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Synthesis, Structure and Reactivity toward Tetrafluoroboric Acid of a New Heterobimetallic Rhenium–Iridium Polyhydride Complex, $(CO)(PPh_3)_2Re(\mu\text{-}H)_3IrH(PPh_3)_2$

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The reaction of $[K][ReH_6(PPh_3)_2]$ with $IrCl(CO)(PPh_3)_2$ leads to the formation of the complex $(CO)(PPh_3)_2Re(\mu\text{-}H)_3IrH(PPh_3)_2$ (1) in 36% yield. Its structure has been established by variable temperature ^1H and ^{31}P NMR and X-ray diffraction; it consists of two distorted octahedra sharing a face containing three bridging hydrides. The iridium atom is bonded to a terminal hydride and to two phosphine ligands. The position of the hydrides has been calculated using the program HYDEX. Crystallographic data for 1: monoclinic C_{2h}^5-$P2_1/n$, $a = 14.818(3)$ Å, $b = 20.750(2)$ Å, $c = 21.693(3)$ Å; $\beta = 96.29(2)°$, $V = 6629$ (2) Å^3, $Z = 4$; $R = 0.0374$, $R_w = 0.0435$ for 3845 observations and 406 variable parameters. The compound 1 reacts with $HBF_4{\cdot}OMe_2$ to give $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3IrH(PPh_3)_2][BF_4]$ which has been isolated as its tetraphenylborate salt and characterized by variable temperature ^1H and ^{31}P NMR spectroscopy. Protonation has induced the formation of a rhenium–terminal hydride bond.

Introduction

Bimetallic polyhydride complexes have recently attracted interest since the presence of terminal and bridging hydride ligands should be a favorable factor of reactivity.[1-3] Moreover, bimetallic activation is expected to lead to unusual stoichiometric or catalytic properties.[4]

For these reasons we have tried to build new heterobimetallic polyhydride complexes retaining as the building block the complex $ReH_7(PPh_3)_2$ which can be easily deprotonated to $[ReH_6(PPh_3)_2]^-$.[1b] Looking for an association of rhenium with a metal able to easily activate hydrogen, we have recently synthesized the new complexes $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$[5-7] and $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3Rh(PPh_3)_2$[8] in good yield by reaction of this anion with the $RuHCl(CO)(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$ complexes respectively.

In order to extend this family of bimetallic compounds we have studied the reaction of $[ReH_6(PPh_3)_2]^-$ toward $IrCl(CO)(PPh_3)_2$ to check the influence of the metal on the structure and reactivity of the bimetallic complexes. The reaction leads to the formation of $(PPh_3)_2(CO)Re(\mu\text{-}H)_3IrH(PPh_3)_2$, 1, which has been fully characterized by NMR and X-ray diffraction. The reactivity of this complex toward tetrafluoroboric acid has also been examined. A recent report on the synthesis, by a different strategy, of the closely related complex $[(PPh_3)_2H_3Re(\mu\text{-}H)_3IrH(PPh_3)_2][SbF_6]$[9] prompted us to report our results in this field.

Results and Discussion

Synthesis and Characterization of $(PPh_3)_2(CO)Re(\mu\text{-}H)_3IrH(PPh_3)_2$, 1. This complex has been synthesized following the strategy used for the synthesis of the Re–Ru and Re–Rh polyhydride complexes[7,8] according to the reaction

$$[K][ReH_6(PPh_3)_2] + IrCl(CO)(PPh_3)_2 \rightarrow (PPh_3)_2(CO)Re(\mu\text{-}H_3)IrH(PPh_3)_2 + H_2 + KCl$$

This occurs at room temperature in THF, and the bimetallic complex is isolated as an air stable red solid in quite good yield (36%). The IR spectrum shows a ν(CO) band at 1810 cm^{-1} which suggests that, as in the Re–Ru and Re–Rh complexes, there is migration of the carbonyl group to the rhenium metal. This is confirmed by ^{13}C NMR: the CO resonance appears as a triplet at 207.2 ppm ($J_{PC} = 11.5$ Hz), and selective phosphorus decoupling experiments show that coupling occurs with the two phosphines bonded to rhenium.

The ^1H and $^{31}P\{^1H\}$ NMR spectra at room temperature give evidence that the molecule is fluxional. In the hydride region at 297 K the spectrum consists of two broad resonances at $\delta = -5.34, -15.67$ ppm and a figure of resonance at -8.40 ppm which can be analyzed as the X part of an AA′XX′ spin system ($J_{AX} = 92.4$ Hz, $J_{AX'} = 12.4$ Hz, $J_{AA'} = 16$ Hz). These signals are in a 1/1/2 intensity ratio. At the same temperature two triplets are observed at 48.8 and 23.0 ppm ($J_{PP} = 4$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum attributed from the chemical shift values, to the phosphines bonded to rhenium and to iridium respectively. Lowering the temperature to 183 K induces the splitting of these two triplets into a singlet at 49.7 ppm, a doublet at 48.4 ppm ($J_{PP} = 22.3$ Hz), a doublet at 23.2 ppm ($J_{PP} = 15.1$ Hz), and a doublet of doublets at 22.4 ppm ($J_{PP} = 22.3$ and 15.1 Hz). At the same temperature in the hydride region the two broad resonances sharpen to a singlet at -5.60 ppm and to an ill-resolved triplet at -15.67 ppm. The other resonance appears as a broad doublet at -8.49 ppm ($J_{PH} = 87.2$ Hz). Even though fully selective ^{31}P decoupling experiments have not been possible due to the proximity of the phosphorus resonances in each group, this has nevertheless

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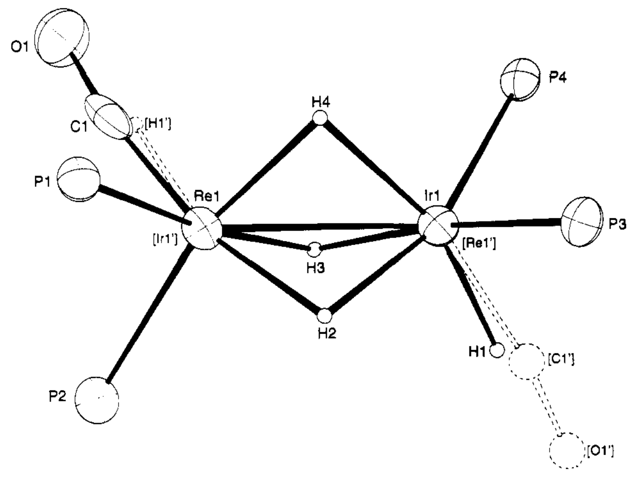


Figure 1. Perspective view of the complex $(CO)(PPh_3)_2Re(\mu\text{-}H)_3IrH(PPh_3)_2$ (**1**) showing the two orientations of the molecule. The dotted lines and the labels in brackets represent respectively the bonds and the atoms corresponding to the 35% contribution. Thermal ellipsoids are shown at the 30% probability level and the phenyl groups have been omitted for clarity.

allowed us to determine that the ill-resolved triplet and the doublet are due to coupling with phosphines bonded to iridium. Decoupling the resonances due to phosphines bonded to rhenium induces just a sharpening of the singlet at −5.60 ppm.

From these experiments and the values of the chemical shifts we deduce that the triplet is due to a terminal hydride bonded to iridium and that the doublet is due to two bridging hydrides in trans position to the two phosphines bonded to iridium. These results are similar to those observed for hydrides in similar positions in $[(PPh_3)_2H_3Re(\mu\text{-}H)_3IrH(PPh_3)_2][SbF_6]$.[9] By comparison with our observations on Re–Ru and Re–Rh polyhydride complexes,[7,8] the third hydride resonance is attributed to a bridging hydride ligand.

These spectroscopic data show that, for the two isoelectronic tetrahydride bimetallic complexes Re–Rh[8] and Re–Ir we have synthesized, the hydride ligands have different location and fluxional behavior. Indeed in the case of the $(PPh_3)_2(CO)HRe(\mu\text{-}H)_3Rh(PPh_3)_2$ compound the terminal hydride is located on rhenium and the three bridging hydrides are fluxional with no or slow exchange with the terminal one.[8] The location of the terminal hydride on iridium in **1** is not unexpected considering the difference in stability of the Ir–H and Rh–H bonds, but in the family of heterobimetallic polyhydride complexes we have developed, **1** is the first case where an exchange between a terminal and a bridging hydride is clearly observed. It has to be mentioned that in the $[(PPh_3)_2H_3Re(\mu\text{-}H)_3IrH(PPh_3)_2][SbF_6]$ [9] complex the bridging hydrides are exchanging with terminal hydride ligands on rhenium but not on iridium.

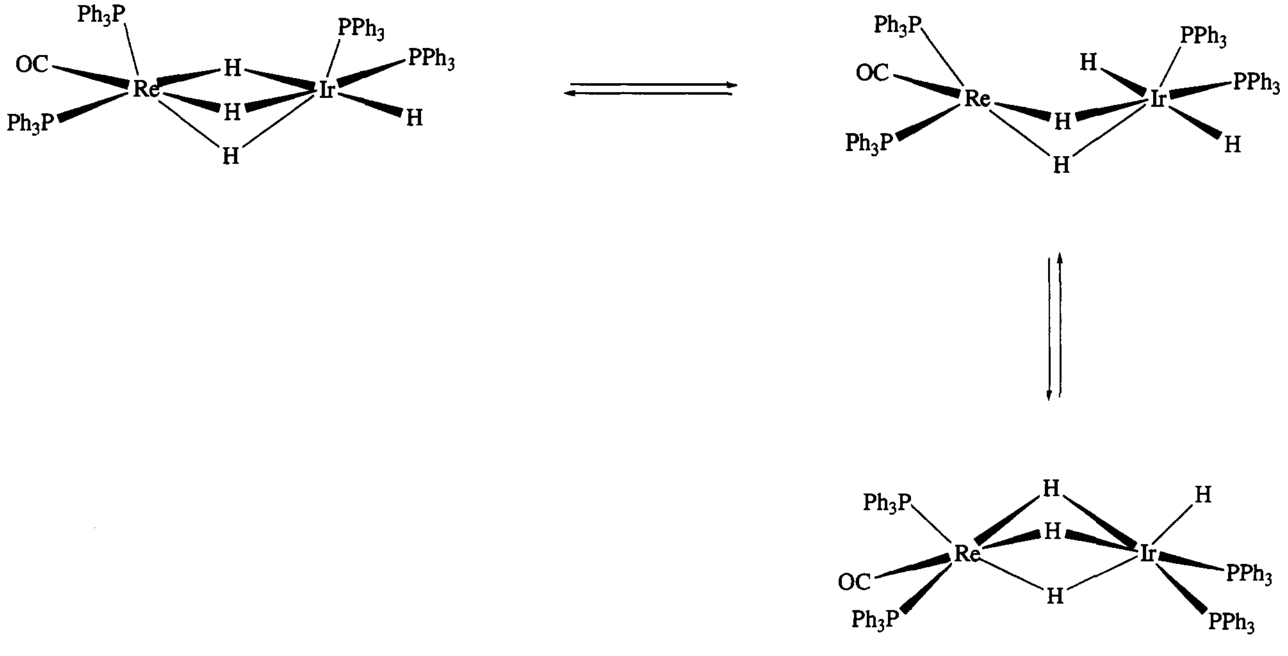
Table 1. Selected Bond Lengths (Å) and Angles (deg) for $(CO)(PPh_3)_2Re(\mu\text{-}H)_3IrH(PPh_3)_2$ (**1**)

Re(1)–Ir(1)	2.5592(9)	Ir(1)–H(4)	1.80
Re(1)–C(1)	1.875(9)	Ir(1)′–H(1)′	1.70
Re(1)–H(2)	1.80	Re(1)–P(1)	2.303(4)
Re(1)–H(3)	1.80	Re(1)–P(2)	2.311(4)
Re(1)–H(4)	1.80	Ir(1)–P(3)	2.298(4)
Re(1)′–C(1)′	1.87(1)	Ir(1)–P(4)	2.294(4)
Ir(1)–H(1)	1.70	C(1)–O(1)	1.151(9)
Ir(1)–H(2)	1.80	C(1)′–O(1)′	1.15(1)
Ir(1)–H(3)	1.80		

C(1)–Re(1)–Ir(1)	119.9(7)	P(3)–Re(1)′–C(1)′	85.2(1)
P(1)–Re(1)–Ir(1)	127.9(1)	P(4)–Re(1)′–C(1)′	97.3(1)
P(1)–Re(1)–C(1)	87.9(8)	P(3)–Ir(1)–Re(1)	129.8(1)
P(2)–Re(1)–Ir(1)	119.1(1)	P(4)–Ir(1)–Re(1)	115.4(1)
P(2)–Re(1)–C(1)	94.3(7)	P(4)–Ir(1)–P(3)	100.1(2)
P(2)–Re(1)–P(1)	99.4(1)	O(1)–C(1)–Re(1)	173.2(2)
H(1)–Ir(1)–Re(1)	112.9	H(1)′–Ir(1)′–Re(1)′	112.3
P(3)–Ir(1)–H(1)	96.5	H(1)′–Ir(1)′–P(1)	94.8
P(4)–Ir(1)–H(1)	95.6	H(1)′–Ir(1)′–P(2)	96.8
Ir(1)–H(2)–Re(1)	90.5	Ir(1)–H(3)–Re(1)	90.5
Ir(1)–H(4)–Re(1)	90.5	C(1)′–Re(1)′–Ir(1)′	121.4(8)
O(1)′–C(1)′–Re(1)′	171.4(3)		

Single crystals of **1** were obtained and an X-ray structure determination was undertaken. The resolution of the structure was complicated by the presence of a disorder due to two orientations of the molecule: one molecule of **1** and the molecule resulting from the rotation of **1** along a C_2 axis passing through the middle of the metal–metal bond and perpendicular to it. The main effect of this disorder is to exchange the Re and Ir centers and the CO bonded to rhenium with the terminal H bonded to Ir. This disorder has been solved by considering that it is the result of the sum of 65% of one orientation and 35% of the other (see experimental section). A perspective view of the sum of the two orientations of the molecule in the crystal is given in Figure 1 along the labeling scheme. Bond lengths and angles of interest are gathered in Table 1. The structure of **1** consists, in accordance with the spectroscopic data, of a dinuclear Re–Ir unit in which

Scheme 1



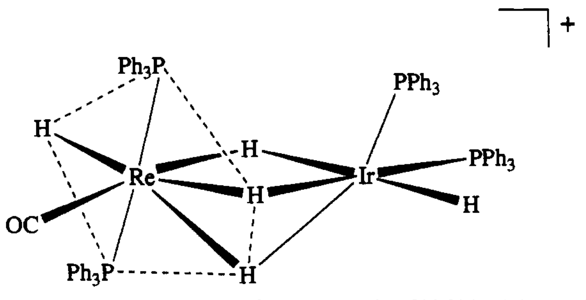


Figure 2. Proposed structure for the complex $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3IrH(PPh_3)_2]^+$ (**2**).

the two metals are bonded to two phosphine ligands and the CO group is on the rhenium atom. The positions of the hydride ligands have been calculated by the use of the program HYDEX[10] (see Experimental Section).

The structure can be described as the union of two distorted octahedra which share a common face defined by the three bridging hydride ligands. The H(2) ligand is trans to the CO group and to P(4), H(3) to P(1) and P(3), and H(4) to H(1) and P(2).

The shortness of the Re–Ir bond (2.5592 (9) Å) compared to the sum of the covalent radii (2.70 Å)[11] suggests a strong metal–metal interaction.

Having now an exact knowledge of the structure of **1** we can reconsider the NMR data. If the structure is consistent with the ^{31}P NMR data at low temperature, there is an apparent discrepancy with the ^1H NMR data for the hydride ligands. From the X-ray structure, we expect three resonances at low temperature for the bridging hydrides. This difference may be due to accidental chemical shift equivalence of H(2) and H(3), the two ligands in trans positions to P(3) and P(4).

Concerning the exchange between the terminal hydride on iridium and one of the bridging hydrides, it concerns the two hydrides H(1) and H(4) which are in trans positions. This is demonstrated by ^1H NMR experiments: in a spin saturation transfer experiment at room temperature, the signal at −15.67 ppm almost disappears upon irradiation of the resonance at −5.58 ppm, the resonance of H(2) and H(3) hydrides being unaffected.

Moreover, variable temperature experiments in deuteriated toluene show a coalescence of these two resonances at ca 320 K which corresponds to a $\Delta G^{\ast}$ value of 13 (±1) kcal·mol^{-1}.[12] A possible mechanism for this exchange passing through an intermediate with two terminal hydrides on iridium, is proposed in Scheme 1. This mechanism is supported by the $\Delta G^{\ast}$ value determined from the coalescence temperature of the resonances of the phosphines bonded to rhenium (218 K) which is close to the value determined from the hydride resonances ($\Delta G^{\ast}$ = 11 (±1) kcal·mol^{-1}).

Synthesis and Characterization of $[(PPh_3)_2(CO)HRe(\mu\text{-}H)_3IrH(PPh_3)_2][BF_4]$, 2. Depending on the associated metals, protonation of the bimetallic polyhydrides leads to the formation of cationic complexes containing either molecular hydrogen (Re–Ru complex)[5] or only hydride ligands (case of Re–Rh systems).[8] So the behavior of **1** toward tetrafluoroboric acid was investigated.

The addition of tetrafluoroboric acid to a solution of **1** leads to the immediate formation of a new complex **2**, which has been isolated as an orange solid after the exchange of the tetrafluoroborate anion by the tetraphenylborate anion. Protonation of **1** has induced a shift of the ν(CO) stretching frequency to 1895 cm^{-1}, consistent with the formation of a cationic complex.

The room temperature ^1H NMR spectrum in the hydride region shows five signals of the same intensity excluding the formation of a molecular hydrogen ligand: two triplets characteristic of terminal hydrides on rhenium and iridium, one singlet, and two broad resonances. At the same temperature, two broad resonances of same intensity are observed in the $^{31}P\{^1H\}$ NMR spectrum.

Table 2. Experimental Data for X-Ray Study of Compound 1

chem formula: $ReIr(CO)H_4(PPh_3)_4{\cdot}C_5H_{12}{\cdot}H_2O$	fw = 1563.8 amu
	space group: $C_{2h}{}^5\text{-}P2_1/n$
a = 14.818(3) Å	T = 22 °C
b = 20.750(2) Å	$\lambda(\text{Mo K}\alpha_1)$ = 0.7093 Å
c = 21.693(3) Å	ρ_{calcd} = 1.536 g·cm^{-3}
β = 96.29(2) deg	abs cor, min–max: 0.935–1.043
V = 6629(2) Å^3	R^a = 0.0374
Z = 4	$R_w{}^b$ = 0.0435

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|^2)]^{1/2}$; unit weights.

Table 3. Fractional Coordinates and Potential Energies of the Hydride Atoms in $(CO)(PPh_3)_2Re(\mu\text{-}H)_3IrH(PPh_3)_2$ (1) Calculated by Molecular Mechanics[10]

atom	x/a	y/b	z/c	PE, kcal·mol^{-1}
H(1)	0.3548	0.2166	0.0817	−0.30
H(2)	0.5055	0.2438	0.1412	0.74
H(3)	0.4605	0.1443	0.1300	1.23
H(4)	0.4773	0.1907	0.2236	0.80
H(1)′	0.5737	0.0969	0.2025	−0.49
H(2)′	0.5058	0.2446	0.1429	0.78
H(3)′	0.4604	0.1440	0.1304	1.18
H(4)′	0.4766	0.1889	0.2235	0.79

When the temperature is lowered to 183 K, in the ^1H NMR spectrum the two broad resonances evolve to two doublets and the triplet of the terminal hydride on iridium evolves to a doublet of doublets. At the same temperature the $^{31}P\{^1H\}$ spectrum shows four multiplets of the same intensity. Selective $^1H\{^{31}P\}$ decoupling experiments indicate that the two doublets are characteristic of two bridging hydride ligands which are trans to the phosphines bonded to iridium.

From these observations we conclude that protonation of **1** has induced the formation of a Re–H terminal bond leading to a complex similar to that obtained by the protonation of $(PPh_3)_2(CO)HRe(\mu\text{-}H)_3Rh(PPh_3)_2$.[8] For the complex **2** we propose the structure shown in Figure 2. This is similar to the structure of $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$[7]: the geometry around the iridium is a distorted octahedron and around rhenium is a distorted pentagonal bipyramid.

In contrast to **1** the fluxional behavior of **2** concerns two bridging hydrides only, similar to $(PPh_3)_2(CO)Re(\mu\text{-}H)_3Ru(CH_3CN)(PPh_3)_2$.[6] By analogy with the mechanism proposed for the isomerization of $[Ph(PEt_3)Pt(\mu\text{-}H)_2IrH(PEt_3)_3]^+$,[13] we have suggested that this exchange occurs through intermediates with hydrides in terminal positions on the metallic centers, the bimetallic frame being maintained by the third bridging hydride. The same explanation holds for **2**.

Conclusion

The complex $(PPh_3)_2(CO)Re(\mu\text{-}H)_3IrH(PPh_3)_2$ is easily synthesized in the reaction of $K[ReH_6(PPh_3)_2]$ with $IrCl(CO)(PPh_3)_2$. Compared with the previously reported similar complex of rhodium $(PPh_3)_2(CO)HRe(\mu\text{-}H)_3Rh(PPh_3)_2$, the substitution of rhodium by iridium induces the migration of the terminal hydride from rhenium to iridium. This observation is the consequence of the greater stability of the Ir–H bond compared to Rh–H. A further illustration of this difference of stability is illustrated by the fluxional behavior of the two complexes: for the Re–Rh compound this phenomenon concerns only the three bridging hydrides, but in the case of the Re–Ir complex it implies an exchange between one of the bridging hydrides with the terminal hydride bonded to iridium.

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Table 4. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å^2 × 100) with Esd's in Parentheses (U(eq) = $^1/_3$ Trace U) for $(CO)(PPh_3)_2Re(\mu\text{-}H)_3IrH(PPh_3)_2$

atom	x/a	y/b	z/c	U(eq)/U(iso)
Re(1)	0.56329(4)	0.17303(3)	0.17341(3)	0.0314
Ir(1)′	0.56329(4)	0.17303(3)	0.17341(3)	0.0314
Ir(1)	0.39802(4)	0.21093(3)	0.15754(3)	0.0301
Re(1)′	0.39802(4)	0.21093(3)	0.15754(3)	0.0301
C(1)	0.591(2)	0.0919(7)	0.208(1)	0.0356
O(1)	0.602(1)	0.0432(7)	0.2336(9)	0.0610
C(1)′	0.340(2)	0.228(2)	0.0784(7)	0.04(1)
O(1)′	0.313(2)	0.234(2)	0.0271(8)	0.07(1)
H(1)	0.3548	0.2166	0.0817	
H(2)	0.5057	0.2442	0.1421	
H(3)	0.4605	0.1442	0.1302	
H(4)	0.4770	0.1898	0.2236	
H(1)′	0.5737	0.0969	0.2025	
H(2)′	0.5058	0.2446	0.1429	
H(3)′	0.4604	0.1440	0.1304	
H(4)′	0.4766	0.1889	0.2235	
P(1)	0.6805(3)	0.2146(2)	0.2401(2)	0.0366
P(2)	0.6396(3)	0.1553(2)	0.0876(2)	0.0366
P(3)	0.3351(3)	0.3065(2)	0.1851(2)	0.0362
P(4)	0.2934(3)	0.1395(2)	0.1880(2)	0.028
C(11)	0.788(1)	0.1712(9)	0.2483(7)	0.041(4)
C(12)	0.807(1)	0.1249(8)	0.2930(8)	0.046(5)
C(13)	0.883(1)	0.084(1)	0.2934(9)	0.068(6)
C(14)	0.939(1)	0.094(1)	0.2486(9)	0.057(5)
C(15)	0.925(1)	0.141(1)	0.2051(9)	0.060(5)
C(16)	0.848(1)	0.1787(9)	0.2031(7)	0.044(4)
C(21)	0.711(1)	0.2979(9)	0.2296(8)	0.047(5)
C(22)	0.644(1)	0.343(1)	0.2103(9)	0.063(6)
C(23)	0.661(1)	0.408(1)	0.205(1)	0.073(6)
C(24)	0.746(2)	0.432(1)	0.217(1)	0.079(7)
C(25)	0.815(1)	0.388(1)	0.236(1)	0.070(6)
C(26)	0.798(1)	0.324(1)	0.2436(8)	0.054(5)
C(31)	0.657(1)	0.2179(8)	0.3220(7)	0.039(4)
C(32)	0.596(1)	0.1780(9)	0.3445(9)	0.057(5)
C(33)	0.580(1)	0.178(1)	0.408(1)	0.080(6)
C(34)	0.633(2)	0.217(1)	0.448(1)	0.081(7)
C(35)	0.694(2)	0.257(1)	0.428(1)	0.096(8)
C(36)	0.709(1)	0.258(1)	0.364(1)	0.073(6)
C(41)	0.557(1)	0.1458(8)	0.0184(7)	0.034(4)
C(42)	0.499(1)	0.0935(9)	0.0164(8)	0.046(5)
C(43)	0.430(1)	0.0853(9)	−0.0310(9)	0.058(5)
C(44)	0.419(1)	0.129(1)	−0.078(1)	0.080(7)
C(45)	0.475(2)	0.181(1)	−0.080(1)	0.088(7)
C(46)	0.546(1)	0.191(1)	−0.030(1)	0.069(6)
C(51)	0.709(1)	0.0837(8)	0.0769(7)	0.034(4)
C(52)	0.730(1)	0.0642(8)	0.0204(8)	0.044(4)
C(53)	0.782(1)	0.0087(9)	0.0133(9)	0.053(5)
C(54)	0.816(1)	−0.024(1)	0.0628(9)	0.061(6)
C(55)	0.798(1)	−0.007(1)	0.1223(9)	0.062(6)
C(56)	0.746(1)	0.0475(9)	0.1287(8)	0.049(5)
C(61)	0.712(1)	0.2229(8)	0.0635(7)	0.040(4)
C(62)	0.679(1)	0.284(1)	0.0705(8)	0.057(5)
C(63)	0.732(1)	0.336(1)	0.0556(9)	0.062(6)
C(64)	0.816(1)	0.326(1)	0.0361(9)	0.066(5)
C(65)	0.850(1)	0.267(1)	0.0308(9)	0.062(6)
C(66)	0.798(1)	0.2135(9)	0.0448(8)	0.051(5)
C(71)	0.361(1)	0.3325(8)	0.2669(7)	0.043(4)
C(72)	0.444(1)	0.3161(9)	0.2972(9)	0.057(5)
C(73)	0.468(1)	0.334(1)	0.359(1)	0.078(6)
C(74)	0.408(1)	0.3710(9)	0.3889(9)	0.058(5)
C(75)	0.327(1)	0.3868(9)	0.3604(9)	0.061(6)
C(76)	0.305(1)	0.3701(9)	0.2981(8)	0.048(5)
C(81)	0.211(1)	0.3154(8)	0.1720(8)	0.042(4)
C(82)	0.158(1)	0.2906(9)	0.2141(8)	0.053(5)
C(83)	0.063(1)	0.292(1)	0.2032(9)	0.067(6)
C(84)	0.025(1)	0.318(1)	0.1490(9)	0.065(6)
C(85)	0.072(1)	0.343(1)	0.106(1)	0.075(7)
C(86)	0.168(1)	0.3428(9)	0.1155(9)	0.060(6)
C(91)	0.3717(8)	0.3781(8)	0.1457(7)	0.060(6)
C(92)	0.4199(9)	0.370(1)	0.0947(8)	0.15(1)
C(93)	0.4498(8)	0.424(1)	0.0641(7)	0.22(2)
C(94)	0.431(1)	0.486(1)	0.084(1)	0.16(1)
C(95)	0.382(1)	0.4938(8)	0.135(1)	0.17(1)
C(96)	0.3515(8)	0.440(1)	0.1654(7)	0.12(1)
C(101)	0.257(1)	0.1539(7)	0.2632(7)	0.027(4)
C(102)	0.166(1)	0.1482(8)	0.2771(8)	0.044(5)
C(103)	0.143(1)	0.167(1)	0.3346(9)	0.056(5)
C(104)	0.205(1)	0.186(1)	0.3812(9)	0.067(6)
C(105)	0.295(1)	0.1913(9)	0.3699(9)	0.063(6)
C(106)	0.321(1)	0.1761(9)	0.3112(7)	0.043(4)
C(111)	0.1871(9)	0.1208(7)	0.1389(7)	0.026(4)
C(112)	0.152(1)	0.1619(8)	0.0934(8)	0.047(5)
C(113)	0.073(1)	0.1454(9)	0.0545(8)	0.049(5)
C(114)	0.028(1)	0.0888(9)	0.0650(9)	0.055(5)
C(115)	0.063(1)	0.0479(9)	0.1119(8)	0.050(5)
C(116)	0.141(1)	0.0631(8)	0.1469(8)	0.041(4)
C(121)	0.344(1)	0.0608(8)	0.1954(7)	0.032(4)
C(122)	0.364(1)	0.0286(9)	0.1407(8)	0.050(5)
C(123)	0.407(1)	−0.0302(8)	0.1450(8)	0.043(4)
C(124)	0.426(1)	−0.0631(9)	0.1995(9)	0.053(5)
C(125)	0.407(1)	−0.0342(9)	0.2529(9)	0.056(5)
C(126)	0.365(1)	0.0259(8)	0.2522(8)	0.042(4)
O(601)	0.536(2)	0.642(2)	0.051(2)	0.11(1)
C(1)s	0.793(5)	0.521(2)	0.062(2)	0.16(1)
C(2)s	0.955(3)	0.503(2)	0.069(2)	0.16(1)
C(3)s	0.703(3)	0.542(2)	0.058(2)	0.19(2)
C(4)s	0.882(6)	0.501(4)	0.106(4)	0.17(3)
C(5)s	0.839(6)	0.510(4)	0.005(4)	0.17(3)
C(6)s	1.038(5)	0.522(3)	0.080(3)	0.12(2)
C(7)s	0.914(7)	0.492(5)	−0.023(5)	0.23(4)
C(8)s	0.664(7)	0.618(5)	0.039(4)	0.25(4)

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 (^1H), and WM 250 (^1H, ^{31}P) instruments. Variable temperature and selective decoupling experiments were carried out on the WM 250 machine. Elemental analysis were performed in our laboratory for the elements C, H. $ReH_7(PPh_3)_2$[14] and $IrCl(CO)(PPh_3)_2$[15] have been prepared according to published procedures.

Synthesis of $(CO)(PPh_3)_2Re(\mu\text{-}H)_3IrH(PPh_3)_2$ (1). To a solution of 0.2 g (0.28 mmol) of $ReH_7(PPh_3)_2$ in 20 mL of THF was added an excess of KH, and the solution was stirred for 40 min, giving a yellow solution. The solution was then filtered to eliminate excess KH and added to 0.22 g (0.33 mmol) of $IrCl(CO)(PPh_3)_2$. After being stirred for 10 h, the red solution was evaporated to dryness. The residue was dissolved in toluene (10 mL) and filtered through Celite to eliminate KCl. Adding 10 mL of hexanes in order to have a two-phase system induced by diffusion the slow precipitation at room temperature of 0.15 g of 1 as dark red crystals (36%). IR ν(CO) (CH_2Cl_2): 1810 cm^{-1}. ^1H NMR (CD_2Cl_2): 293 K, δ −5.58 (broad, 1 H), −8.40 (2 H, AA′XX′ system, see text), −15.67 (broad, 1 H); 183 K, δ −5.59 (1H), −8.49 (d, J = 87.2 Hz, 2H), −15.67 (unresolved triplet, 1H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 293 K, δ 48.9 (t, J = 4 Hz), 23 (t, J = 4 Hz); 183 K, δ 49.7, 48.4 (d, J = 22.3 Hz), 23.7 (d, J = 15.1 Hz), 23.3 (dd, J_1 = 22.3, J_2 = 15.1 Hz). Anal. Calcd. for $C_{73}H_{64}IrOP_4Re$: C, 60.07; H, 4.42. Found: C, 59.87; H, 4.12.

Synthesis of $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3IrH(PPh_3)_2][BPh_4]$ (2). To 0.1 g (0.01 mmol) of 1 dissolved in 10 mL of dichloromethane was added 10 μL of HBF_4,OMe_2 (0.082 mmol). The solution turned to a pale orange color. After being stirred for 10 mn, the solution was evaporated to dryness under vacuum. After redissolution in acetone, 0.03 g (0.09 mmol) of $NaBPh_4$ was added and the solution was stirred for 1 h. The solution was then evaporated to dryness and then redissolved in 10 mL of dichloromethane. After filtration through Celite, 10 mL of methanol was added and the mixture cooled to 4 °C. Then 0.1 g of 2 was obtained as orange crystals (80% yield). IR ν(CO) (CH_2Cl_2): 1895 cm^{-1}. ^1H NMR (CD_2Cl_2): 293 K, −2.93 (1 H), −3.73 (t, J = 49.8 Hz, 1 H), −5.48 (broad, 1H), −7.53 (broad, 1 H), −18.94 (t, J = 22.6 Hz, 1 H); 183 K, δ −3.01 (1H), −3.96 (t, J = 48.2 Hz, 1H), −5.32 (d, J = 68.1 Hz, 1 H), −7.37 (d, J = 85 Hz, 1 H), −18.68 (dd, J = 26.6, 14.8 Hz, 1H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 293 K, δ 33.7, 17.9; 183 K, δ 38.1 (t, J = 16.4), 36.8 (dd, J = 4.2, 16.4 Hz), 21.2 (dt, J = 4.2, 16.4 Hz), 17.6 (d, J = 16.4 Hz).

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Anal. Calcd for $C_{96}H_{85}BIrOP_4Re$: C, 65.46; H, 4.81. Found: C, 64.94; H, 4.26.

Crystallographic Studies. Crystals of **1** suitable for X-ray diffraction were obtained through recrystallization from a THF/hexanes 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 $20° < 2\theta(\text{Mo K}\alpha_1) < 24°$. 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 CRYSTALS crystallographic computing package.[16] Empirical absorption correction were applied using the program DIFABS.[17] Table 2 presents further crystallographic informations.

The structure was solved by using the SHELXS-86 program,[18] which revealed the positions of two metal centers and four phosphorus atoms. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses by using the CRYSTALS program.[16] At the early stages of the refinement, the atomic scattering factors used for both metal centers were the ones of rhenium since we had no possibility to discriminate rhenium and iridium atoms before the carbonyl ligand was located. In fact, a Fourier difference map showed that each metal center bore a carbonyl ligand. Since the spectroscopic data clearly showed a unique carbonyl ligand bonded only to rhenium (*vide supra*), the observation of two carbonyl ligands in the Fourier difference map could only be explained by a disorder between the Ir–(H) and Re–CO fragments in the molecule. The carbonyl ligands correctly refined with structure occupancy factor of 65% for C(1)-O(1), and 35% for C(1)'-O(1)'. Finally, the metal center attached to P(1), P(2), and C(1) was refined as a mixture of rhenium atom with a site occupancy factor of 65% (Re(1)) and an iridium atom with a site factor of 35% (Ir(1)') using a riding model, while, in a similar manner, the second metal center was refined as a mixture of iridium atom with a site occupancy factor of 65% (Ir(1)) and a rhenium atom with a site occupancy factor of 35% (Re(1)'). A difference Fourier map also revealed several strong peaks situated at nonbonding distances from any atoms of the molecule: these peaks have been attributed to the oxygen atom of a water molecule and to the carbon atoms of a disordered hexane molecule or of a mixture of hexane isomers. Atomic scattering factors were taken from the standard tabulations.[19] Anomalous dispersion terms for Re, Ir, and P atoms were included in the calculated structure factors.[20] 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.[21]

The hydride ligands could not be located unambiguously. Their positions have been inferred from molecular mechanics calculations using the program HYDEX.[10] The positions of the four potential energy minima thus obtained in the unprimed and the primed molecule, respectively, are given in Table 3. The positions of minima H(2) and H(2)', H(3) and H(3)', H(4) and H(4)' were finally averaged, then introduced as the bridging hydrides H(2), H(3) and H(4), along with H(1) (with an s.o.f. fixed to 65%) and H(1)' (with an s.o.f. fixed to 35%), in the last cycle of refinement. No attempt has been made to refine the positions of the hydride ligands.

Final atomic coordinates and thermal parameters U_{eq} (×100) for Ir, Re, P, O, and C atoms in compound **1** are given in Table 4, along with the calculated positions of the hydride ligands. 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, anisotropic thermal parameters for compound **1**, Table S2, hydrogen positions for compound **1**, Table S3, a full Table of crystal and intensity data, Table S4, a full list of bond distances and angles, and a full Ortep presentation (8 pages). Ordering information is given on any current masthead page.

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