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Synthesis and Reactivity of the New Unsaturated Heterobimetallic Polyhydride Complex $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$

Zhongli He, Sergeï Nefedov,[‡] Noël Lugan, Denis Neibecker, and René Mathieu*

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

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The reaction of $[K][ReH_6(PPh_3)_2]$ with $RuHCl(CO)(PPh_3)_3$ leads to the formation of the 30-electron complex $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ (1) in good yield. Its structure has been established by an X-ray structure determination. Most of the bridging hydrides were located in a difference Fourier map. The position of the terminal hydrides has been calculated using the program HYDEX. Crystallographic data for 1: monoclinic C_{2h}^5–$P2_1/n$, $a = 21.938(6)$ Å, $b = 13.046(2)$ Å, $c = 44.804(10)$ Å; $\beta = 96.50(1)°$, $V = 12740$ Å^3, $Z = 8$; $R = 0.053$, $R_w = 0.068$ for 4683 observations and 425 variable parameters. Compound 1 is inactive toward alkynes, but with ethylene the substitution of two hydride ligands and not the expected addition reaction is observed, leading to $(CO)(PPh_3)_2Re(\mu\text{-}H)_3Ru(C_2H_4)(PPh_3)_2$ (2). The reaction is reversible under hydrogen at atmospheric pressure. With chloroform 1 gives selectively the 34-electron complex $(CO)(PPh_3)_2Re(\mu\text{-}Cl)_2(\mu\text{-}H)RuH(PPh_3)_2$ (3). Compounds 1 and 3 react with $HBF_4{\cdot}OEt_2$ to give $[(CO)(PPh_3)_2Re(\mu\text{-}X)_2(\mu\text{-}H)Ru(H_2)(PPh_3)_2][BF_4]$ (X = H (4); X = Cl (5)), the first examples of heterobimetallic complexes containing molecular hydrogen as a ligand. Contrary to 5, the molecular hydrogen ligand in 4 is labile and can be replaced by ligands L like acetone, acetonitrile, or ethylene, leading to $[(CO)(PPh_3)_2Re(\mu\text{-}H)_3Ru(L)(PPh_3)_2][BF_4]$ complexes.

Introduction

The concept of bimetallic activation has led in the last several years to intensive investigations of the synthesis of new homo- and heterobimetallic systems, in which unusual stoichiometric or catalytic properties may be expected to exist.[1]

Among these systems, bimetallic polyhydride complexes have recently attracted interest since the presence of both terminal and bridging hydride ligands should be a factor favoring enhanced reactivity.[2] In addition to the expected classical reactivity of hydride ligands toward unsaturated organic molecules, polyhydride complexes generally offer the property of leading to unsaturated compounds, as they quite easily eliminate molecular hydrogen under photolysis[3] or protonation, occasionally through the formation of complexes containing a labile molecular hydrogen ligand.[4]

For these reasons we have tried to build new heterobimetallic polyhydride complexes, and as a building block, we have used $ReH_7(PPh_3)_2$ which can be easily deprotonated to $[ReH_6(PPh_3)_2]^-$.[2b] It has already been shown that this anion can be a source of bimetallic complexes, as it readily reacts with halogenide complexes of uranium[5] or zirconium[6] to give heterobimetallic polyhydride compounds in good yield.

Looking for an association of rhenium with a metal able to easily activate molecular hydrogen, we have retained in a first approach the ruthenium and we have observed that the $[ReH_6(PPh_3)_2]^-$ anion reacts with $RuHCl(CO)(PPh_3)_3$, leading to the new unsaturated complex $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ (1) in good yield.

This paper describes the characterization and some properties of this complex. Some preliminary results about its reactivity have already been published.[7,8]

Results and Discussion

Synthesis and Structure of $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ (1). This complex has been synthesized in 72% yield according to the reaction shown in eq 1 which occurs at room temperature in THF.

$$K[ReH_6(PPh_3)_2] + RuHCl(CO)(PPh_3)_3 \rightarrow ReRuH_5(CO)(PPh_3)_4 + PPh_3 + H_2 \quad (1)$$

In this reaction, one molecule of triphenylphosphine is liberated and hydrogen is certainly eliminated, as no other products have been detected by NMR. Note that the

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[‡] On leave from N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Leninsky Prosp. 31, Moscow 117907, Russia.

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Table I. Spectroscopic Data for the Isolated Complexes (*J* in Hz)

compd	IR (THF) νCO (cm^{-1})	NMR ^{1}H δ (ppm)	NMR ^{31}P{^{1}H} δ (ppm)	*T* (K)
1	1865	H_a −4.92 (t) (J_{PH} = 52.4) $H_b + H_c + H_d$ −6.12 (l) H_e −17.21 (dt) (J_{HH} = 5.3; J_{PH} = 33.0)	$P_a + P_b$ 71.9 $P_c + P_d$ 37.1	293
		H_b −4.25 (ddd) (J_{HbHe} = 5.3; J = 15.0; 18.0 (J_{HbPc} and J_{HbPd})) H_a −4.92 (t) ($J_{HaPc} = J_{HaPd}$ = 52.4) H_c −6.21 (dt) (J = 15.0 (J_{HcPa} or J_{HcPb}); $J_{HcPc} = J_{HcPd}$ = 24.0) He −17.13 (dt) (J_{HeHb} = 5.3; $J_{HePa} = J_{HePb}$ = 33.0)	P_a 70.7 (dd) (J_{PaPd} = 5.1; J_{PaPc} = 14.1) P_b 70.5 (s) P_c 40.8 (dd) (J_{PcPa} = 14.1; J_{PcPd} = 21.0) P_d 37.1 (dd) (J_{PdPa} = 5.0; J_{PdPc} = 21.0)	193
2	1820	C_2H_4 2.69 (s) H_2 −5.80 (s) H_1 (or H_3) −6.75 (d) (J_{PH} = 60.0) H_3 (or H_1) −6.85 (d) (J_{PH} = 60.0)	$P_1 + P_2$ 61.3 (1) $P_3 + P_4$ 47.3 (s)	296
		C_2H_4 3.19 H_1 −5.66 (bd) ($J_{H_1P_1}$ = 59.0) H_2 −5.84 (multiplet) H_3 −6.94 (dd) ($J_{H_3P_2}$ = 62.0; $J_{H_3P_1}$ = 10.0)	P_1 67.9 (multiplet) P_2 58.5 (multiplet) $P_3 + P_4$ 48.0 (s)	193
3	1870	H_1 −4.59 (t) ($J_{H_1P_3} = J_{H_1P_4}$ = 66.3) H_2 −5.46 (ddt) ($J_{H_2P_1}$ = 31.0; $J_{H_2P_2}$ = 9.4; $J_{H_2P_3} = J_{H_2P_4}$ = 32) H_3 − 18.95 (ddd) ($J_{H_3P_1}$ = 32.2; $J_{H_3P_2}$ = 27.3; $J_{H_3P_4}$ = 3.0)	P_1 74.0 (d) ($J_{P_1P_2}$ = 37.6) P_2 59.3 (ddd) ($J_{P_2P_1}$ = 37.6; $J_{P_2P_3}$ = 7.5; $J_{P_2P_4}$ = 28.1) P_3 21.8 (dd) ($J_{P_3P_2}$ = 7.6; $J_{P_3P_4}$ = 9.2) P_4 14.0 (dd) ($J_{P_4P_3}$ = 9.2; $J_{P_4P_2}$ = 28.1)	293
4	1892	H_1 −4.85 (ddt) ($J_{H_1P_1}$ = 42.8; $J_{H_1P_2}$ = 14.0; $J_{H_1P_3} \approx J_{H_1P_4}$ = 12) H_2 −5.12 (t) ($J_{H_2P_3} = J_{H_2P_4}$ = 50.6) H_3 −6.09 (dd) ($J_{H_3P_1}$ = 11.4; $J_{H_3P_2}$ = 52.9) H_4 −8.10 (b) ($J_{H_4P_3}$ = 9; $J_{H_4P_4}$ = 5.0) (H_2) −9.34 (b)	P_1 56.6 (ddd) ($J_{P_1P_2}$ = 24.7; $J_{P_1P_3}$ = 10.6; $J_{P_1P_4}$ = 4.6) P_2 48.7 (d) ($J_{P_2P_1}$ = 24.7) P_3 39.9 (dd) ($J_{P_3P_1}$ = 10.6; $J_{P_3P_4}$ = 10.5) P_4 35.4 (dd) ($J_{P_4P_1}$ = 4.6; $J_{P_4P_3}$ = 10.5)	193
5	1898	H_1 −3.29 (t) ($J_{H_1P_3} = J_{H_1P_4}$ = 59.0) 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) (H_2) −11.75 (b)	P_1 59.3 (d) ($J_{P_1P_2}$ = 24.5) P_2 32.3 (ddd) ($J_{P_2P_1}$ = 24.5; $J_{P_2P_3}$ = 26.9; $J_{P_2P_4}$ = 4.7) P_3 25.8 (d) ($J_{P_3P_2}$ = 26.9) P_4 20.1 (d) ($J_{P_4P_2}$ = 4.7)	293
6	1895	C_2H_4 2.40 (s) H_2 −4.72 (t) (J_{PH} = 53.4) H_3 −6.07 (t) (J_{PH} = 12.0) $H_1 + H_4$ −6.5 (1)	$P_1 + P_2$ 54.2 (s) $P_3 + P_4$ 33.7 (s)	294
		C_2H_4 2.45 (s); 2.31 (s) H_1 −4.68 (dd) ($J_{H_1P_1}$ = 42.5; $J_{H_1P_2}$ = 11.0) H_2 −5.00 (t) ($J_{H_2P_3} = J_{H_2P_4}$ = 54.0) H_3 −6.15 (tl) ($J_{H_3P_1} = J_{H_3P_2}$ 11.0) H_4 −8.36 (dd) ($J_{H_4P_1} \approx$ 5; $J_{H_4P_2}$ = 57.2)	P_1 63.0 (dd) ($J_{P_1P_2}$ = 24.9; $J_{P_1P_3}$ = 9.6) P_2 46.7 (d) ($J_{P_2P_1}$ = 24.9) P_3 39.9 (dd) ($J_{P_3P_2}$ = 9.6; $J_{P_3P_4}$ = 9.6) P_4 30.2 (d) ($J_{P_4P_3} \approx$ 9.6)	188
7	2272 (νCN) 1886 (νCO)	CH_3CN 1.52 (s) $H_1 + H_3$ −4.8 (b) H_2 −4.93 (t) (J_{PH} = 52.4) H_4 −14.0 (b)		297
		CH_3CN 1.52 (s) H_1 −4.64 (dd) (J_{H_1P} = 12.0; J_{H_1P} = 20.0) H_2 −4.92 (t) ($J_{H_2P_3} = J_{H_2P_4}$ = 52.6) H_3 −5.22 (multiplet) H_4 −13.98 (b)	P_1 56.8 (ddd) ($J_{P_1P_2}$ = 24.7; $J_{P_1P_3}$ = 15.7; $J_{P_1P_4}$ = 4.0) P_2 55.9 (d) ($J_{P_2P_1}$ = 24.7) P_3 39.5 (dd) ($J_{P_3P_1}$ = 15.7; $J_{P_3P_4}$ = 14.0) P_4 31.8 (b) ($J_{P_4P_1}$ = 4.0; $J_{P_4P_3}$ = 14.0)	183
8	1886 (ν CO) 1632 (νC=O)	$(CH_3)_2CO$ 2.05 (s) $H_1 + H_2$ −4.5 (bd) (J_{PH} = 40.0) H_3 −5.44 (t) (J_{PH} = 56.6) H_4 −20.85 (t) (J_{PH} = 13.5)	$P_1 + P_2$ 56.8 $P_3 + P_4$ 36.1	294
		$(CH_3)_2CO$ 2.20 (s) H_1 −3.65 (dd) ($J_{H_1P_1}$ <5; $J_{H_1P_2}$ = 54.0) H_2 −4.64 (dq) ($J_{H_2P_1}$ = 48.8; $J_{H_2P_2} \approx J_{H_2P_3} \approx J_{H_2P_4} \approx$ 13) H_3 −5.57 (t) ($J_{H_3P_3} = J_{H_3P_4}$ = 57.0) H_4 −20.68 (m)	P_1 57.5 (ddd) (J_{P_1P2} = 26.3; $J_{P_1P_3}$ = 16.9; $J_{P_1P_4}$ = 5.0) $J_{P_1P_3}$ = 16.9; $J_{P_1P_4}$ = 5.0) P_2 55.2 (d) ($J_{P_2P_1}$ = 26.3) P_3 40.3 (dd) ($J_{P_3P_1}$ = 16.9; $J_{P_3P_4}$ = 3.0) P_4 32.8 (dd) ($J_{P_4P_1}$ = 5.0; $J_{P_4P_3}$ = 3.0)	213

reaction of $RuHCl(CO)_2(PPh_3)_2$ gives the same complex in lower yield, but in this case with CO departure.

^{1}H and ^{31}P{^{1}H} NMR spectra (Table I) indicate the occurrence of a fluxional process: at room temperature the hydride resonances appear as a triplet (H_a, δ = −4.92 ppm, J = 52 Hz), a broad resonance centered at −6.12 ppm ($H_b + H_c + H_d$), and a double triplet at −17.21 ppm (H_e, J_1 = 5.3 Hz, J_2 = 33 Hz) in the 1/3/1 intensity ratio. The ^{31}P{^{1}H} NMR spectrum displays two broad resonances of the same intensity at 71.9 and 37.1 ppm. By lowering the temperature to 193 K, we observe in the ^{1}H NMR spectrum a splitting of the broad resonance at −6.12 ppm into three multiplets of equal intensity at −4.25 (H_b), −6.21 (H_c), and −7.86 (H_d) ppm. The two other triplet resonances are not modified except for a slight modification of the chemical shift. At the same temperature the ^{31}P{^{1}H} NMR shows that the two broad resonances have split into four multiplets of equal intensity, giving evidence of the presence of four phosphine ligands. By comparison with the chemical shift of the phosphines in the starting complexes we attribute the two multiplets at low field to the two phosphines bound to ruthenium.

Selective ^{31}P decoupling experiments at 193 K show that the H_a ligand is equally coupled to the two phosphines bound to rhenium and that the H_e ligand is equally coupled to the two phosphines bound to ruthenium. This is consistent with a terminal position of these two ligands on rhenium and ruthenium, respectively. For the other three hydride ligands, the values of the J_{PH} coupling constants[2c] and the fact that one of them (H_c) is coupled to three phosphine ligands are consistent with bridging positions for these ligands. As the hydride signals do not coalesce at 293 K, there is no fast exchange between the terminal and bridging hydride positions at this temperature. The same type of phenomenon has been observed by Caulton et al.[9] for the $(PPh_3)_2HRu(\mu\text{-}H)_3Ru(PPh_3)_3$ complex, and the authors propose a mechanism in which the exchange between the bridging hydride ligands occurs through an

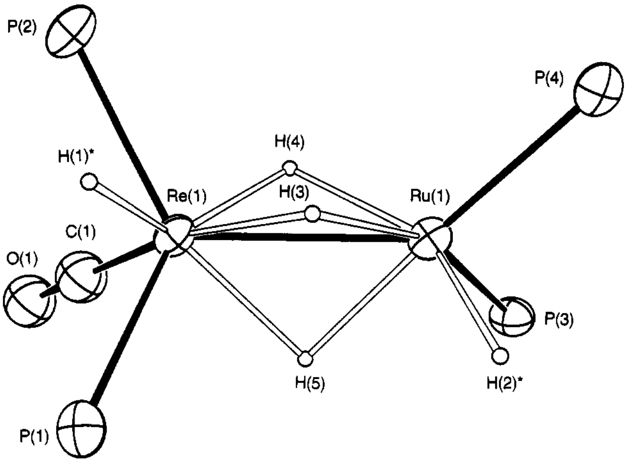

Figure 1. Perspective view of the complex $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ (1) (atoms flagged with an asterisk (*) have been located by molecular mechanics). Thermal ellipsoids are shown at the 30% probability level, and the phenyl groups have been omitted for clarity.

intermediate in which one of the hydrides is in the terminal position on the $Ru(PPh_3)_3$ center. In our case, this mechanism cannot be considered, as it would certainly imply an exchange with one of the terminal hydride ligands on rhenium or ruthenium. A possible mechanism could be a rotation of the terminal ligands around the metal–metal bond. Such a mechanism has been proposed for $Re_2H_4(PMePh_2)_4[P(OCH_2)_3CEt]_2$ and its conjugate acid.[10]

The carbonyl region of the IR spectrum exhibits one absorption at 1865 cm^{-1}, which is an important shift compared to the CO absorption of the starting ruthenium complex (1930 cm^{-1}). This initially suggested to us, in the absence of an X-ray structure determination, that the carbonyl group was in a bridging position,[7] but we found later by an X-ray structure determination that in the product of the reaction of 1 with benzonitrile, $(CO)(PPh_3)_2Re(\mu\text{-}H)_2(\mu\text{-}N{=}CHPh)Ru(PhCN)(PPh_3)_2$, the CO ligand was in the terminal position on rhenium.[8]

Having now in hand suitable crystals of 1, an X-ray structure determination was undertaken to confirm this observation. The unit cell contains two independent molecules of 1. The two independent molecules are almost identical. A perspective view of one of these molecule (molecule A) is given in Figure 1 along with the labeling scheme. Bond lengths and angles of interest are gathered in Table II.

The structure of 1 consists of, in accordance with the spectroscopic data, a dinuclear ReRu unit in which the two metals are bridged by three hydride ligands which were located in a difference Fourier search of molecule A (in the case of molecule B only two bridging hydride ligands have been located). The positions of the two terminal hydride ligands have been calculated by the use of the program HYDEX,[11] and this program also located the bridging hydrides in good agreement with the experimentally determined positions (see Experimental Section).

Table II. Selected Bond Lengths (Å) and Angles (deg) for $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$[a] (1)

	molecule A	molecule B
	Bond Distances	
Re(1)–Ru(1)	2.593(2)	2.585(2)
Re(1)–P(1)	2.385(7)	2.396(7)
Re(1)–P(2)	2.373(7)	2.372(8)
Re(1)–C(1)	1.79(3)	1.91(2)
Ru(1)–P(3)	2.269(7)	2.266(7)
Ru(1)–P(4)	2.237(7)	2.258(7)
C(1)–O(1)	1.21(3)	1.17(3)
Re(1)–H(1)	1.7*	1.7*
Re(1)–H(3)	1.8	1.9
Re(1)–H(4)	1.5	1.8*
Re(1)–H(5)	1.8	1.9
Ru(1)–H(2)	1.6*	1.6*
Ru(1)–H(3)	1.7	1.8
Ru(1)–H(4)	1.6	1.8*
Ru(1)–H(5)	1.7	1.9
	Bond Angles	
C(1)–Re(1)–P(1)	89.9(8)	84.9(7)
C(1)–Re(1)–P(2)	83.7(9)	85.5(8)
C(1)–Re(1)–Ru(1)	125.8(8)	125.7(7)
P(1)–Re(1)–P(2)	124.5(2)	135.6(2)
P(1)–Re(1)–Ru(1)	110.3(2)	106.0(2)
P(2)–Re(1)–Ru(1)	117.7(2)	114.6(2)
C(1)–Re(1)–H(1)	117*	113*
C(1)–Re(1)–H(3)	166	167
C(1)–Re(1)–H(4)	109	106*
C(1)–Re(1)–H(5)	99	84
O(1)–C(1)–Re(1)	178(2)	175(2)
H(1)–Re(1)–H(3)	75*	76*
H(1)–Re(1)–H(4)	120*	123*
H(1)–Re(1)–H(5)	128*	142*
H(1)–Re(1)–P(1)	68*	73*
H(1)–Re(1)–P(2)	67*	71*
H(1)–Re(1)–Ru(1)	117*	120*
H(3)–Re(1)–H(4)	64	71*
H(3)–Re(1)–P(1)	90.3	91.6
H(3)–Re(1)–P(2)	107	104.9
H(4)–Re(1)–P(1)	147	149*
H(4)–Re(1)–P(2)	84	74*
H(5)–Re(1)–H(3)	67	83
H(5)–Re(1)–H(4)	73	76*
H(5)–Re(1)–P(1)	78	76
H(5)–Re(1)–P(2)	157	145
P(3)–Ru(1)–P(4)	100.1(2)	98.8(3)
P(3)–Ru(1)–Re(1)	120.3(2)	119.8(2)
P(4)–Ru(1)–Re(1)	132.2(2)	133.4(2)
H(2)–Ru(1)–H(3)	86*	88*
H(2)–Ru(1)–H(4)	142*	155*
H(2)–Ru(1)–H(5)	79*	86*
H(2)–Ru(1)–P(3)	92*	95*
H(2)–Ru(1)–P(4)	91*	89*
H(2)–Ru(1)–Re(1)	110*	111*
H(3)–Ru(1)–H(4)	62	75*
H(3)–Ru(1)–H(5)	70	85
H(3)–Ru(1)–P(3)	160	168
H(3)–Ru(1)–P(4)	99	92
H(4)–Ru(1)–H(5)	71	74*
H(4)–Ru(1)–P(3)	111	98*
H(4)–Ru(1)–P(4)	112	109*
H(5)–Ru(1)–P(3)	89	84
H(5)–Ru(1)–P(4)	167	174
Ru(1)–H(3)–Re(1)	91	91
Ru(1)–H(4)–Re(1)	91	91*
Ru(1)–H(5)–Re(1)	91	91

[a] Values marked with an asterisk refer to bond distances and bond angles from calculated values of the hydride ligands.

The structure can be described as the union of a distorted octahedron ($(\mu\text{-}H)_3RuH(PPh_3)_2$) and a distorted pentagonal bipyramid ($(CO)(PPh_3)_2HRe(\mu\text{-}H)_3$) via a triangular face defined by the bridging hydride ligands. The approximately planar pentagon consists of Re(1), P(1), P(2), H(1), H(4), and H(5) atoms (the maximum deviations from the mean plane defined by Re(1), P(1), P(2) atoms are observed for H(1) at 0.619 Å (molecule A) and 0.528 Å (molecule B) (see supplementary material)). A similar geometry has been found for $Re_2H_4(PMePh_2)_4[P(OCH_2)_3CEt]_2$,[10] and a distorted pentagonal bipyramid geometry around rhenium has also been found in the $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]^+$ cation.[12] This struc-

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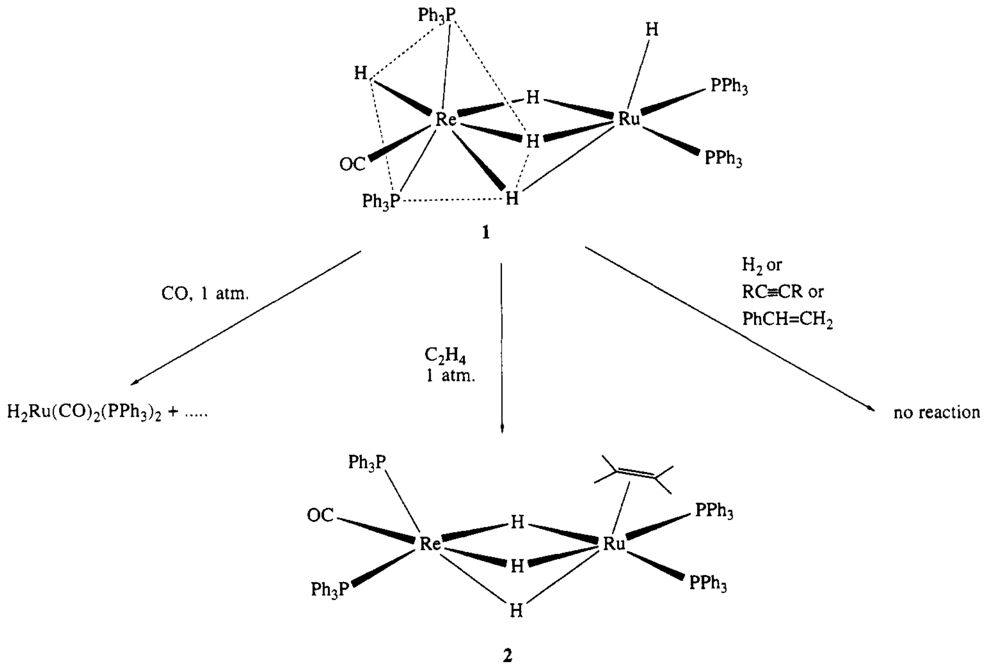
[9] Van Der Sluys, L. S.; Kubas, G. J.; Caulton, K. G. *Organometallics* **1991**, *10*, 1033.

[10] Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2319.

[11] Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

Scheme I



ture further confirms that, during the synthesis of 1, there is migration of the carbonyl ligand from ruthenium to rhenium.

The Re–P distances seem rather insensitive to the environment of rhenium, as they are very similar to those found in the $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]^+$ cation (2.372(3) Å) and in the $(CO)(PPh_3)_2Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)$ complex (2.345(4) Å).[8] In contrast, the Ru–P distances are very short compared to the case of the 32-electron complex $(CO)(PPh_3)_2Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)$ (2.354(4) Å), even though the phosphine ligands are trans to bridging hydrides in the both cases. In the last complex the benzonitrile ligand occupies the same position as the terminal hydride ligand in 1 and we could expect the reverse effect on the Ru–P distances. Nevertheless these Ru–P distances are in the range found for mononuclear ruthenium complexes.[13]

The electronic unsaturation of 1 is reflected by the Re–Ru distance (2.593(2) Å in molecule A and 2.585(2) Å in molecule B) which is shorter than the sum of the atomic radii (2.73 Å)[14] and also shorter than the value found in the 32-electron complex $(CO)(PPh_3)_2Re(\mu\text{-}H_2)(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)$ (2.654(1) Å). This is in agreement with a formal ReRu triple bond expected to give the dimer a 36-electron count.

Having now an exact knowledge of the structure, it is possible to propose an assignment of the observed NMR signals at low temperature. The assignment of the H_a and H_e resonances to H(1) and H(2) is obvious. In agreement with the observation of a coupling constant between H_b and H_e we attribute the H_b resonance to H(4) which is trans to H(2). The assignment of the two other hydride resonances is less easy, as only one of them experiences coupling with the phosphines bound to rhenium, but we have assigned H_c to H(3) and H_d to H(5) on the basis of the following arguments: (1) H_c, which is equally coupled to the two phosphines bound to rhenium, is consistent with the H(3) position which is on the axis of the pentagonal bipyramid. (2) The coupling of H_c with one phosphine bound to ruthenium is lower than that of H_d, which is consistent with the fact that the H(3)–Ru–P(3) angle (160°) is smaller than the H(5)–Ru–P(4) angle (167°). The only problem with this assignment, which is nevertheless the most realistic, is the fact that the H_b and H_d ligands are in similar situations in the approximate plane of the pentagonal bipyramid but only H_b is significantly coupled to the two phosphines bound to rhenium. The same problem is observed for the phosphorus resonances, as only one of the two phosphines bound to ruthenium has measurable coupling constants with the two phosphines bound to rhenium. On the basis of the hydride assignments, we attribute the P_a and P_b resonances to P(4) and P(3), respectively, but it is not possible to assign the other ^{31}P resonances for the phosphines bound on rhenium on the basis of NMR data.

Study of the Reactivity of 1 toward H_2, CO, Alkynes, and Alkenes. The electronic unsaturation of 1 prompted us to study its reactivity toward hydrogen and a range of electron donor molecules like carbon monoxide, alkynes, and alkenes. The results are summarized in Scheme I. No reaction is observed with hydrogen even under pressure and the reaction with carbon monoxide at room temperature and at atmospheric pressure leads to complete breaking of the dinuclear unit. Only one component of the mixture has been identified as $H_2Ru(CO)_2(PPh_3)_2$ by comparison of its IR and NMR parameters with literature values.[15] Unexpectedly, no reaction occurs with alkynes, even with an activated one like dimethyl acetylenedicarboxylate.

In the case of alkenes, styrene is not reactive but a reaction is observed with ethylene. It occurs at room temperature and a new compound 2 is formed which is slightly soluble in dichloromethane and quite soluble in THF. Analytical and spectroscopic data (Table I) are in

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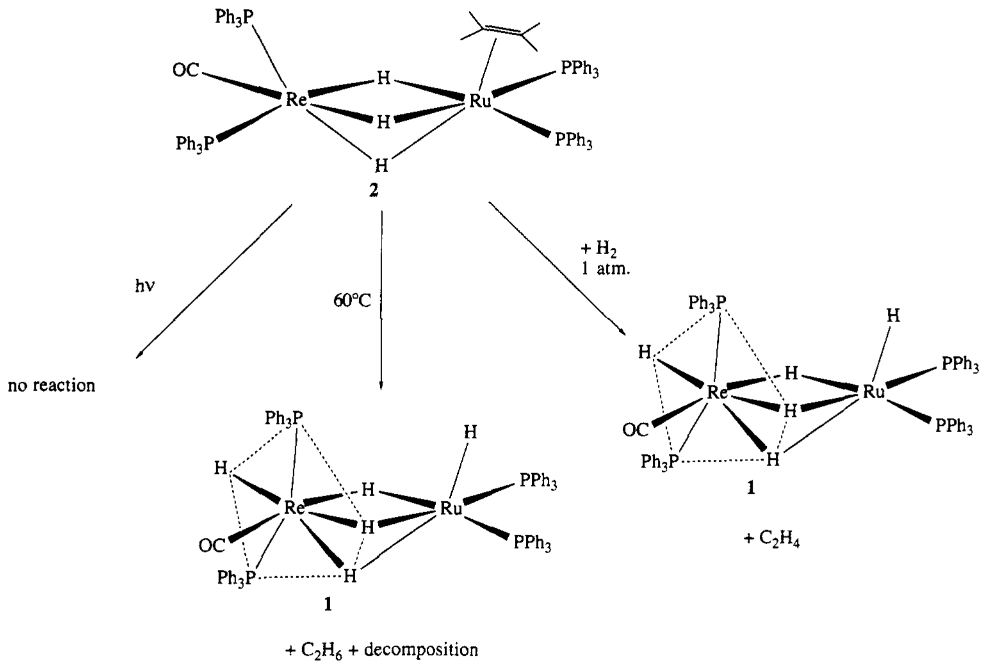
(12) Allison, J. D.; Cotton, F. A.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1984**, *23*, 159.

(13) Guggenberger, L. J. *Inorg. Chem.* **1973**, *12*, 1317.

(14) *Comprehensive Inorganic Chemistry*; Bailar C. J., Emeléus H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, England, 1973; Vol. 3.

(15) Cenini, S.; Porta, F.; Pizzotti, M. *Inorg. Chim. Acta* **1976**, *20*, 119.

Scheme II



agreement with the $(CO)(PPh_3)_2Re(\mu\text{-}H)_3Ru(C_2H_4)(PPh_3)_2$ structure for **2**. Indeed, a CO absorption is observed at 1820 cm^{-1}, which corresponds to a lowering of 45 cm^{-1} compared to **1**, consistent with the decrease of the formal oxidation number of rhenium. In the ^1H NMR spectrum at room temperature we observe, besides the phenyl resonances, a broad signal at 2.69 ppm for the ethylene protons, and for the hydride ligands a broad unresolved multiplet at −5.80 ppm and two broad doublets centered at −6.75 and −6.85 ppm with the 1/1/1 ratio of intensity. The $^{31}P\{^1H\}$ NMR spectrum displays two broad resonances of the same intensity at 61.3 and 47.3 ppm. When the temperature is lowered to 193 K, the first resonance splits into two ill-defined multiplets but the second resonance is not noticeably modified.

At the same temperature, the ^1H NMR spectrum shows that the ethylene resonance sharpens but gives only one signal at 3.19 ppm. In the hydride region, the broad multiplet is unchanged and the two other hydrides appear now as a doublet and a doublet of doublets at −5.66 and −6.94 ppm, respectively. Selective ^{31}P decoupling experiments at 193 K indicate that coupling occurs with the two phosphines bound to ruthenium.

All these spectroscopic data are very similar to those of $(CO)(PPh_3)_2Re(\mu\text{-}H)_3Ru(CH_3CN)(PPh_3)_2$,[8] and we propose for **2** the same type of structure shown in Scheme I. In this molecule the ethylene is rotating with a low barrier of energy, as only one signal has been detected for the methylene protons at 193 K.

To summarize the results observed for the reactivity of **1** toward unsaturated hydrocarbons, it appears that although this complex is electronically unsaturated, it is inert toward reactive molecules like alkynes. Nevertheless it reacts with ethylene by a substitution reaction of two hydride ligands and not an addition reaction as expected. (We have monitored the reaction in a NMR tube, and there is no evidence of the presence of ethane during the formation of **2**.) The same behavior was observed with the acetonitrile ligand.[8]

Since complex **2** is unsaturated, we have checked if CH activation could occur as in the reaction of the unsaturated complex $(C_5Me_5)Ru(\mu\text{-}H)_4Ru(C_5Me_5)$ with ethylene.[16] By photochemical activation no reaction was observed and thermal activation was checked in a sealed NMR tube in deuterated toluene. The reaction is very complex: after 24 h at 70 °C we have observed extensive decomposition to a black precipitate and the solution is a mixture of **2** and, unexpectedly, of complex **1**. Ethane is also detected. Under hydrogen at room temperature, there is displacement of ethylene and **1** is regenerated. These observations are summarized in the Scheme II.

Reactivity of 1 toward Chloroform. It is well-known that polyhydride complexes can react with polyhalogenated hydrocarbons to give halogen–hydride exchange reactions. In our case, the reaction was first monitored by ^1H NMR in deuteriated chloroform. A clean reaction is observed with formation of a new complex and with the simultaneous appearance of $CHDCl_2$. Synthesis on a preparative scale leads to the isolation of the complex $(CO)(PPh_3)_2Re(\mu\text{-}Cl)_2(\mu\text{-}H)RuH(PPh_3)_2$ (**3**). The spectroscopic data for this complex are gathered in Table I.

^1H and $^{31}P\{^1H\}$ NMR spectra show that this molecule is rigid on the NMR time scale: four multiplets are observed at room temperature in the $^{31}P\{^1H\}$ spectrum, and we observe in the ^1H spectrum two signals characteristic of terminal hydride ligands on rhenium and ruthenium and a multiplet due to coupling of a hydride with four phosphine ligands characteristic of a bridging position. From these data we propose for **3** the structure shown in Figure 2 in which two bridging hydrides are replaced by two chloride ligands. In this structure we propose that the geometry of **1** is maintained. The remaining bridging hydride has been located by considering the J_{PH} values.

In this reaction the selective substitution of two hydride by two chloride ligands can be explained by the fact that in the **1** → **3** transformation we obtain a 34-electron structure consistent with the presence of a single metal-metal bond.

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[16] Suzuki, H.; Omori, H.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2579.

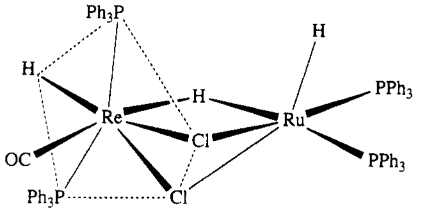

Figure 2. Proposed structure for the complex (CO)$(PPh_3)_2Re(\mu\text{-}Cl)_2(\mu\text{-}H)RuH(PPh_3)_2$ (3).

Having in hand two bimetallic Re–Ru polyhydride complexes, it was tempting to check if protonation could induce the formation of cationic complexes containing molecular hydrogen as a ligand. Indeed, it is well-known that rhenium[17] and ruthenium[18] are metals able to stabilize this ligand. For this reason we have checked the reactivity of 1 and 3 with tetrafluoroboric acid. A preliminary report of this work has already been published.[7]

Reactivity of 1 and 3 toward Tetrafluoroboric Acid. Protonation of 1 or 3 with 1 equiv of tetrafluoroboric acid induces a shift of the ν(CO) absorption toward higher frequencies in accordance with the formation of new cationic complexes 4 and 5. The reaction can be reversed by adding a slight excess of triethylamine.

The room temperature ^{1}H NMR spectrum of 4 shows in the hydride region one triplet at −4.85 ppm and a very broad resonance at −7 ppm. When the temperature is lowered to 193 K, the triplet is unchanged but the broad resonance splits into three multiplets and one broad resonance with the intensity ratio 1/1/1/2 (Table I). In the $^1H\{^{31}P\}$ spectrum all the multiplets transform into singlets but there is no change for the broad resonance. This suggests the presence of a bound dihydrogen molecule which is confirmed by T_1 measurements at 250 MHz. A minimum value of T_1 of 10 ms is observed at 213 K, which is fully characteristic of molecular hydrogen η^2-bound to a metal.[19] The T_1 values for the other resonances are, at the same temperature 116, 116, 104, and 109 ms, respectively. Four multiplets are observed in the ^{31}P spectrum at 193 K (Table I), showing that the dinuclear unit has been maintained. Selective $^1H\{^{31}P\}$ decoupling measurements have allowed the assignment of J_{PH} coupling constants for the hydride resonances, and they are consistent with a structure similar to the structure of 1, the hydride ligand being replaced by the dihydrogen ligand on ruthenium: $[(CO)(PPh_3)_2Re(\mu\text{-}H)_3Ru(H_2)(PPh_3)_2][BF_4]$ (4). This structure is shown in Figure 3.

The thermal instability of 4 at temperatures higher than 40 °C has not allowed us to check if there is exchange between molecular hydrogen and hydride ligands at higher temperatures. It should be pointed out that in a closely related dinuclear complex $H(PR_3)_2Ru(\mu\text{-}Cl)_2(\mu\text{-}H)Ru(PR_3)_2(\eta^2\text{-}H_2)$, complete scrambling of the hydride ligands with the dihydrogen ligands or scrambling of only the bridging hydride ligand has been observed, depending on the nature of the phosphine.[20]

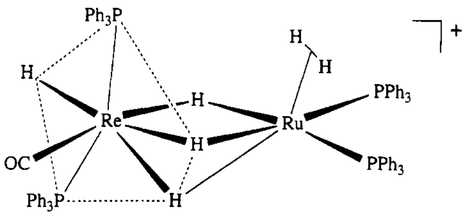

Figure 3. Proposed structure for the complex $[(CO)(PPh_3)_2Re(\mu\text{-}H)_3Ru(H_2)(PPh_3)_2][BF_4]$ (4).

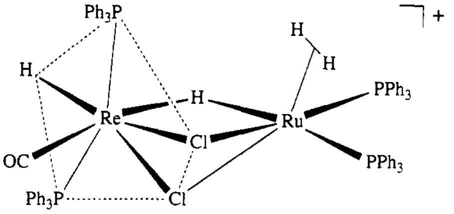

Figure 4. Proposed structure for the complex $[(CO)(PPh_3)_2Re(\mu\text{-}Cl)_2(\mu\text{-}H)Ru(H_2)(PPh_3)_2][BF_4]$ (5).

In the case of complex 5, the room temperature ^{1}H NMR spectrum is very similar in the hydride region to that of 4 except for the resonance at high field, which is replaced by a broad resonance at −11.75 ppm with a relative intensity of 2. T_1 measurements at 250 MHz are in agreement with the presence of a molecular hydrogen ligand, with a minimum value of 9 ms being observed at 213 K for this broad signal. The T_1 values for the two other hydride signals are respectively 88 and 140 ms at the same temperature.

Four multiplets are observed in the $^{31}P\{^1H\}$ spectrum of 5 at room temperature which confirms that, like 3, the complex is not fluxional at room temperature. Moreover there is no exchange between the η^2-bound molecular hydrogen and the hydride ligands in its domain of thermal stability. A structure $[(CO)(PPh_3)_2Re(\mu\text{-}Cl)_2(\mu\text{-}H)Ru(H_2)(PPh_3)_2][BF_4]$, shown in Figure 4 and consistent with the spectroscopic data, is proposed for 5. It results from the replacement in 3 of the terminal hydride ligand on ruthenium by molecular hydrogen.

Complexes 4 and 5 constitute the first examples of heterobimetallic complexes containing the molecular hydrogen ligand. Since dihydrogen ligands are generally labile,[4] we have checked the reactivity of 4 and 5 toward ethylene, acetonitrile, and acetone. It should be pointed out that no reaction has been observed with dinitrogen, a reaction which often occurs with molecular hydrogen complexes.[21]

Reactivity of 4 and 5 toward Ethylene, Acetonitrile, and Acetone. Complex 4 reacts immediately at room temperature with L = ethylene, acetonitrile, or acetone: this leads to the isolation of three products 6–8 which are stable in the case of acetonitrile (7) and acetone (8) but quite unstable in the case of ethylene (6) (Scheme III). The replacement of a molecular hydrogen ligand by acetonitrile has already been observed in the case of ruthenium compounds.[22]

All these complexes 6–8 have the common feature of being fluxional at room temperature (Table I). In the $^{31}P\{^1H\}$ NMR spectra we observe two broad signals of the

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[17] See for instance: (a) Michos, D.; Luo, X. L.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **1992**, 1735. (b) Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991**, 241. (c) Kim, Y.; Deng, H. B.; Meek, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 2798.

[18] See for instance: (a) Chaudret, B.; Chung, G.; Eisenstein, O.; Jackson, S. A.; Lahoz, F. J.; Lopez, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2314. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166. (c) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161. (d) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1992**, *31*, 2.

[19] Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.

[20] Hampton, C.; Cullen, W. R.; James, B. R. *J. Am. Chem. Soc.* **1988**, *110*, 6918.

[21] Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581.

[22] Jia, G.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 582.

Scheme III

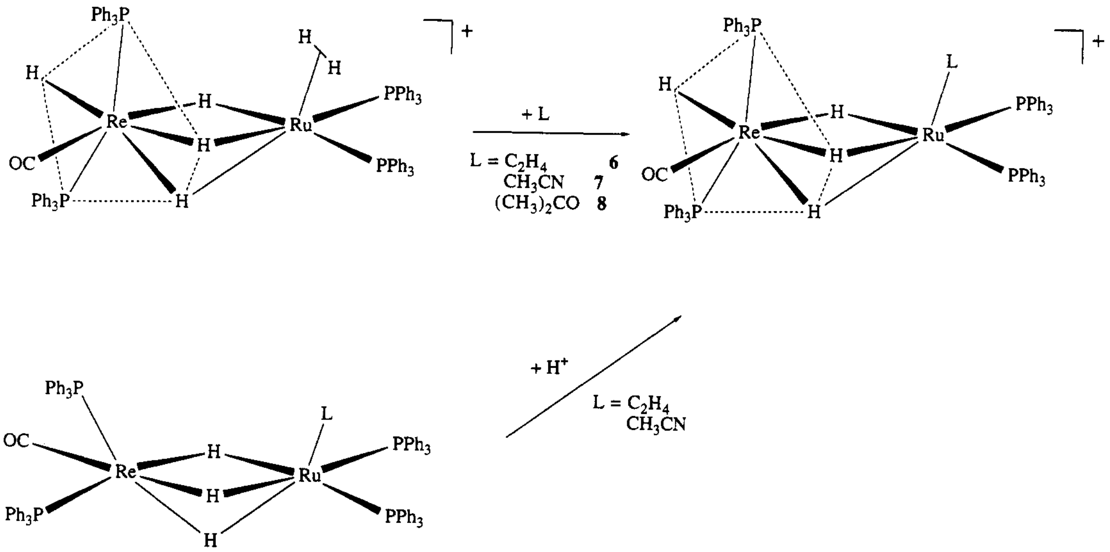

Table III. Experimental Data for X-ray Study of Compound 1

formula	$C_{73}H_{65}OP_4ReRu$
F_w	1369.50
cryst syst	monoclinic
space group	$C_{2h}^5 - P2_1/n$
a, Å	21.938(6)
b, Å	13.046(2)
c, Å	44.804(10)
β, deg	96.50(1)
V, Å^3	12740(5)
Z	8
ρ_{calcd}, g·cm^{-3}	1.428
t, °C	22
radiation	Cu Kα
linear abs coeff, cm^{-1}	67.72
transm factors[a]	0.688–0.999
scan mode	ω–2θ
2θ limit, deg	2–90
no. of unique data used in final refinement, $F_o^2 > 3\sigma(F_o^2)$	4683
final no. of variables	425
R (on F_o, $F_o^2 > 3\sigma(F_o^2)$)[b]	0.053
R_w (on F_o, $F_o^2 > 3\sigma(F_o^2)$)[c]	0.068
error in observ of unit weight, e^2	1.52

[a] Ψ-scan method, transission coefficients normalized to a maximum value of unity. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|^2)]^{1/2}$, unit weights.

same intensity and in the ^{1}H NMR spectra it appears that only two bridging hydrides are exchanging. As in the case of 1, there is no exchange with the terminal hydride bound to rhenium.

When the temperature is lowered, the $^{31}P\{^1H\}$ resonances split into four multiplets and the two equivalent bridging hydrides split into two multiplets. ^{31}P selective decoupling experiments show that each of these two hydrides are trans to one of the phosphines bound to ruthenium. The resonances of the other hydrides are only slightly affected by the variation of temperature. As in the $(CO)(PPh_3)_2Re(\mu\text{-}H)_3Ru(CH_3CN)(PPh_3)_2$ complex,[8] the fluxionality of the hydride ligands may be explained by an exchange between the two bridging ligands occurring through an intermediate with a hydride in a terminal position on ruthenium, the bimetallic frame being maintained by the third hydride ligand. A similar mechanism was proposed for $[Ph(PEt_3)Pt(\mu\text{-}H)_2IrH(PEt_3)_3]^+$.[23]

Concerning the mode of bonding of acetonitrile and acetone, the ν(CN) and ν(CO) frequencies observed (Table I) are consistent with a terminal mode of bonding. It also has to be pointed out that the ethylene signal split into two broad resonances at 183 K, showing that the rotation of ethylene is noticeably slowed down. All these data show that the three molecules have similar geometries and we propose the structure shown in Scheme III which is derived from the structure of 4 by the substitution of the molecular hydrogen ligand on ruthenium. In this structure we propose that the bridging hydride which is trans to the ligand L is the nonexchanging bridging hydride ligand: this is consistent with the fact that increasing the basicity of L induces a shift of its resonance to a higher field. It has to be pointed out that the same complexes 6 and 7 have been obtained by protonation of 2 and $(CO)(PPh_3)_2Re(\mu\text{-}H)_3Ru(CH_3CN)(PPh_3)_2$.

Finally, in the case of complex 5 no reaction is observed with the same ligands before thermal decomposition occurs, showing that in this case the molecular hydrogen ligand is not labile. The observed difference of reactivity between 4 and 5 is not clear but two reasons can be invoked: contrary to 4, 5 is electronically saturated, and if our proposal about the structures of 4 and 5 is correct, the molecular hydrogen ligand in 5 is trans to a chloride ligand which has a weaker trans effect than the hydride.

Experimental Section

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. IR spectra were recorded on a Perkin-Elmer 225 spectrometer. NMR spectra were recorded on Bruker AC 80 (^{31}P), AC 200 (^{1}H), and WM 250 (^{1}H, ^{31}P) instruments. Variable temperature and selective decoupling experiments were carried out on the WM 250 machine. Elemental analyses were performed in our laboratory for the elements C, H, and N and by the Service Central de Microanalyses du CNRS for the other elements. $ReH_7(PPh_3)_2$[5] and $RuHCl(CO)(PPh_3)_3$[24] have been prepared according to published procedures.

Synthesis of $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ (1). To a solution of 0.24 g (0.33 mmol) of $ReH_7(PPh_3)_2$ in 30 mL of THF was added an excess of KH and the solution was stirred for 1 h, giving a yellow solution. The solution was then filtered to eliminate excess KH and added to 0.32 g (0.33 mmol) of $RuHCl(CO)(PPh_3)_3$. After stirring for 1 h, the red brown solution was evaporated to dryness. The residue was dissolved in toluene (10 mL) and filtered through Celite to eliminate KCl. Addition

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(23) Boron, P.; Musco, A.; Venanzi, L. *Inorg. Chem.* **1982**, *21*, 4192.

(24) Hallmann, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143.

Table IV. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å² × 100) with Esds in Parentheses for (CO)(PPh$_3$)$_2$HRe(μ-H)$_3$RuH(PPh$_3$)$_2$ (1)

atom	*x/a*	*y/b*	*z/c*	U_{eq}/U_{iso}	atom	*x/a*	*y/b*	*z/c*	U_{eq}/U_{iso}
Re(1)a	0.16323(5)	0.85614(9)	0.13498(3)	3.15(8)	Re(1)b	0.73191(5)	0.29711(9)	0.10054(3)	3.29(8)
Ru(1)a	0.22470(8)	0.7282(2)	0.10572(4)	3.1(1)	Ru(1)b	0.64980(9)	0.2615(2)	0.13632(4)	3.5(1)
P(1)a	0.1115(3)	0.9779(5)	0.1014(2)	3.9(5)	P(1)b	0.7257(3)	0.4767(5)	0.0895(2)	3.9(5)
P(2)a	0.1268(3)	0.7975(6)	0.1799(2)	4.5(5)	P(2)b	0.7666(3)	0.1494(6)	0.0766(2)	4.4(5)
P(3)a	0.3267(3)	0.7512(5)	0.1039(2)	3.7(5)	P(3)b	0.6782(3)	0.2448(6)	0.1863(2)	4.2(5)
P(4)a	0.2181(3)	0.5584(5)	0.0993(1)	3.4(5)	P(4)b	0.5641(3)	0.1643(5)	0.1325(2)	3.8(5)
C(1)a	0.195(1)	0.959(2)	0.1585(6)	5.4(8)	C(1)b	0.817(1)	0.324(2)	0.1125(5)	4.3(8)
O(1)a	0.2186(8)	1.026(1)	0.1743(4)	6.2(6)	O(1)b	0.8681(8)	0.346(1)	0.1200(4)	6.6(6)
H(3)a	0.1476	0.7568	0.1074		H(3)b	0.6422	0.2846	0.0963	
H(4)a	0.2044	0.7656	0.1387		H(5)b	0.7199	0.3568	0.1382	
H(5)a	0.2147	0.8634	0.1047		C(11)b	0.7363(7)	0.555(1)	0.1236(5)	5.3(8)
C(11)a	0.0492(7)	0.927(1)	0.0751(3)	3.6(7)	C(12)b	0.6896(7)	0.557(1)	0.1423(5)	8(1)
C(12)a	0.0284(7)	0.827(1)	0.0777(3)	4.2(8)	C(13)b	0.6984(7)	0.609(1)	0.1697(5)	9(1)
C(13)a	−0.0195(7)	0.790(1)	0.0575(3)	6.8(9)	C(14)b	0.7539(7)	0.658(1)	0.1784(5)	11(1)
C(14)a	−0.0465(7)	0.853(1)	0.0346(3)	8(1)	C(15)b	0.8006(7)	0.656(1)	0.1597(5)	10(1)
C(15)a	−0.0257(7)	0.953(1)	0.0319(3)	7.0(9)	C(16)b	0.7918(7)	0.605(1)	0.1323(5)	9(1)
C(16)a	0.0222(7)	0.990(1)	0.0522(3)	5.9(9)	C(21)b	0.7801(7)	0.532(1)	0.0660(4)	3.4(7)
C(21)a	0.1560(7)	1.045(1)	0.0754(4)	4.5(8)	C(22)b	0.8165(7)	0.466(1)	0.0509(4)	4.5(8)
C(22)a	0.1541(7)	1.152(1)	0.0723(4)	7.2(9)	C(23)b	0.8539(7)	0.507(1)	0.0306(4)	5.6(8)
C(23)a	0.1876(7)	1.199(1)	0.0516(4)	9(1)	C(24)b	0.8549(7)	0.612(1)	0.0254(4)	7(1)
C(24)a	0.2229(7)	1.141(1)	0.0340(4)	9(1)	C(25)b	0.8184(7)	0.677(1)	0.0406(4)	8(1)
C(25)a	0.2248(7)	1.035(1)	0.0371(4)	8(1)	C(26)b	0.7810(7)	0.637(1)	0.0609(4)	5.8(8)
C(26)a	0.1913(7)	0.987(1)	0.0578(4)	6.8(9)	C(31)b	0.6531(7)	0.527(1)	0.0706(3)	4.0(7)
C(31)a	0.0739(5)	1.082(1)	0.1201(4)	4.2(7)	C(32)b	0.6325(7)	0.626(1)	0.0760(3)	5.4(8)
C(32)a	0.1114(5)	1.153(1)	0.1366(4)	4.8(8)	C(33)b	0.5794(7)	0.663(1)	0.0595(3)	8(1)
C(33)a	0.0852(5)	1.235(1)	0.1507(4)	7(1)	C(34b)	0.5469(7)	0.602(1)	0.0376(3)	8(1)
C(34)a	0.0216(5)	1.1245(1)	0.1484(4)	5.8(8)	C(35)b	0.5676(7)	0.503(1)	0.0322(3)	6.9(9)
C(35)a	−0.0159(5)	1.174(1)	0.1319(4)	5.4(8)	C(36)b	0.6206(7)	0.466(1)	0.0487(3)	4.6(8)
C(36)a	0.0103(5)	1.092(1)	0.1177(4)	5.4(8)	C(41)b	0.8153(7)	0.057(1)	0.1012(4)	3.7(7)
C(41)a	0.0637(8)	0.710(1)	0.1752(3)	5.0(8)	C(42)b	0.8163(7)	0.062(1)	0.1323(4)	5.8(9)
C(42)a	0.0168(8)	0.708(1)	0.1938(3)	5.6(8)	C(43)b	0.8477(7)	−0.012(1)	0.1505(4)	9(1)
C(43)a	−0.0303(8)	0.636(1)	0.1888(3)	9(1)	C(44)b	0.8781(7)	−0.092(1)	0.1375(4)	8(1)
C(44)a	−0.0304(8)	0.566(1)	0.1653(3)	10(1)	C(45)b	0.8771(7)	−0.097(1)	0.1064(4)	10(1)
C(45)a	0.0165(8)	0.568(1)	0.1468(3)	9(1)	C(46)b	0.8458(7)	−0.023(1)	0.0882(4)	8(1)
C(46)a	0.0636(8)	0.640(1)	0.1517(3)	7.3(9)	C(51)b	0.7067(9)	0.067(1)	0.0563(4)	4.4(8)
C(51)a	0.1813(6)	0.734(1)	0.2076(4)	3.4(7)	C(52)b	0.6457(9)	0.098(1)	0.0561(4)	7(1)
C(52)a	0.1607(6)	0.669(1)	0.2290(4)	5.3(8)	C(53)b	0.5985(9)	0.036(1)	0.0429(4)	6.9(9)
C(53)a	0.2019(6)	0.631(1)	0.2524(4)	7.2(9)	C(54)b	0.6123(9)	−0.057(1)	0.0298(4)	7(1)
C(54)a	0.2637(6)	0.658(1)	0.2544(4)	6.9(9)	C(55)b	0.6733(9)	−0.088(1)	0.0300(4)	13(2)
C(55)a	0.2843(6)	0.723(1)	0.2330(4)	6.8(9)	C(56)b	0.7204(9)	−0.026(1)	0.0433(4)	12(1)
C(56)a	0.2431(6)	0.761(1)	0.2097(4)	6.4(9)	C(61)b	0.8183(5)	0.176(1)	0.0479(4)	3.3(7)
C(61)a	0.0982(8)	0.895(2)	0.2024(3)	5.8(9)	C(62)b	0.7934(5)	0.187(1)	0.0180(4)	5.6(8)
C(62)a	0.0491(8)	0.952(2)	0.1886(3)	7(1)	C(63)b	0.8312(5)	0.213(1)	−0.0039(4)	7.0(9)
C(63)a	0.0283(8)	1.038(2)	0.2031(3)	10(1)	C(64)b	0.8939(5)	0.228(1)	0.0042(4)	5.9(9)
C(64)a	0.0566(8)	1.067(2)	0.2313(3)	9(1)	C(65)b	0.9188(5)	0.217(1)	0.0340(4)	6.2(9)
C(65)a	0.1058(8)	1.010(2)	0.2450(3)	8(1)	C(66)b	0.8810(5)	0.191(1)	0.0559(4)	6.0(9)
C(66)a	0.1266(8)	0.924(2)	0.2306(3)	7.0(9)	C(71)b	0.7620(9)	0.265(1)	0.1946(4)	4.9(8)
C(71)a	0.3475(8)	0.873(2)	0.1237(3)	5.7(8)	C(72)b	0.8015(9)	0.188(1)	0.2067(4)	8(1)
C(72)a	0.3322(8)	0.964(2)	0.1082(3)	8(1)	C(73)b	0.8648(9)	0.203(1)	0.2097(4)	12(1)
C(73)a	0.3362(8)	1.057(2)	0.1235(3)	10(1)	C(74)b	0.8886(9)	0.296(1)	0.2007(4)	7.3(9)
C(74)a	0.3554(8)	1.059(2)	0.1542(3)	7(1)	C(75)b	0.8491(9)	0.373(1)	0.1886(4)	8(1)
C(75)a	0.3707(8)	0.969(2)	0.1697(3)	8(1)	C(76)b	0.7858(9)	0.357(1)	0.1856(4)	7.2(9)
C(76)a	0.3667(8)	0.875(2)	0.1544(3)	8(1)	C(81)b	0.6710(8)	0.120(1)	0.2043(4)	5.4(8)
C(81)a	0.3840(8)	0.666(1)	0.1231(3)	4.4(8)	C(82)b	0.6510(8)	0.113(1)	0.2327(4)	9(1)
C(82)a	0.4375(8)	0.639(1)	0.1109(3)	5.7(8)	C(83)b	0.6454(8)	0.017(1)	0.2460(4)	11(1)
C(83)a	0.4801(8)	0.574(1)	0.1269(3)	6.7(9)	C(84)b	0.6598(8)	−0.072(1)	0.2309(4)	10(1)
C(84)a	0.4692(8)	0.537(1)	0.1549(3)	9(1)	C(85)b	0.6798(8)	−0.065(1)	0.2025(4)	9(1)
C(85)a	0.4157(8)	0.564(1)	0.1671(3)	9(1)	C(86)b	0.6854(8)	0.031(1)	0.1892(4)	6.1(9)
C(86)a	0.3731(8)	0.629(1)	0.1512(3)	6.5(9)	C(91)b	0.6483(8)	0.329(1)	0.2138(3)	5.2(8)
C(91)a	0.3573(7)	0.769(1)	0.0683(3)	3.1(7)	C(92)b	0.5879(8)	0.365(1)	0.2093(3)	5.4(8)
C(92)a	0.4099(7)	0.828(1)	0.0667(3)	6.6(9)	C(93)b	0.5635(8)	0.419(1)	0.2320(3)	8(1)
C(93)a	0.4360(7)	0.834(1)	0.0398(3)	9(1)	C(94)b	0.5993(8)	0.437(1)	0.2592(3)	12(1)
C(94)a	0.4095(7)	0.782(1)	0.0144(3)	7(1)	C(95)b	0.6596(8)	0.402(1)	0.2637(3)	13(2)
C(95)a	0.3569(7)	0.723(1)	0.0160(3)	7.1(9)	C(96)b	0.6841(8)	0.348(1)	0.2410(3)	10(1)
C(96)a	0.3308(7)	0.717(1)	0.0429(3)	4.9(8)	C(101)b	0.5703(6)	0.024(1)	0.1327(4)	3.3(7)
C(101)a	0.1408(8)	0.517(1)	0.0835(4)	4.5(8)	C(102)b	0.6229(6)	−0.016(1)	0.1223(4)	5.4(8)
C(102)a	0.1102(8)	0.576(1)	0.0606(4)	4.9(8)	C(103)b	0.6303(6)	−0.122(1)	0.1204(4)	7.1(9)
C(103)a	0.0531(8)	0.544(1)	0.0467(4)	5.8(9)	C(104)b	0.5851(6)	−0.188(1)	0.1288(4)	7.1(9)
C(104)a	0.0267(8)	0.454(1)	0.0558(4)	9(1)	C(105)b	0.5326(6)	−0.147(1)	0.1393(4)	4.7(7)
C(105)a	0.0574(8)	0.395(1)	0.0788(4)	9(1)	C(106)b	0.5252(6)	−0.042(1)	0.1412(4)	5.3(8)
C(106)a	0.1145(8)	0.426(1)	0.0926(4)	6.3(9)	C(111)b	0.5140(6)	0.181(1)	0.0966(4)	3.3(7)
C(112)a	0.3247(7)	0.468(1)	0.0843(3)	4.4(8)	C(112)b	0.5224(6)	0.264(1)	0.0778(4)	4.1(7)
C(113)a	0.3646(7)	0.432(1)	0.0645(3)	6.6(9)	C(113)b	0.4856(6)	0.274(1)	0.0504(4)	7(1)
C(114)a	0.3446(7)	0.424(1)	0.0339(3)	8(1)	C(114)b	0.4403(6)	0.201(1)	0.0420(4)	7.1(9)
C(115)a	0.2845(7)	0.450(1)	0.0231(3)	6.9(9)	C(115)b	0.4320(6)	0.118(1)	0.0608(4)	9(1)
C(116)a	0.2445(7)	0.486(1)	0.0429(3)	4.7(8)	C(116)b	0.4688(6)	0.108(1)	0.0881(4)	10(1)
C(111)a	0.2646(7)	0.494(1)	0.0735(3)	3.6(7)	C(121)b	0.5082(8)	0.187(1)	0.1603(3)	4.6(8)
C(121)a	0.2321(7)	0.4735(9)	0.1330(4)	3.3(7)	C(122)b	0.4639(8)	0.263(1)	0.1546(3)	5.1(8)
C(122)a	0.2281(7)	0.5192(9)	0.1609(4)	4.4(8)	C(123)b	0.4271(8)	0.291(1)	0.1768(3)	7.1(9)
C(123)a	0.2369(7)	0.4605(9)	0.1870(4)	5.6(8)	C(124)b	0.4348(8)	0.242(1)	0.2047(3)	6.5(9)
C(124)a	0.2498(7)	0.3561(9)	0.1854(4)	7.1(9)	C(125)b	0.4791(8)	0.166(1)	0.2104(3)	6.8(9)
C(125)a	0.2538(7)	0.3104(9)	0.1575(4)	6.5(9)	C(126)b	0.5159(8)	0.138(1)	0.1882(3)	5.1(8)
C(126)a	0.2450(7)	0.3690(9)	0.1313(4)	4.9(8)					

of 20 mL of methanol and cooling to 0 °C gave 0.33 g of 1 as orange crystals (72%).

Using the same procedure except adding 0.24 g of $RuHCl(CO)_2(PPh_3)_2$ (0.33 mmol) gave 0.17 g of 1 (37%).

Anal. Calcd for $C_{73}H_{65}OP_4ReRu$: C, 65.68; H, 4.99; P, 8.48; Re, 12.73; Ru, 6.91. Found: C, 65.55; H, 5.06; P, 8.78; Re, 12.81; Ru, 6.71.

Synthesis of $(CO)(PPh_3)_2Re(\mu\text{-}H)_3Ru(C_2H_4)(PPh_3)_2$ (2). Ethylene was bubbled for 1 h through a stirred solution of 0.3 g (0.21 mmol) of 1 in 10 mL of dichloromethane. A red brown precipitate appeared. The solution was concentrated to 5 mL, and the precipitate was filtered and dried (0.25 g, 80%).

Anal. Calcd for $C_{75}H_{67}OP_4ReRu$: C, 64.55; H, 4.84; P, 8.88; Re, 13.34; Ru, 6.91. Found: C, 64.12; H, 4.67; P, 8.50; Re, 12.78; Ru, 6.89.

Synthesis of $(CO)(PPh_3)_2Re(\mu\text{-}Cl)_2(\mu\text{-}H)RuH(PPh_3)_2$ (3). 1 (0.2 g) was dissolved in 5 mL of chloroform, and the solution was stirred for 1 h. The solvent was then evaporated to dryness, leaving a dark orange solid 3 in quantitative yield. Anal. Calcd for $C_{73}H_{63}Cl_2OP_4ReRu$: C, 60.96; H, 4.41; Cl, 4.93; P, 8.61; Re, 12.95; Ru, 7.03. Found: C, 59.32; H, 4.33; Cl, 5.33; P, 8.53; Re, 11.88; Ru, 7.66.

Synthesis of $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3Ru(H_2)(PPh_3)_2][BF_4]$ (4). To 0.15 g (0.11 mmol) of 1 dissolved in 10 mL of dichloromethane was added 22 μL of $HBF_4{\cdot}OEt_2$ at room temperature. The solution immediately turned red and was evaporated to dryness, leaving 4 in quantitative yield as an orange solid.

Anal. Calcd for $C_{73}H_{66}BF_4OP_4ReRu$: C, 60.17; H, 4.56; F, 5.21; P, 8.50; Re, 12.78; Ru, 6.94. Found: C, 59.81; H, 4.50; F, 5.19; P, 8.23; Re, 11.95; Ru, 7.13.

Synthesis of $[(CO)(PPh_3)_2Re(\mu\text{-}Cl)_2(\mu\text{-}H)Ru(H_2)(PPh_3)_2][BF_4]$ (5). This compound was synthetized in the same way 4 and was isolated as an orange powder.

Anal. Calcd for $C_{73}H_{64}BCl_2F_4OP_4ReRu$: C, 57.45; H, 4.23; Cl, 4.65; F, 4.98; P, 8.12; Re, 12.20; Ru, 6.62. Found: C, 56.30; H, 4.12; Cl, 4.43; F, 4.89; P, 7.78; Re, 11.97; Ru, 6.92.

Synthesis of $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3Ru(C_2H_4)(PPh_3)_2][BF_4]$ (6). This compound was synthesized by bubbling ethylene through a freshly prepared dichloromethane solution of 4. The solution turned red brown and after 10 min was concentrated to 5 mL. Adding diethyl ether induced the precipitation of a brown powder 6 which was not stable enough to get a good analysis.

Synthesis of $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3Ru(CH_3CN)(PPh_3)_2][BF_4]$ (7) and $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3Ru((CH_3)_2CO)(PPh_3)_2][BF_4]$ (8). Complex 4 was synthesized as previously described from 0.2 g of 1, 5 mL of acetonitrile was then added, and the solution turned maroon. The solution was stirred for 30 min and then evaporated to dryness, leaving 7 as a dark brown powder. The product was purified by crystallization in a dichloromethane–diethyl ether mixture, leaving 0.16 g (73%) of 7.

Anal. Calcd for $C_{75}H_{67}BF_4NOP_4ReRu$: C, 60.20; H, 4.51; F, 5.08; N, 0.94; P, 8.26; Re, 12.44; Ru, 6.75. Found: C, 59.21; H, 4.50; F, 4.90; N, 1.05; P, 8.22; Re, 11.73; Ru, 7.41.

Complex 8 was synthesized in the same manner and isolated as a green solid in quantitative yield by evaporation of the solvents. Further purification by recrystallization was prevented by the instability of the complex on standing in solution in the absence of excess acetone.

Anal. Calcd for $C_{76}H_{70}BF_4O_2P_4ReRu$: C, 60.32; H, 4.66; F, 5.02; P, 8.19; Re, 12.30; Ru, 6.68. Found: C, 59.91; H, 4.59; F, 4.90; P, 7.61; Re, 11.79; Ru, 6.81.

Crystallographic Studies. Crystals of 1 suitable for X-ray diffraction were obtained through recrystallization from a dichloromethane/ether mixture at room temperature. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22 °C. Cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range $8° < 2\theta$ (Mo $K\alpha_1$) $< 28°$. The space group was determined by careful examination of systematic extinctions in the listing of the measured reflections. All calculations were performed on a MicroVax 3400. Data reductions were carried out using the SDP crystallographic computing package.[25] The intensities were corrected from absorption by using the empirical Ψ-scan method.[26] Table III presents further crystallographic informations.

The structure was solved by using the SHELXS-86 program[27] and refined by using the SHELX-76 program.[28] The positions of the Re, Ru, and P atoms were determined by direct methods. There are two independent molecules of 1 per unit cell. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses. Atomic scattering factors were taken from the standard tabulations.[29] Anomalous dispersion terms for Re, Ru, and P atoms were included in the calculated structure factors,[30] and the Re, Ru, and P atoms were allowed to vibrate anisotropically. The carbon atoms of the phenyl rings were refined as isotropic rigid groups (C_6H_5 ring: imposed D_{6h} symmetry, C–C = 1.395 Å), and the hydrogen atoms attached to the phenyl rings were entered in idealized positions (C–H = 0.97 Å). The scattering factors for the hydrogen atoms were taken from Stewart et al.[31]

At the final stage of the refinement, a Fourier difference map clearly showed, respectively, three strong peaks in molecule A and two strong peaks in molecule B (molecule A: $x = 0.1476$, $y = 0.7568$, $z = 0.1074$; $x = 0.2044$, $y = 0.7656$, $z = 0.1387$; $x = 0.2147$, $y = 0.8634$, $z = 0.1047$. Molecule B: $x = 0.6422$, $y = 0.2846$, $z = 0.0963$; $x = 0.7199$, $y = 0.3568$, $z = 0.1382$). They were situated at reasonable distances from the Re and Ru atoms for bridging hydrides. It was not possible to locate unambiguously any terminal hydrides on the Re or Ru atoms, whose presence was indicated by the ^1H NMR spectra. The possible location of all hydride ligands in 1 was also confirmed by molecular mechanics calculations using Orpen's program HYDEX.[11] The positions of the five potential energy minima for each of the two independent molecules of 1 have been refined to the values given in Table IV. The positions of some of them (the ones attributed to H(3)a, H(4)a, H(5)a, H(3)b, and H(5)b) were indeed in good agreement with the positions of the residual peaks found in the final difference Fourier map.

The hydride ligands were finally introduced in the last cycle of refinement, on the positions given by the program HYDEX, with fixed coordinates and thermal parameters (arbitrarily set to 0.06 Å²).

Final atomic coordinates and thermal parameters $U_{eq} \times 100$ for non-hydrogen atoms in compounds 1 are given in Table IV. Thermal parameters for atoms which were refined anisotropically and hydrogen positions are available as supplementary material.

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Supplementary Material Available: Table S1, listing anisotropic thermal parameters, Table S2, giving hydrogen positions, and Table S3, giving least-squares planes for compound 1 and a figure of the structure of molecule B (6 pages). Ordering information is given on any current masthead page.

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