Synthesis of the First Heterobimetallic Rhenium–Ruthenium η^2-Dihydrogen Complexes

Martine Cazanoue, Zhongli He, Denis Neibecker and René Mathieu*

Laboratoire de Chimie de Coordination du CNRS, UP 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne 31077 Toulouse Cedex, France

The complex $[(PPh_3)_2HRe(\mu\text{-}H)_3(\mu\text{-}CO)RuH(PPh_3)_2]$ **1**, resulting from the reaction of $[ReH_6(PPh_3)_2]^-$ with $[RuHCl(CO)(PPh_3)_3]$, reacts with chloroform to give $[(PPh_3)_2HRe(\mu\text{-}Cl)_2(\mu\text{-}H)(\mu\text{-}CO)RuH(PPh_3)_2]$ **2**; protonation of **1** and **2** with $HBF_4{\cdot}Et_2O$ leads to the formation of the fluxional $[(PPh_3)_2HRe(\mu\text{-}H)_3(\mu\text{-}CO)Ru(\eta^2\text{-}H_2)(PPh_3)_2][BF_4]$ **3**, and the rigid $[(PPh_3)_2HRe(\mu\text{-}H)(\mu\text{-}Cl)_2(\mu\text{-}CO)Ru(\eta^2\text{-}H_2)(PPh_3)_2]$ $[BF_4]$ **4** complexes.

The search for new heterobimetallic systems with unusual stoichiometric or catalytic properties is currently under intensive investigation.[1] Bimetallic polyhydride complexes are of special interest since the presence of terminal or bridging hydride ligands should be a favourable factor for reactivity.[2]

Using the strategy allowing the ReU[3] or ReZr[4] bimetallic polyhydrides to be obtained, we have synthesized a bimetallic ReRu polyhydride complex by the reaction of $[ReH_6(PPh_3)_2]^-$ with a complex containing a metal–halogen bond. The reaction of $[ReH_6(PPh_3)_2]^-$ with $[RuHCl(CO)(PPh_3)_3]$ at room temperature leads to the synthesis of $[ReRuH_5CO(PPh_3)_4]$ **1**, in 72% yield. The structure of **1** has been deduced from spectroscopic data since it has not been possible to obtain crystals suitable for an X-ray crystal structure determination. The spectroscopic data for **1** are gathered in Table 1. The ν_{CO} stretching frequency indicates that the carbonyl group is in bridging position. At room temperature, the ^1H and ^{31}P NMR spectra show that the molecule is fluxional while lowering the temperature to 193 K

Table 1 Spectroscopic data for the complexes isolated

Compound	IR: ν_{CO}/cm^{-1}	^1H NMR (δ)[a] (hydride region)	^{31}P NMR (δ)	T/K
1	1865	−4.92 (t) (J 52.4), −6.12 (br), −17.21 (dt) (J^1 5.3, J^2 33)	71.9 and 37.1	293
		H^1 −4.25 (ddd); $J(H^1H^5)$ 5.3, J 15 and 18 $[J(H^1P^3) + J(H^1P^4)]$	P^1 70.7 (dd) (J_{14} 5.1, J_{13} 14.1)	193
		H^2 −4.92 (t); J 52.4 $[J(H^2P^3) + J(H^2P^4)]$	P^2 70.5 (s)	
		H^3 −6.21 (dt); J 15 $[J(H^3P^1)$ or $J(H^3P^2)]$, J 24 $[J(H^3P^3) + J(H^3P^4)]$	P^3 40.8 (dd) (J_{13} 14.1, J_{34} 21)	
		H^4 −7.86 (d); J 38 $[(J(H^4P^1)$ or $J(H^4P^2)]$	P^4 37.1 (dd) (J_{14} 5, J_{34} 21)	
		H^5 −17.13 (dt); J 5.3 $[J(H^1H^5)$, J 33 $[J(H^5P^1) + J(H^5P^2)]$		
2	1870	H^1 −4.59 (t); J 66.3 $[J(H^1P^3) + J(H^1P^4)]$	P^1 74.0 (d) (J_{12} 37.6)	293
		H^2 −5.46 (dddd); $J(H^2P^1)$ 23, $J(H^2P^2)$ 9.4, $J(H^2P^3)$ 30.6, $J(H^2P^4)$ 30.6	P^2 59.3 (ddd) J_{12} 37.6, J_{23} 7.6, J_{24} 28.1)	
		H^3 −18.95 (ddd); $J(H^3P^1)$ 32.2, $J(H^3P^2)$ 27.3, $J(H^3P^4)$ 3	P^3 21.8 (dd) (J_{23} 7.6, J_{34} 9.2)	
			P^4 14.0 (dd) (J_{24} 28.1, J_{34} 9.2)	
3	1892	H^1 −4.85 (ddt); $J(H^1P^1)$ 42.8, $J(H^1P^2)$ 14, $J(H^1P^3) \approx J(H^1P^4) \approx 12$	P^1 56.6 (ddd) (J_{12} 24.7, J_{13} 10.6, J_{14} 4.6)	193
		H^2 −5.12 (t); $J(H^2P^3) = J(H^2P^4) = 50.6$	P^2 48.7 (d) (J_{12} 24.7)	
		H^3 −6.09 (dd); $J(H^3P^1)$ 11.4, $J(H^3P^2)$ 52.9	P^3 39.9 (dd) (J_{13} 10.6, J_{34} 10.5)	
		H^4 −8.10 (br.); $J(H^4P^3) \approx J(H^4P^4) \approx 5$	P^4 35.4 (dd) (J_{14} 4.6, J_{34} 10.5)	
		(H_2) −9.34 (br.)		
4	1898	H^1 −3.29 (t); $J(H^1P^3) = J(H^1P^4) = 59$	P^1 59.3 (d) (J_{12} 24.5)	
		H^2 −6.55 (ddt); $J(H^2P^1)$ 15.3, $J(H^2P^2)$ 45.5, $J(H^2P^3) \approx J(H^2P^4) \approx 11.4$	P^2 32.3 (ddd) (J_{12} 24.5, J_{23} 26.9, J_{24} 4.7)	
		(H_2) −11.75 (br.)	P^3 25.8 (d) (J_{23} 26.9)	
			P^4 20.1 (d) (J_{24} 4.7)	

[a] J values in Hz.

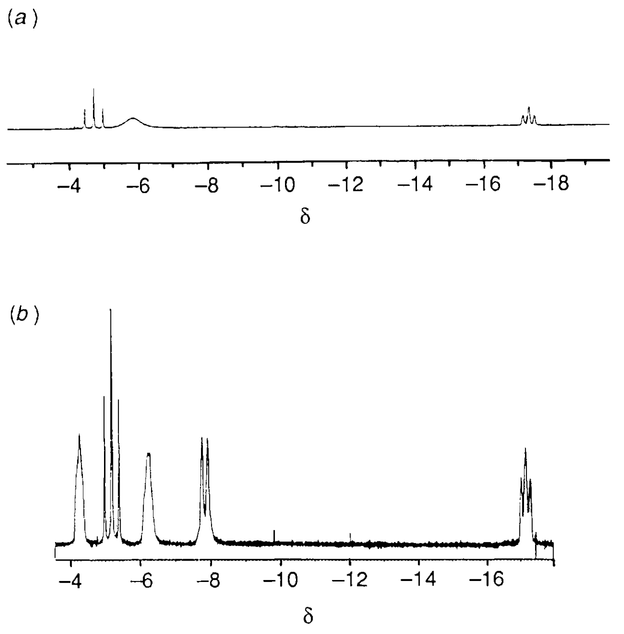

Fig. 1 250 MHz ^{1}H NMR spectra in the high field region for **1**: (*a*) at 293 K, (*b*) at 193 K

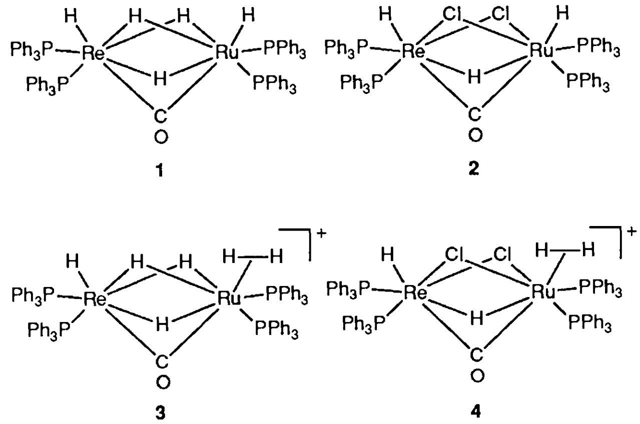

Fig. 2 Proposed structures for complexes **1–4**

freezes the motion. Four phosphorus signals are observed and, from chemical shift values, P^1 and P^2 are attributed to phosphorus atoms bonded to Ru and P^3 and P^4 to phosphorus atoms bonded to Re.

In the ^{1}H NMR spectrum (Fig. 1), the broad signal observed at room temperature at δ −6.12 splits into three signals centred at δ −4.25, and −6.21 and −7.86 at 193 K, while the other two signals are only slightly affected by lowering the temperature. ^{1}H NMR spectroscopy with selective decoupling of $P^1 + P^2$ and $P^3 + P^4$ phosphorus atoms has allowed all the coupling constants to be attributed. The results obtained (Table 1) are consistent with H^2 and H^5 being in terminal positions on the Re and Ru centres, respectively, and the other three hydride ligands being in bridging positions. More specifically, the data observed for the hydride resonances compare well with those found in the literature for $Re_2H_{8-2x}(PR_3)_{4+x}$ complexes.[5] We propose for **1** the structure shown in Fig. 2 in which the two metals are bridged by three hydride and one CO ligands. Complex **1** is electronically unsaturated (30 valence electrons) and in the absence of an X-ray structure determination it is difficult to know if there is some degree of multiplicity in the metal–metal bond or even a metal–metal bond. (There is a recent example of a 30 valence electrons dirhenium complex in which there is no metal–metal bond).[6]

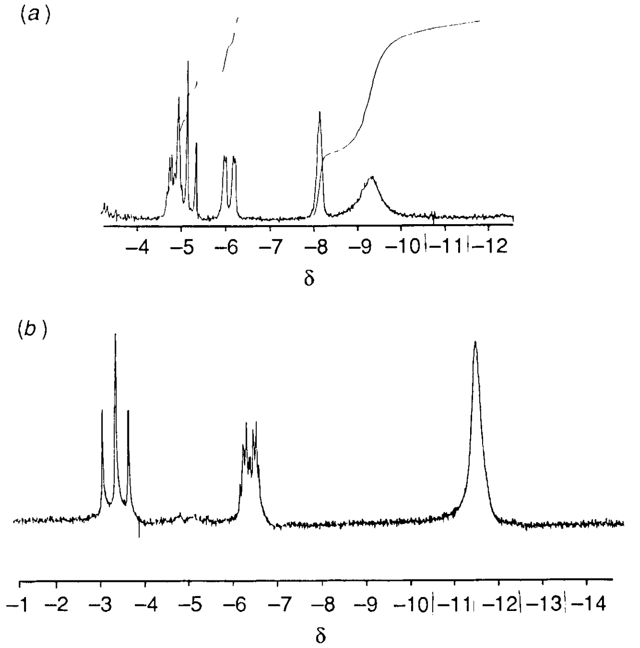

Fig. 3 250 MHz ^{1}H NMR spectra in the high field region: (*a*) for **3** at 193 K; (*b*) for **4** at 293 K

Without an X-ray structure, it is also difficult to be certain of the relative positions of the various ligands in **1** and to propose a mechanism for its fluxionality. Nevertheless, there are some similarities with the fluxional $[Re_2H_5(PMe_2Ph)_4\{P(OCH_2)_3CEt\}_2]^+$ cation where the terminal hydride remains distinct from bridging hydrides in the room temperature ^{1}H NMR spectrum.[5b]

Complex **1** reacts cleanly with chloroform to give a new product, **2**, analysing for $[ReRuH_3Cl_2CO(PPh_3)_4]$. Again, the structure was deduced from spectroscopic data since no crystal suitable for an X-ray structure determination was obtained. The ν_{CO} stretching frequency is only slightly modified compared to **1** and the CO ligand is still in a bridging position. The NMR data (Table 1) show that **2** is not a fluxional molecule and four resonances are observed in the ^{31}P NMR spectrum at room temperature. The ^{1}H NMR spectrum is consistent with the replacement of two bridging hydrides by two bridging chlorine ligands. Like H^2 in **1**, H^1 is in a terminal position on the Re atom, while, like H^5 in **1**, H^3 is in a terminal position on Ru. H^2 is in a bridging position since it is coupled to all the phosphorus atoms.

From these observations we propose for **2** the structure shown in Fig. 2 in which the Re–Ru metal–metal bond is bridged by one CO, one hydride and two chlorine ligands. Owing to the replacement of two bridging hydride ligands by two chlorine ligands, the Re–Ru bond is now a single metal–metal bond. This certainly explains the selectivity of the reaction of chloroform with **1**. As for **1**, it is difficult to assign the relative positions of the ligands in **2**.

Considering the structures of **1** and **2** and the fact that the two metals are able to stabilize η^2-bonded molecular hydrogen,[4,7] it was tempting to study their reactivity towards Brønsted acids to check whether protonation could induce the formation of complexed molecular hydrogen.

The reaction of stoichiometric amounts of $HBF_4 \cdot Et_2O$ with **1** or **2** led to the formation of two new complexes **3** and **4**, analysing $[(PPh_3)_2HRe(\mu\text{-}H)_3(\mu\text{-}CO)Ru(\eta^2\text{-}H_2)(PPh_3)_2][BF_4]$ **3** and $[(PPh_3)_2HRe(\mu\text{-}H)(\mu\text{-}Cl)_2(\mu\text{-}CO)Ru(\eta^2\text{-}H_2)(PPh_3)_2][BF_4]$ **4**. Protonation induces a shift of the CO IR absorption of 26 and 28 cm^{-1} respectively to higher frequencies which is consistent with the cationic formulation and the CO remaining in a bridging position. The region of hydride resonances of the ^{1}H NMR spectrum of **3** at room temperature shows a triplet centred at δ −4.77 (J_{PH} 51.3 Hz) and a very broad and asymmetric resonance centred at δ −7 (5 ppm broad at half-height). Lowering the temperature to 193 K (Table 1; Fig. **3a**) induces a slight shift of the triplet to δ −5.12 but the broad resonance is then split into a multiplet overlapping with the triplet, a double doublet centred at δ −6.09, a broad resonance at δ −8.10 and a very broad resonance at δ −9.34, the relative intensity of the last three signals being 1:1:2. Decoupling all the phosphorus nuclei gives sharp signals at δ −4.85 (H^1), −5.12 (H^2), −6.09 (H^3) and −8.10 (H^4) but the resonance at δ −9.34 remains very broad, suggesting that it could be a signal due to molecular hydrogen.

T_1 measurements at 250 MHz confirm this hypothesis since the minimum value observed at 213 K is 10 ms, which is fully characteristic of molecular hydrogen η^2-bonded to a metal.[8] The T_1 values for the other signals are, under the same conditions, 116 (H^1 and H^2), 104 (H^3) and 109 (H^4).

Four multiplets are apparent from the ^{31}P NMR spectrum (Table 1). The ^{1}H NMR spectrum with selective decoupling experiments of the phosphorus nucleus shows that H^1 is coupled with all the phosphorus atoms, H^2 with P^3 and P^4, H^3 with P^1 and P^2, and H^4 with P^3 and P^4. These results are consistent with H^2 being terminally bonded to Re and H^1, H^3 and H^4 being in a bridging position. So, we can conclude that protonation has occurred on the Ru metal centre and that the molecular hydrogen ligand is η^2-bonded to this centre. Furthermore at room temperature exchange occurs between bonded molecular hydrogen and bridging hydride ligands.

As for **1**, we propose for **3** a structure shown in Fig. 2 in which the two metals are bridged by three hydride and one CO ligands, but the relative positions of the phosphine and hydride ligands is difficult to ascertain in the absence of any X-ray crystal structure determination.

The ^{1}H NMR spectrum of **4** (Fig. 3*b* and Table 1) shows roughly the same pattern as **2** at room temperature except for H^3 resonance which is replaced by a broad signal of intensity 2 centred at δ −11.75, suggesting again the formation of η^2-bonded molecular hydrogen. T_1 measurements at 250 MHz give a minimum value of 9 ms at 213 K, the other two hydride ligands having T_1 values of 88 and 140 ms under the same conditions.

The ^{31}P NMR spectrum shows four resonances (Table 1) while the ^{1}H NMR spectrum, with selective phosphorus decoupling, indicates that H^1 is terminally bonded to Re and that H^2 is in a bridging position.

These results show that, here again, protonation has induced the formation of molecular hydrogen η^2-bonded to the ruthenium metal centre and we propose the structure shown in Fig. 2. In contrast to **3**, and as for **2**, the molecule is non-fluxional on the NMR time-scale and there in no apparent exchange between the bridging hydride ligand and the η^2-bonded molecular hydrogen on the NMR time-scale.

This situation has to be contrasted with that found for the closely related binuclear complexes, $[(R_3P)_2(H)Ru(\mu\text{-}Cl)_2(\mu\text{-}H)Ru(\eta^2\text{-}H_2)(PR_3)_2]$, where, depending on the phosphine ligands, complete exchange of all the hydride ligands with η^2-H_2 or limited exchange between the bridging hydride ligand and η^2-H_2 has been observed.[7c]

Finally, **3** and **4** are deprotonated to give **1** and **2** by triethylamine and, contrary to many molecular hydrogen complexes,[9] there is no exchange for **3** and **4** between molecular hydrogen η^2-bonded and dinitrogen.

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