i}Pr-CH); 1.79/1.15 (6H/6H, d/d, 6 Hz, ^{i}Pr-CH$_3$); −15.06 (1H, s, Ru–H)
9^b	8.31 (1H, s, σ-N=CH); 3.86 (1H, s, η^2-N=CH); 3.68/3.21 (1H/1H, sept/sept, 6 Hz, ^{i}Pr-CH); 1.63 (9H, s, ^{t}Bu-CH$_3$); 1.14/1.05 (6H/6H, d/d, 6 Hz, ^{i}Pr-CH$_3$; −15.79 (1H, s, Ru–H)

^{a}C$_6$D$_6$, 100.13 MHz. ^{b}CDCl$_3$, 100.13 MHz. ^{c}CDCl$_3$, 300.13 MHz.

TABLE 7. ^{13}C NMR data of the complexes **3a–f**, **4a**, **4c**, **6**, **7**, **8** and **9**

3a^a	22.3/22.6/25.5/27.2 (^{i}Pr-CH$_3$); 60.6/66.7 (2×^{i}Pr-CH+η^2-N=CH); 173.7 (σ-N=CH); 190.1/191.4/196.2/197.5/197.9 (CO)
3b^a	14.9 (N=C(CH$_3$)); 20.4/23.8/25.2/27.4 (^{i}Pr-CH$_3$); 55.0 (η^2-N=CH); 65.4/66.5 (^{i}Pr-CH); 183.0 (σ-N=C(Me)); 190.7/191.2/195.7/198.0/198.3 (CO)
3c^a	22.1/22.2/25.2/29.7 (^{i}Pr-CH$_3$); 61.0 (η^2-N=CH); 60.0/67.3 (^{i}Pr-CH); 172.7 (σ-N=CH); 190.4/191.1/196.8/197.9/198.3 (CO)
3d^c	22.3/22.5/25.1/28.6 (^{i}Pr-CH$_3$); 60.5/62.2 (^{i}Pr-CH); 64.2 (η^2-N=CH); 172.7 (σ-N=CH); 190.8 (Ru–CO (2×)); 191.4 (Ru–CO) (3×)); 198 (br, Co–CO)
3e^c	21.7/21.9/22.8/30.6 (^{i}Pr-CH$_3$); 56.8/65.0 (^{i}Pr-CH); 64.2 (η^2-N=CH); 171.0 (σ-N=CH); 192.1/192.8/200.7/203.7/205.7 (Ru–CO); 223 (br, Mn–CO)
3f^{c,d}	23.1/23.2/26.8/28.3 (^{i}Pr-CH$_3$); 61.8/62.0 (^{i}Pr-CH); 68.5 (η^2-N=CH); 174.9 (σ-N=CH); 189.8/191.3/194.2/196.2/197.4 (CO)
4a^b	21.8/24.3 (^{i}Pr-CH$_3$); 51.9 (N-CH$_2$CH$_2$-N); 66.1 (^{i}Pr-CH); 190.3 (Ru–CO (2×)); 196.3 (Ru–CO (3×))
4c^a	24.1/24.4 (^{i}Pr-CH$_3$); 54.7 (N-CH$_2$CH$_2$-N); 66.2 (^{i}Pr-CH); 190.8 (Ru–CO (3×)); 197.5 (Ru–CO (3×))
6^b	22.5/25.7 (^{i}Pr-CH$_3$); 59.5 (η^2-N=CH); 61.3/65.6 (^{i}Pr-CH); 176.1 (σ-N=CH); 187.9/190.2/193.5/195.1/195.2 (Ru–CO)
7^c	20.9/24.4 (^{i}Pr-CH$_3$); 51.1 (N-CH$_2$CH$_2$-N); 66.3 (^{i}Pr-CH); 186.4 (CO (1×)); 189.3 (CO (2×)); 194.5 (CO (2×))
8^b	22.4/22.7/27.0/28.1 (^{i}Pr-CH$_3$); 62.1/67.7 (^{i}Pr-CH); 62.3 (η^2-N=CH); 181.3 (σ-N=CH); 184.5/186.4/187.2/188.6/189.3/194.1 (CO)
9^b	22.4/22.8/27.1/27.8 (^{i}Pr-CH$_3$); 30.2 (^{t}Bu-CH$_3$); 61.2 (C(Me$_3$)); 61.8/62.3 (^{i}Pr-CH); 67.3 (η^2-N=CH); 168.2 (Ru–C–N); 179.6 (σ-N=CH); 188.0/190.0/190.4/192.6/195.3 (CO)

^{a}C$_6$D$_6$, 25.17 MHz. ^{b}CDCl$_3$, 263 K, 25.17 MHz. ^{c}CDCl$_3$, 263 K, 75.46 MHz. ^{d}Cyanide-carbon atom not observed.

and the imine proton of the η^2-coordinated imine moiety and a similar coupling has been observed for H$_2$Ru$_2$(CO)$_5$(^{i}Pr-DAB) (**1a**) [3]. The presence of the small coupling between the bridging hydride ligand and the imine proton of the η^2-coordinated imine moiety within **3a** justifies the use of this coupling as an argument for the bridging nature of one of the hydride ligands within **1a** [3]. The bridging character of the hydride ligand of **3a** was confirmed by its chemical shift and further by the proton coupled ^{13}C NMR spectrum and the 2D ^{1}H–^{13}C correlations of the carbonyl region of **3a**, which were compared with the data obtained for **1a** [3]. From the chemical shifts it may be safely deduced that in complexes **3b–f**, **6**, **8** and **9** the hydride ligand is also bridging.

Both the ^{1}H NMR spectra and the ^{13}C NMR spectra of complexes **4a**, **4c** and **7** show the characteristic features of a hydrogenated DAB ligand. The C$_2$H$_4$ moiety appears in the ^{1}H NMR spectrum as two sets of signals, both looking like doublets of doublets but obviously broadened due to second order coupling effects. The corresponding C atoms have been observed around 53 ppm in the ^{13}C NMR spectrum.

The carbonyl region of the ^{13}C NMR spectrum of complexes **3d** shows a slightly broadened signal whereas the spectrum of **3e** contains a very broad signal in this region. These signals are attributed to the carbonyls coordinated to cobalt and manganese, respectively, since it is well known that these metals have a broadening effect on ^{13}C resonances of carbonyl ligands [26].

Preparation of HRu$_2$(X)(CO)$_5$(^{i}Pr-DAB{H, R}) (X=Cl, R=H (3a); X=Cl, R=Me (3b); X=I, R=H (3c)) and reactions with H$_2$ and D$_2$

The preparation of complexes **3a–c** from H$_2$Ru$_2$(CO)$_5$(^{i}Pr-DAB{H,R}) (R = H (**1a**); R = Me (**1b**)) involves the substitution of one hydride ligand by a halide atom of CX$_4$. This reaction is a strong indication that **1a, b** contain one bridging and one terminal hydride atom, since bridging hydrides are generally less reactive than terminal ones [3, 27]. The deuteride derivatives could also be prepared by treatment of the dideuteride complexes **1′** with CX$_4$, whereas alternatively the reaction of HRu$_2$(Cl)(CO)$_5$(^{i}Pr-DAB) (**3a**) with D$_2$ at 70 °C also eventually afforded DRu$_2$(Cl)(CO)$_5$(^{i}Pr-DAB) (**3a′**).

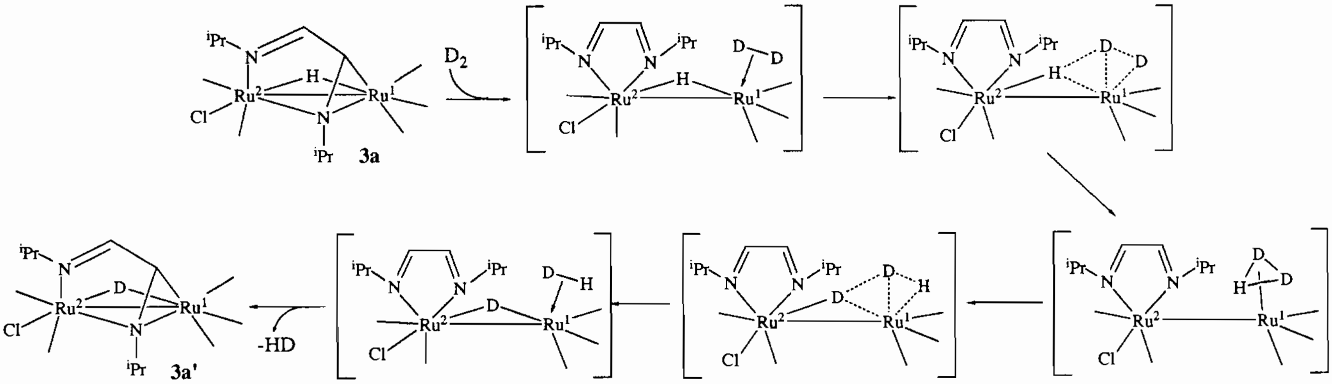
When following this H/D exchange process at 70 °C by ^{1}H NMR, e.g. for the reverse exchange of **3a′** with H$_2$, the appearance and slow increase of the signal at the known bridging hydride position at −19.0 ppm was observed without the reduction of the DAB ligand occurring. This exchange requires some comment, because it is not directly obvious how this reaction takes cause it is not directly obvious how this reaction takes place. In this respect it should be noted that during the reversible exchange of $H_2Ru_2(CO)_5$(^{i}Pr-DAB) (**1a**) with D_2 and of $D_2Ru_2(CO)_5$(^{i}Pr-DAB) (**1a'**) with H_2 at 70 °C the terminal hydride/deuteride, respectively, exchanged with D_2/H_2 much less rapidly than the bridging hydride/deuteride [3].

We propose that this H/D exchange process proceeds via a mechanism outlined in Scheme 5. D_2 coordinates in an η^2-fashion to the Ru atom which does not carry the chloride atom, and close to the bridging hydride atom. In order to create an empty coordination site the α-diimine changes its coordination mode to a σ-N,σ-N′ 4e donor mode, which is thermally induced (Scheme 5). In order to rationalize the H–D exchange we assume subsequent formation of an H$\cdots$D–D interaction or a HD_2 type of moiety [28] from which HD may escape with the formation of a bridging deuteride species. It is clear that the suggested mechanism enables the bridging hydride both in the case of **3a**, which contains a terminal chloride atom, and in the case of $H_2Ru_2(CO)_5$(^{i}Pr-DAB) (**1a**), which contains a terminal hydride atom [3], to be involved in an exchange process with molecular deuterium.

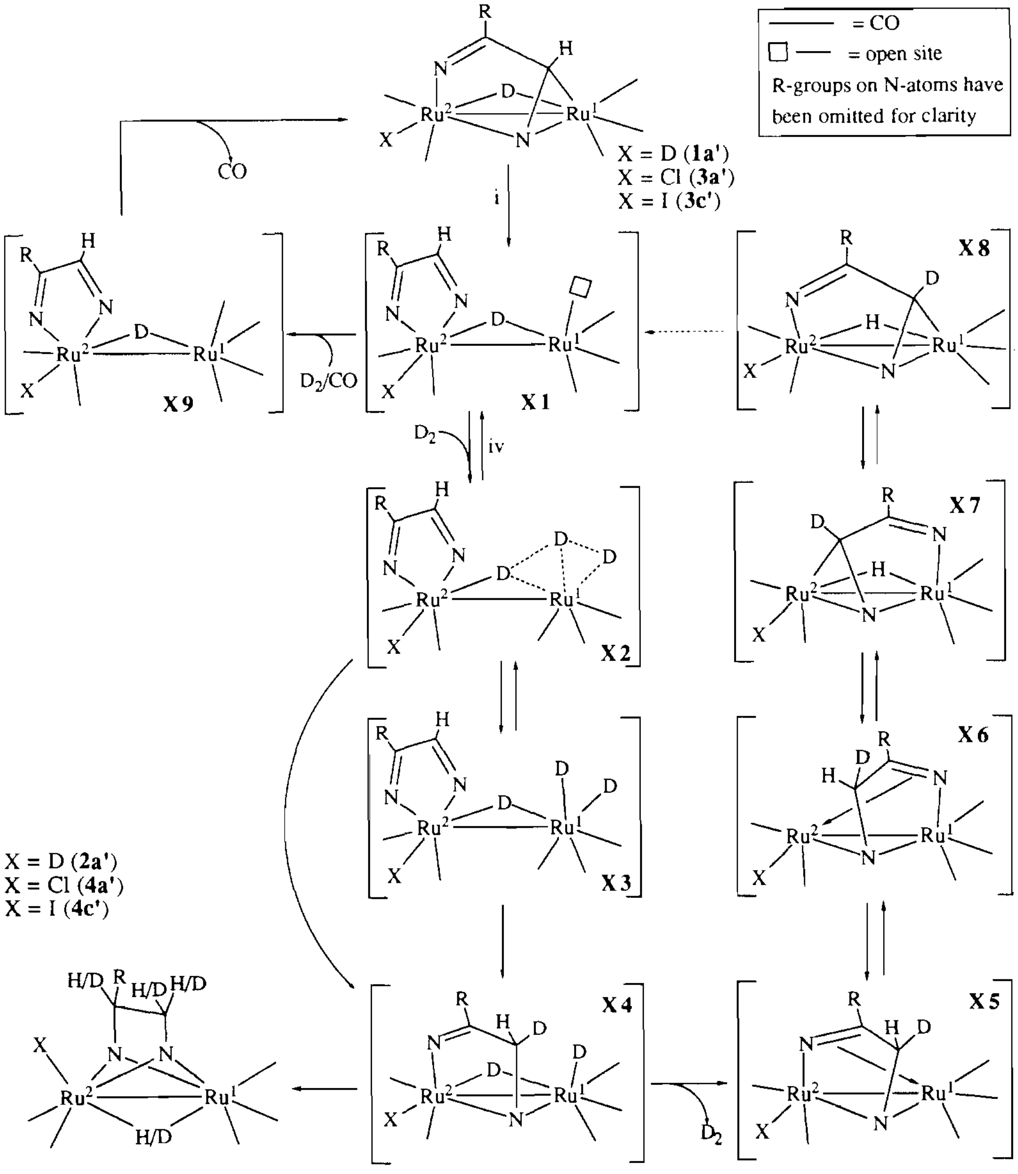
When we now increase the reaction temperature to 90 °C the compounds **3a** and **3c** are converted to $HRu_2(X)(CO)_5$(^{i}Pr-N-CH_2CH_2-N-^{i}Pr) (X = Cl (**4a**); X = I (**4c**)) and small amounts of the side product $Ru_2(CO)_6$(^{i}Pr-N-CH_2CH_2-N-^{i}Pr) (**5a**) (Scheme 3). This result implies that **4a** and **4c** are more stable than $H_2Ru_2(CO)_5$(^{i}Pr-N-CH_2CH_2-N-^{i}Pr) (**2a**), which easily converts to $Ru_2(CO)_6$(^{i}Pr-N-CH_2CH_2-N-^{i}Pr) (**5a**) in the presence of some CO formed by decomposition [3]. Furthermore, although **4a** and **4c** can eventually be converted to **5a**, higher temperatures and longer reaction times are required. Interestingly the reduction of the methylated ^{i}Pr-DAB{H,Me} ligand in **3b** only yielded the hexacarbonyl complex $Ru_2(CO)_6$(^{i}Pr-N-C(H)-(Me)CH_2-N-^{i}Pr) (**5b**). Why in this case $HRu_2(Cl)(CO)_5$(^{i}Pr-N-C(H)(Me)CH_2-N-^{i}Pr) is not formed is not clear. A reason could be that in the latter compound a steric interaction between the methyl group and the terminal chloride atom causes the complex to be unstable with respect to the hexacarbonyl complex. In this respect it should be noted that $H_2Ru_2(CO)_5$(^{i}Pr-N-C(H)(Me)CH_2-N-^{i}Pr) does exist, but is clearly unstable, probably due to steric interaction between the terminal hydride and the methyl group [3].

With respect to the mechanism it is essential to mention that carbon monoxide completely inhibits the reduction reaction, as has also been observed for the reaction systems involving $H_2Ru_2(CO)_5$(^{i}Pr-DAB) [3] and $FeRu(CO)_6$(^{i}Pr-DAB) [4]. In the case of the reaction system containing, for example, **3a**, H_2 and CO, only a small amount of $Ru_2(CO)_6$(^{i}Pr-DAB) was formed, whereas no evidence was found for the formation of complexes containing a reduced DAB ligand. This inhibiting effect of carbon monoxide on the reduction process may be rationalized by coordination of the carbon monoxide to an open coordination site that is formed by breaking the η^2-C=N coordination of the DAB ligand, thus blocking the attack of hydrogen (Scheme 6; *vide infra*).

Essential for the understanding of the stereochemistry of the reduction process involves the use of D_2. We have already mentioned the H/D exchange process occurring on the bridging hydride position of **3a** and in our mechanism we should incorporate this finding. At 90 °C $DRu_2(Cl)(CO)_5$(^{i}Pr-DAB) (**3a'**) reacted with D_2 to **4a'** together with a small amount of **5a'**. Fortunately we were able to isolate pure **4a'** from the reaction mixture, which in contrast to the non-halogenated analogue **2a'** [3], enables us to obtain detailed information about the presence of H and D atoms on the C_2 moiety of the reduced ligand. The ^{1}H NMR spectrum of **4a'** showed the presence of some hydride intensity at the bridging hydride/deuteride position (integral 0.25 H)*, whereas for the C_2 moiety of the hydrogenated DAB ligand two small signals were observed with relative intensities of about 0.4 H (3.55



Scheme 5. Proposed mechanism for the observed H/D exchange of the bridging hydride in **3a**.



Scheme 6. Proposed mechanism for the deuteration of complexes **1a'** (X = D) [3] and **3a'**/**3c'** (X = Cl/I).

ppm)* and 0.25 H (2.43 ppm)*. The ^{1}H NMR spectrum of **5a'** showed a broad signal for the C_2 moiety with an integral of less than one proton*. The inescapable conclusion is that during the deuteration process, which is clearly not as stereoselective as for the FeRu systems [1, 4], in one of the key intermediates not only C–D bond making occurs, but also C–H bond breaking, since we find that in the final product H has been transferred from the C_2 moiety to the bridging hydride position.

The proposed mechanism for the reduction of complexes **3a–c** is shown in Scheme 6 [3]. The D_2 attacks the empty position on Ru(1) which is formed by breaking the Ru(1)–η^2-C=N bond. Then η^2-coordinated D_2 may now form a D_3 kind of species (**X2**) (see also Scheme 5) after which D is transferred to one imine C atom. Alternatively the coordinated D_2 may be oxidatively added to Ru(1) (**X3**) after which D-transfer occurs. When now the non-coordinated imine unit becomes coordinated to Ru(1) a species **X5** is formed, analogous to $Ru_2(CH_3C{=}C(H)\text{-}CH_2\text{-}N\text{-}^iPr)$ [29] containing an enyl-amido group which may carry out a windscreen wiper type of motion converting **X5** to **X6**. Subsequently transfer of H may occur to give **X7** and finally **X8**, whereafter the cycle may start again. As soon as the final product **4** is formed the bridging hydride of **4** does not exchange anymore with D_2 gas, while also no C–H/C–D bond rupture/formation takes place. This

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*Based on the integral of the overlapping signals of the two ^{i}Pr-CH protons, which was set on 2.00.

finding nicely shows that an empty position must be formed for H/D exchange to occur, which is possible for **3a**/**3a′**, but not for **4**. Finally, we wish to mention that in the presence of carbon monoxide a carbonyl ligand may coordinate to the open site vacated by the H_2–C=N moiety, thus forming **X9** and inhibiting the hydrogenation process.

Upon comparing Schemes 1 and 6 it can be seen that the proposed reaction mechanisms for the FeRu and Ru_2 systems are very similar, especially with respect to the way the open coordination site is created, and with respect to the presence of intermediates containing a partially reduced DAB ligand (i.e. **X4** in Scheme 6). However, in the case of the Ru_2 system the presence of hydride/deuteride ligands within the partially hydrogenated species **X4** provides an additional pathway via which the above mentioned bond making/breaking processes may occur.

It was found that the reaction of **3a′** with H_2 leads to the same result as the reaction of **3a** with H_2 since a completely non-deuterated product was observed in both cases whereas at the same time reaction of **3a** with D_2 gave the same results as the reaction of **3a′** with D_2. This is obviously a consequence of the occurrence of the above mentioned H/D exchange process (Scheme 5) between the bridging hydride and the gas atmosphere, which occurs more easily than the reduction process (*vide supra*). The occurrence of this H/D exchange process also explains that for the reaction of **3a′** with D_2 the total proton content in the product is lower than in the starting compound, showing that the H atoms cannot only be transferred from the ligand to the hydride site but may subsequently even be transferred to the gas atmosphere.

An important conclusion that can be drawn at this stage is that the results obtained for the reaction of **3a′** with D_2 may be explained via the same mechanism that has been proposed for the reaction of $D_2Ru_2(CO)_5$(^{i}Pr-DAB) (**1a′**) with D_2 [3]. This agrees very well with the assumption that the atom at the terminal position, i.e. a D atom for **1a′** and a Cl atom for **3a′**, does not play any role in the reduction of the DAB ligand, as we proposed earlier [3].

Preparation of [OTF][HRu$_2$(CO)$_5$(^{i}Pr-DAB) (6) and reactions of 6 with CO, ^{t}Bu-NC, Co(CO)$_4$$^-$, Mn(CO)$_5$$^-$, CN$^-$ and hydrogen

In order to probe the reactivity of the derivatives of $HRu_2(Cl)(CO)_5$(^{i}Pr-DAB) (**3a**) towards H_2 and D_2, we prepared first [OTF][$HRu_2(CO)_5$(^{i}Pr-DAB)] (**6**) from **3a** and AgOTF. Subsequent reactions of **6** with CO and ^{t}Bu-NC afforded [OTF][$HRu_2(CO)_5$(L)(^{i}Pr-DAB)] (L = CO (**8**); L = ^{t}Bu-NC (**9**)), whereas neutral complexes $HRu_2(X)(CO)_5$(^{i}Pr-DAB) could be formed by reaction of **6** with $Co(CO)_4^-$ (**3d**), $Mn(CO)_5^-$ (**3e**) and CN^- (**3f**) (Scheme 4).

The structure of the novel trimetallic heteronuclear $CoRu_2$ and $MnRu_2$ complexes is not exactly known, but they should be similar to that of **3a** in view of the ^{1}H NMR spectra. The IR spectra indicate the presence of terminal CO groups, although in the case of **3d** a bridging CO group may be present.

Reaction of complexes **3d** and **3e** at 65 °C with H_2 yielded $H_2Ru_2(CO)_5$(^{i}Pr-DAB) together with $Co_2(CO)_8$ and $Mn_2(CO)_{10}$, respectively, whereas **3f**, which in contrast to **3d** and **3e** proved to be stable up to 95 °C, did react with H_2 without giving, however, identifiable products.

Finally, reaction of **6** with H_2 at 90 °C afforded [OTF][$HRu_2(CO)_5$(^{i}Pr-N-CH_2CH_2-N-^{i}Pr)] (**7**) together with the side product **5a** (about 25%). The reaction has also been performed using D_2 and the results were similar to those obtained for **1a** and **3a** with D_2. Even when only deuterium was used, both for the preparation of [OTF][$DRu_2(CO)_5$(^{i}Pr-DAB)] (**6′**) and for the ligand reduction, the resulting **7′** showed some proton intensity at the hydride position (relative intensity about 0.6 H)*. In addition both the main product **7′** and the side product **5a′** showed a shortage of proton intensity on the C_2 moiety of hydrogenated DAB ligand (relative intensity about 0.7 H)*.

Some comment is required on the purification of the mixture obtained in the treatment of **6** with hydrogen. Due to the cationic nature of the main product **7** column chromatography proved to be unsuitable as a method for purification. For this reason **7** was converted to **4a** by treatment with [NH_4][Cl]. Subsequently the reaction mixture was purified by means of column chromatography, and finally the purified **4a** was reconverted to **7** by treatment with AgOTF.

The reaction times and reaction conditions for the reaction of **6** with hydrogen did not differ substantially from the reactions of **1a** and **3a** with hydrogen, indicating that ligand effects appear to be of little importance. Only for the halide compounds **3a, 3c, 4a** and **4c**, it is clear that the halide increases the stability of the complexes as compared to their dihydride analogues.

Concluding remarks

A fascinating difference between the hydrogenation of all Ru_2 systems and all FeRu systems studied is that in the latter case use of D_2 leads to stereoselective *trans* addition of two D atoms to the central C–C bond of the coordinated DAB ligand (Scheme 1) [1, 4], whereas in the case of the Ru_2 systems the D atoms are randomly substituted on the C_2 moiety (ref. 3 and this paper). Furthermore, more than two D atoms arrive on the C_2 unit, whereas at the same time H, originally

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*Based on the integral of the overlapping signals of the two ^{i}Pr-CH protons, which was set on 2.00.

bonded in the former C_2H_2 unit, has been transferred to the bridging deuteride position of, for example, $DRu_2(X)(CO)_5(^iPr\text{-}DAB)$ (X = H, Cl) (Scheme 6).

Therefore at this stage it is of interest to address ourselves to the question of why these systems differ. In our view the main cause of difference lies in the existence of stable hydride/deuteride intermediates in the case of Ru_2 complexes, whereas these species have never been observed for the FeRu compounds with DAB ligands [1]. Up to intermediate **X4** of Scheme 6 both Scheme 1 and Scheme 6 are rather similar. However, in the case of Ru_2 after **X4** H/D exchange may occur between the C_2 moiety and the bridging hydride/deuteride, which is not possible for the FeRu system (Scheme 1). In the FeRu case a cycle like presented in Scheme 6 from **X4** to **X8** is not feasible.

These results therefore, when considered in a broader context, offer a nice model of how on catalytic surfaces (partial) reversible hydrogen exchange may occur depending on the stability of the metal–hydride intermediates.

Supplementary material

Tables of crystal data, anisotropic thermal parameters, all H atom parameters, bond lengths and bond angles of **3a** (6 pages) are available from the authors on request. Listings of observed and calculated structure factor amplitudes for **3a** (28 pages) can be obtained from author A.L.S.

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