2118 *Inorg. Chem.* **1993,** *32,* 2118–2122

Synthesis and Solution Structure of Heterobimetallic Rhenium–Iridium Polyhydride Complexes

Demetrius Michos, Xiao-Liang Luo,*[1] and Robert H. Crabtree

Sterling Chemistry Laboratory, Department of Chemistry, Yale University,
New Haven, Connecticut 06511-8118

Received October 16, 1992

The reaction of $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ with $ReH_7(PPh_3)_2$ or $ReH_7(dppf)$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) is extremely rapid and leads to the quantitative formation of the heterobimetallic polyhydride complexes $[L_2H_3Re(\mu\text{-}H)_3IrH(PPh_3)_2]SbF_6$ (L = PPh_3 (**1**), $^1/_2$ dppf (**2**)), which have been characterized by IR and variable-temperature ^1H and ^{31}P NMR spectroscopy. The spectroscopic data for compounds **1** and **2** suggest that they contain three bridging and four terminal hydride ligands. The coordination polyhedron about rhenium is a dodecahedron, and that about iridium is an octahedron; the two polyhedra are fused by sharing a face containing the three bridging hydride ligands, which is an equilateral (E) triangular face of the dodecahedron and a triangular face of the octahedron. Compounds **1** and **2** are most likely formed by a formal dinuclear H_2 elimination mechanism, which involves initial displacement of the labile acetone ligands from $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ by the hydride ligands of ReH_7L_2 to give a transient hydride-bridged dinuclear $\eta^2\text{-}H_2$ species which subsequently undergoes facile H_2 elimination. The geometric factors favoring or disfavoring $M(\mu\text{-}H)_nM'$ (n = 3–5) bridging systems are discussed.

Introduction

Heterobimetallic complexes have been intensively studied[2] due in part to the promise of enhanced stoichiometric or catalytic reactivity as a result of the cooperation between the two electronically different metal centers. Of particular interest are heterobimetallic hydride complexes,[3] some of which have been shown to exhibit novel structures,[4] reactivity patterns,[5] and catalytic properties.[6]

Dirhenium polyhydride complexes of the general type $L_2H_2Re(\mu\text{-}H)_4ReH_2L_2$ are unusual in having four hydride ligands bridging the two rhenium centers,[7] whereas the diiridium polyhydride complexes of the type $[L_2HIr(\mu\text{-}H)_3IrHL_2]^+$ have three hydride ligands in the bridging positions.[8] We were interested to see which structure would be adopted in a heterobimetallic rhenium–iridium system. Here we report the synthesis and spectroscopic characterization of two heterobimetallic rhenium–iridium polyhydride complexes.

Results and Discussion

Synthesis of Heterobimetallic Rhenium–Iridium Polyhydride Complexes. A variety of bimetallic hydride complexes have been synthesized by coupling a hydride complex with a complex containing labile ligands, as shown in eq 1, where the M′–H

$$MS_xL_m + M'H_yL'_n \rightarrow L_mM(\mu\text{-}H)_zM'H_lL'_n + xS \quad (1)$$

bonds of $M'H_yL'_n$ act as two-electron ligands displacing the labile ligands S from MS_xL_m.[3a] With this synthetic strategy, we have synthesized two heterobimetallic rhenium–iridium polyhydride complexes.

The addition of 1 mol equiv of $ReH_7(PPh_3)_2$[9] or $ReH_7(dppf)$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene)[10] to a pale-yellow solution of $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$[11] in CH_2Cl_2 at room temperature resulted in instantaneous evolution of hydrogen along with formation of a deep red or green solution, from which the heterobimetallic rhenium–iridium polyhydride complexes $[L_2H_3Re(\mu\text{-}H)_3IrH(PPh_3)_2]SbF_6$ (L = PPh_3 (**1**), $^1/_2$ dppf (**2**)) were isolated in excellent yields (>90%) as red and green solids, respectively (eq 2).

$$[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6 + ReH_7L_2 \rightarrow$$
$$[L_2H_3Re(\mu\text{-}H)_3IrH(PPh_3)_2]SbF_6 + H_2 + 2Me_2CO \quad (2)$$

$$L = PPh_3\ (\mathbf{1}),\ ^1/_2\ \mathrm{dppf}\ (\mathbf{2})$$

---

(1) Present address: Inorganic and Structural Chemistry Group (INC-1), Mail Stop C346, Los Alamos National Laboratory, Los Alamos, NM 87545.

(2) (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry;* Wilkinson, G., Stone, F. G. A., Abel, W. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 6, Chapter 40. (b) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41.

(3) (a) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251. (b) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167. (c) Alvarez, D., Jr.; Lundquist, E. G.; Ziller, J. W.; Evans, W. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 8392.

(4) (a) Cazanoue, M.; He, Z.; Neibecker, D.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1991**, 307. (b) Delavaux, B.; Chaudret, B.; Dahan, F.; Poilblanc, R. *J. Organomet. Chem.* **1986**, *317*, 69. (c) Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F.; Albinati, A. *Inorg. Chem.* **1992**, *31*, 3841 and references therein.

(5) (a) Lundquist, E. G.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1986**, *108*, 8309. (b) Poulton, J. T.; Folting, K.; Caulton, K. G. *Organometallics* **1992**, *11*, 1364. (c) He, Z.; Neibecker, D.; Lugan, N.; Mathieu, R. *Organometallics* **1992**, *11*, 817. (d) Delavaux, B.; Arliguie, T.; Chaudret, B.; Poilblanc, R. *Nouv. J. Chim.* **1986**, *10*, 619. (e) Alvarez, D., Jr.; Caulton, K. G.; Evans, W. J.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 5500 and references therein.

(6) (a) Casey, C. P.; Rutter, E. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 8917. (b) Casey, C. P.; Whiteker, G. T. *Inorg. Chem.* **1990**, *29*, 876 and references therein.

(7) (a) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963. (b) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872. (c) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 4522. (d) Lyons, D.; Wilkinson, G. *J. Chem. Soc., Dalton. Trans.* **1985**, 587. (e) Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 3203. (f) Costello, M. T.; Moehring, G. A.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 1578. (g) Cotton, F. A.; Luck, R. L.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 43. (h) Meyer, K. E.; Root, D. R.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 3067 and references therein.

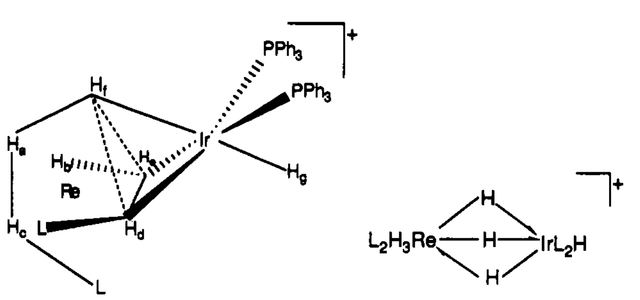
(8) (a) Crabtree, R. H.; Felkin, H.; Morris, G. *J. Organomet. Chem.* **1977**, *141*, 205. (b) Wang, H. H.; Pignolet, L. H. *Inorg. Chem.* **1980**, *19*, 1470. (c) Wang, H. H.; Mueting, A. M.; Casalnuovo, J. A.; Yan, S.; Barthelmes, J. K.-H.; Pignolet, L. H. *Inorg. Synth.* **1990**, *27*, 22.

(9) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Organomet. Chem.* **1982**, *224*, 363.

(10) (a) Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3775. (b) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 4813.

(11) (a) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (b) Crabtree, R. H.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994. (c) Crabtree, R. H.; Hlatky, G. G.; Parnell, B. E.; Segmullar, B. E.; Uriarte, R. J. *Inorg. Chem.* **1984**, *23*, 354. (d) Shapley, J. R.; Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2816.

0020-1669/93/1332-2118$04.00/0



(a) (b)

Figure 1. (a) Sketch of the structure of compounds **1** (L = PPh_3) and **2** (L = $^1/_2$ dppf). The lines connecting the ligands around the rhenium atom are the selected edges of the dodecahedron and not chemical bonds. (b) Representation of the bonding model in compounds **1** and **2** for the purpose of electron counting.

The reaction of eq 2 is extremely rapid with no intermediate species observed by ^1H and ^{31}P NMR spectroscopy, and the formation of compounds **1** and **2** is quantitative. When the reaction was carried out in CD_2Cl_2 in a sealed NMR tube, the ^1H NMR spectrum of the reaction mixture exhibited a singlet resonance at δ 4.60 assigned to free H_2 and a singlet resonance at δ 1.99 assigned to free acetone, in addition to the resonances from compound **1** or **2**. The reaction is irreversible, because no deuterium incorporation occurs for **1** and **2** when the reaction mixture is maintained in the presence of D_2 for several days at room temperature.

Characterization of Heterobimetallic Rhenium–Iridium Polyhydride Complexes. Compounds **1** and **2** are air-stable both in solid state and in solution, and their identities were established by IR and variable-temperature ^1H and ^{31}P spectroscopy and elemental analysis. The IR spectrum (Nujol mull) of each of compounds **1** and **2** shows a ν(Ir–H) band (2166 cm^{-1} for **1** and 2169 cm^{-1} for **2**) and three ν(Re–H) bands (1999, 1902, 1818 cm^{-1} for **1** and 2024, 1910, 1810 cm^{-1} for **2**). As in the case of $L_2H_2Re(\mu\text{-}H)_4ReH_2L_2$[7] and $[L_2HIr(\mu\text{-}H)_3IrHL_2]^+$,[8] no stretching bands due to the bridging hydride ligands can be located with confidence. This is not surprising because these bands may be hidden under other ligand resonances or they may be too weak and broad to be detected.[12]

The variable-temperature ^1H and ^{31}P NMR spectroscopic data for compounds **1** and **2** (vide infra) are most consistent with a structure shown in Figure 1a. Green et al.[13] have introduced an electron-counting convention for hydride-bridged compounds in which a bridging hydride ligand is considered as a two-electron donor to a second metal and the bonding is represented by a half-arrow notation. Using this convention, the bonding model for compounds **1** and **2** can be described by Figure 1b. With the formal cationic charge assigned to the Ir center, compounds **1** and **2** can be regarded as complexes of Re(V) and Ir(III). This designation leads to an 18-electron count at both metal centers. The most common coordination geometry about Re(V) is eight-coordinate dodecahedral,[3c,14] and that about Ir(III) is six-coordinate octahedral.[15] These two coordination geometries are consistent with but not uniquely defined by the spectroscopic data for compounds **1** and **2**.

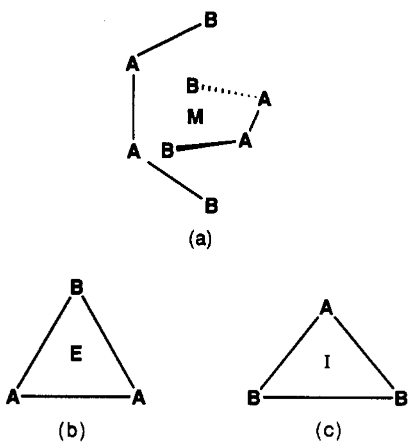


Figure 2. (a) The two mutually orthogonal BAAB trapezoids that constitute the dodecahedral coordination geometry. (b) The equilateral (E) polyhedral face. (c) The isosceles (I) polyhedral face.

The dodecahedral coordination geometry has an S_4 axis which divides the coordination sites into two inequivalent sets, A and B.[16] Figure 2 shows the two mutually orthogonal BAAB trapezoids that constitute the dodecahedral coordination geometry and the two types of triangular polyhedral faces, equilateral (E) and isosceles (I). In the ReH_6L_2 dodecahedral fragment, the two bulky L ligands are expected to occupy the sterically less hindered B sites. Because the two L ligands are inequivalent as shown by ^{31}P NMR spectroscopy at low temperature (vide infra), they must occupy two B sites that are in two different and orthogonal trapezoids (see Figure 1a). A possible explanation for this arrangement is that the ReH_6L_2 fragment organizes itself in such fashion in order to minimize the steric repulsion between the bulky L ligands and the incoming $IrH(PPh_3)_2^+$ unit. In the case of compound **2**, this arrangement is also dictated by the bite angle (95–103°) of the dppf ligand[17] which is far smaller than the angle (140–156°) between the two B sites within the same trapezoid but very close to that (typically ~100°) between the two B sites that are in two different and orthogonal trapezoids.[3c,14] Similar arrangements are also adopted in $K(THF)_2ReH_6(PPh_3)_2$,[3c] $(\eta^5\text{-}C_5H_5)_2(THF)Y(\mu\text{-}H)_2ReH_4(PPh_3)_2$,[5c] and $Me_2Al(\mu\text{-}H)_2\text{-}ReH_4(PMePh_2)_2$.[14e]

The two coordination polyhedra in each of compounds **1** and **2** can only be fused if they share congruent faces. In the dodecahedral ReH_6L_2 unit described above and shown in Figure 1a, the three sterically least encumbered hydride ligands for bridging to the $IrH(PPh_3)_2^+$ unit are H_e, H_b, and H_f, which occupy one A site and two B sites. However, it must be recognized that these hydride ligands form an I face (see Figure 2c) which does not match an equilateral triangular face of the octahedron. We therefore believe that bridging is most likely to occur with the hydride ligands H_f, H_d, and H_e, which occupy one B site and two A sites and thus form an E face (see Figure 2b) that closely matches an equilateral triangular face of the octahedron. Therefore, as has been observed with many other hydride-bridged bimetallic complexes,[3–8] the conventional coordination geometries about the both metal centers are preserved in compounds **1** and **2**, with the three bridging hydride ligands disposed in positions

---

[12] (a) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415. (b) Cooper, C. B.; Shriver, D. F.; Onaka, S. *Adv. Chem. Ser.* **1978**, *167*, 232.

[13] (a) Berry, M.; Cooper, N. J.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29. (b) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

[14] (a) Emge, T. J.; Koetzle, T. F.; Bruno, J. W.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 4012. (b) Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5757. (c) Kim, Y.; Deng, H.; Meek, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 2798. (d) Luo, X.-L.; Michos, D.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 4286. (e) Skupinski, W. A.; Huffman, J. C.; Bruno, J. W.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8128. (f) Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *Inorg. Chem.* **1987**, *26*, 2930.

[15] (a) Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335. (b) Deutsch, P. P.; Eisenberg, R. *Chem. Rev.* **1988**, *88*, 1147. (c) Luo, X.-L.; Michos, D.; Crabtree, R. H.; Hall, M. B. *Inorg. Chim. Acta* **1992**, *198–200*, 429 and references therein.

[16] (a) Drew, M. G. B. *Coord. Chem. Rev.* **1977**, *24*, 179. (b) Hoard, J.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235. (c) Crabtree, R. H.; Hlatky, G. G.; Holt, E. M. *J. Am. Chem. Soc.* **1983**, *105*, 7302.

[17] (a) Butler, I. R.; Cullen, W. R.; Kim, T.-J.; Rettig, S. J.; Trotter, J. *Organometallics* **1985**, *4*, 972. (b) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158. (c) Cullen, W. R.; Kim, T.-J.; Einstein, F. W. B.; Jones, T. *Organometallics* **1985**, *4*, 346. (d) Longato, B.; Pilloni, G.; Valle, G.; Corain, B. *Inorg. Chem.* **1988**, *27*, 956. (e) Bandini, A. L.; Banditelli, G.; Cinellu, M. A.; Sanna, G.; Minghetti, G.; Demartin, F.; Manassero, M. *Inorg. Chem.* **1989**, *28*, 404.

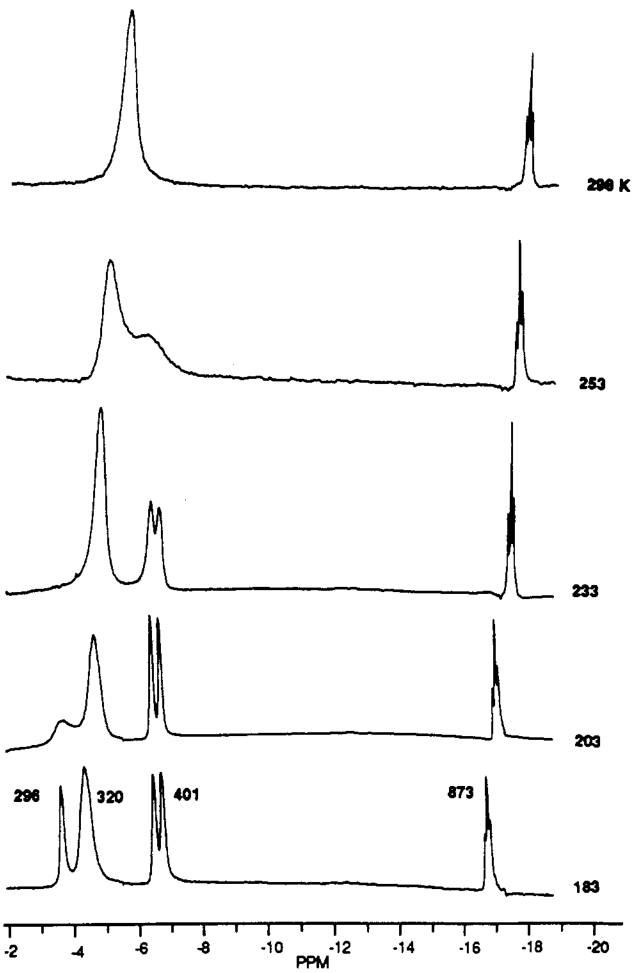


Figure 3. Variable-temperature ^1H NMR spectra of $[(PPh_3)_2H_3Re(\mu\text{-}H)_3IrH(PPh_3)_2]SbF_6$ (**1**) in CD_2Cl_2 at 250 MHz in the hydride region. The T_1 values (ms) are written on the peaks for the spectrum at 183 K.

which satisfy the normal coordination geometries of both metal centers.

The hydride region of the variable-temperature ^1H NMR spectra of compound **1** in CD_2Cl_2 at 250 MHz is shown in Figure 3. The spectrum at 298 K consists of a broad resonance at δ -5.46 (6 H) and a triplet resonance at δ -18.13 ($^2J_{PH}$ = 21.8 Hz, 1 H). The broad resonance is assigned to the three terminal hydride ligands (H_a, H_b, H_c) bound to the rhenium and the three bridging hydride ligands (H_d, H_e, H_f) which are rapidly exchanging. Similar exchange between bridging and terminal hydride ligands has been observed with $L_2H_2Re(\mu\text{-}H)_4ReH_2L_2$.[7] The triplet resonance has a chemical shift within the range observed[8] for the terminal hydride ligands in $[L_2HIr(\mu\text{-}H)_3IrHL_2]^+$ and thus is assigned to the terminal hydride ligand (H_g) bound to the iridium. While the triplet resonance shows almost no change down to 183 K, lowering the temperature causes the broad resonance to undergo decoalescence. Thus, when the sample is cooled to 233 K, the broad resonance decoalesces into a broad resonance at δ -4.71 (4 H) assigned to H_a, H_b, H_c, and H_f and a doublet at δ -6.42 ($^2J_{PH}$ = 66.5 Hz, 2 H) assigned to H_d and H_e which are trans to one PPh_3 ligand and so give rise to the doublet. Upon further cooling to 183 K, the resonance at δ -4.71 splits into a broad resonance at δ -3.61 (1 H) assigned to H_f and a broad resonance at δ -4.35 (3 H) assigned to H_a, H_b, and H_c, while the doublet resonance at δ -6.42 remains unchanged.

The $^{31}P\{^1H\}$ NMR spectrum of compound **1** at 298 K shows two singlet resonances of equal intensity at δ 34.1 and 18.8 which are assigned to the PPh_3 ligands bound to rhenium and iridium, respectively. When the sample is cooled to 183 K, the former splits into two broad resonances at δ 37.3 and 33.0, while the latter does not change significantly. The assignment of the ^{31}P resonances was established by selectively ^{31}P-decoupled ^1H NMR experiments: at 298 K, decoupling the ^{31}P resonance at δ 18.8 leads to collapse of the triplet Ir–*H* resonance at δ -18.20 into a singlet resonance, while decoupling the ^{31}P resonance at δ 34.1 has no effect on the Ir–*H* resonance; at 183 K, decoupling the ^{31}P resonance at δ 18.5 leads to collapse of both the doublet resonance at δ -6.42 (H_d and H_e) and the triplet Ir–*H* resonance at δ -18.13 into singlet resonances, while decoupling the ^{31}P resonances at δ 37.3 or 33.0 has no appreciable effect on either of the two hydride resonances.

Mathieu et al.[4a] recently reported the synthesis of the first heterobimetallic η^2-H_2 complexes from the protonation of corresponding neutral precursors. We wondered whether the broad hydride resonance at δ -4.35 (3 H) observed for compound **1** at 183 K arises from an η^2-H_2 ligand and a terminal hydride ligand which are rapidly exchanging. ^1H NMR spin–lattice relaxation times (T_1) of hydride resonances have been shown to provide useful structural information about transition-metal hydride complexes as to whether they contain one or more nonclassical η^2-H_2 ligands.[18,19] The T_1 values of the hydride resonances of compound **1** at 183 K are shown in Figure 3. The T_1 value of the broad resonance at δ -4.35 is 320 ms, which is comparable to the values observed under the same conditions for the resonances of other classical terminal and bridging hydride ligands within the same molecule and thus rules out the presence of an η^2-H_2 ligand.

As shown in Figure 4, the hydride region of the ^1H NMR spectrum of compound **2** at 298 K in CD_2Cl_2 exhibits a pattern similar to that of compound **1**. The broad resonance at δ -4.85 (6 H) is assigned to the three terminal Re–H and the 3 bridging H ligands, and the triplet at δ -16.81 ($^2J_{PH}$ = 21.3 Hz, 1 H) is assigned to the terminal Ir–H. When the sample is cooled to 183 K, the broad hydride resonance at δ -4.85 splits into five resonances of relative intensities 1:2:1:1:1, while the triplet resonance at δ -16.81 becomes a broad resonance.

The $^{31}P\{^1H\}$ NMR spectrum of compound **2** at 298 K shows two singlet resonances of equal intensity at δ 28.4 and 22.1. The former is assigned to the dppf ligand bound to rhenium, while the latter is assigned to the PPh_3 ligands bound to iridium. When the sample is cooled to 183 K, each resonance splits into a pair of broad resonances of equal intensity. As for compound **1**, the assignment of ^{31}P resonances has been established by selective ^{31}P-decoupled ^1H NMR spectroscopy.

Both the ^1H and ^{31}P NMR spectroscopic data suggest that compound **2** is less fluxional than compound **1**. Clearly, the replacement of the two PPh_3 ligands in compound **1** by the chelating diphosphine ligand dppf in compound **2** leads to an increase in the rearrangement barriers. We have previously shown that dppf is particularly effective in slowing down the fluxional processes in polyhydride complexes.[10]

Geometric Factors Favoring or Disfavoring $M(\mu\text{-}H)_nM'$ (n = 3–5) Bridging Systems. Up to now there have been examples of

---

(18) (a) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031. (b) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (c) Luo, X.-L.; Howard, J. A. K.; Crabtree, R. H. *Magn. Reson. Chem.* **1991**, *29*, S89. (d) Luo, X.-L.; Liu, H.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 4740. (e) Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 2788.

(19) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (d) Crabtree, R. H.; Luo, X.-L.; Michos, D. *Chemtracts*: *Anal., Phys., Inorg. Chem.* **1991**, *3*, 245.

(20) (a) Wilson, R. B.; Sattelberger, A. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 858. (b) Scioly, A. J.; Luetkens, M. L.; Wilson, R. B.; Huffman, J. C.; Sattelberger, A. P. *Polyhedron* **1987**, *6*, 741. (c) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1982**, 1388. (d) Chaudret, B.; Devillers, J.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1983**, 641. (e) Holmes, S. J.; Schrock, R. R. *Organometallics* **1983**, *2*, 1463. (f) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Moro-Oka, Y. *Organometallics* **1988**, *7*, 2243. (g) Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1992**, *11*, 1559. (h) Marsh, R. E. *Organometallics* **1989**, *8*, 1583.

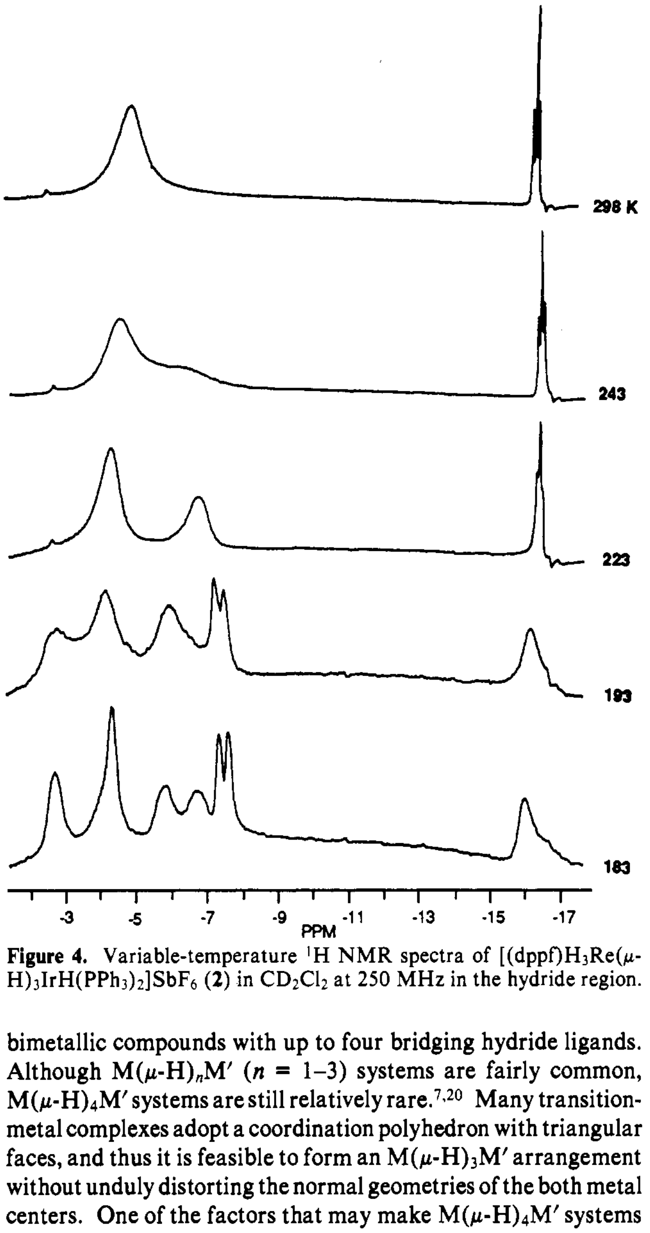


Figure 4. Variable-temperature ^1H NMR spectra of [(dppf)$H_3Re(\mu$-$H)_3IrH(PPh_3)_2]SbF_6$ (**2**) in CD_2Cl_2 at 250 MHz in the hydride region.

bimetallic compounds with up to four bridging hydride ligands. Although $M(\mu$-$H)_nM'$ (n = 1–3) systems are fairly common, $M(\mu$-$H)_4M'$ systems are still relatively rare.[7,20] Many transition-metal complexes adopt a coordination polyhedron with triangular faces, and thus it is feasible to form an $M(\mu$-$H)_3M'$ arrangement without unduly distorting the normal geometries of the both metal centers. One of the factors that may make $M(\mu$-$H)_4M'$ systems so rare is that only the rare square antiprism in eight-coordination and the four-legged piano stool in (η^5-$C_5R_5)MH_4$ systems appear to have a square face suitable for accommodating an $M(\mu$-$H)_4M'$ arrangement. The fact that bimetallic compounds with five bridging hydride ligands remain elusive[21] may be related to the fact that no transition-metal complexes adopt a coordination polyhedron with a pentagonal face suitable for forming an $M(\mu$-$H)_5M'$ arrangement. Hoffmann et al. have probed the possible existence of $M(\mu$-$H)_5M'$ systems using extended Huckel calculations and concluded that although there is no a priori electronic reason that an $M(\mu$-$H)_5M'$ system cannot exist, its existence may be precluded by undue steric demands.[22]

Mechanism for the Formation of Heterobimetallic Rhenium–Iridium Polyhydride Complexes. A common feature of the reaction chemistry of polyhydride complexes is their ability to generate a reactive intermediate species containing a vacant coordination site by elimination of H_2 through thermolysis, photolysis, or acidolysis.[23] The rate of thermal elimination of H_2 from complexes ReH_7L_2 with monophosphine ligands is usually low,[7a,24,25] and complexes ReH_7L_2 with a chelating diphosphine ligand do not eliminate H_2 even at elevated temperatures.[7a,10,25,26] In spite of this, the reaction between ReH_7L_2 and $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ (eq 2) proceeds rapidly even at room temperature. Thus, elimination of H_2 from ReH_7L_2 to form ReH_5L_2 as an intermediate which subsequently reacts with $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ can be precluded as a mechanism for the formation of compounds **1** and **2**.

Caulton, Chaudret, and co-workers have studied the modification of the structure and reactivity of transition-metal polyhydride complexes with metallic Lewis acids.[27] They have shown that interaction of a polyhydride complex with a Lewis acid reduces the electron density at the metal center, which in turn increases the tendency of the complex to undergo an intramolecular reductive coupling of two hydride ligands to form an η^2-H_2 complex and thus facilitates loss of H_2. In this respect, complexes ReH_7L_2 have been shown to react with a range of metallic Lewis acids such as $[Cu(CH_3CN)_4]PF_6$, $AgPF_6$, and AgI.[27c,28] The complex $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ contains very labile acetone ligands which undergo rapid exchange with free acetone and other ligands,[11,29] and the 14-electron fragment $[IrH_2(PPh_3)_2]^+$ has been shown to be a versatile Lewis acid that can accommodate a wide variety of ligands.[30] It is thus conceivable that the hydride ligands of ReH_7L_2 may displace the labile acetone ligands to give a transient dinuclear η^2-H_2 complex $[L_2H_3(\eta^2$-$H_2)Re(\mu$-$H)_2$-$IrH_2(PPh_3)_2]SbF_6$, and subsequently a terminal iridium hydride ligand displaces the η^2-H_2 ligand by moving into a bridging position, giving the observed product $[L_2H_3Re(\mu$-$H)_3$-$IrH(PPh_3)_2]SbF_6$. This mechanism is in accord with the observation that, under the same conditions used for $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$, complexes $[IrH_2S_2(PPh_3)_2]SbF_6$ (S = MeCN, 2,2′-bipyridyl) do not react with $ReH_7(PPh_3)_2$ or ReH_7(dppf), because MeCN and 2,2′-bipyridyl, which are more tightly bound and dissociate far more slowly than acetone,[11,29] cannot be displaced by the hydride ligands of ReH_7L_2. Howarth et al. have also shown that the reaction of $[IrH_2(Me_2CO)_2$-$(PPh_3)_2]PF_6$ with $MH_2(\eta^5$-$C_5H_5)_2$ (M = Mo or W) requires dissociation of the acetone ligands.[31]

Conclusion

The cationic heterobimetallic rhenium–iridium polyhydride complexes $[L_2H_3Re(\mu$-$H)_3IrH(PPh_3)_2]SbF_6$ (L = PPh_3 (**1**), $^1/_2$

---

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

[22] Dedieu, A.; Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141.

[23] (a) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1. (b) Crabtree, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2, Chapter 19. (c) Halpern, J.; Cai, L.; Desrosiers, P. J.; Lin, Z. *J. Chem. Soc., Dalton Trans.* **1991**, 717.

[24] Zeiher, E. H. K.; DeWit, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 7006.

[25] Luo, X.-L.; Baudry, D.; Bordell, P.; Charpin, P.; Nierlich, M.; Ephritikhine, M.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 1511.

[26] Baudry, D.; Boydell, P.; Ephritikhine, M.; Felkin, H.; Guihem, J.; Pascard, C.; Bau, E. T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 670.

[27] (a) He, X. D.; Fernandez-Baeza, J.; Chaudret, B.; Folting, K. Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 5000. (b) Chaudret, B.; Commenges, G.; Jalon, F.; Otero, A. *J. Chem. Soc., Chem. Commun.* **1989**, 210. (c) Rhodes, L. F.; Bansemer, R. L.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chim. Acta* **1992**, *191*, 31 and references therein.

[28] Connelly, N. G.; Howard, J. A. K.; Spencer, J. L.; Woodley, P. K. *J. Chem. Soc., Dalton Trans.* **1984**, 2003.

[29] (a) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1481. (b) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1982**, 745. (c) Crabtree, R. H.; Habib, A. *Inorg. Chem.* **1986**, *25*, 3698.

[30] (a) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361. (b) Burk, M. J.; Segmuller, B.; Crabtree, R. H. *Organometallics* **1987**, *6*, 2241. (c) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986. (d) Crabtree, R. H.; Davis, M. W.; Mellea, M. F.; Mihelcic, J. M. *Inorg. Chim. Acta* **1983**, *72*, 223. (e) Luo, X.-L.; Schulte, G. K.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 682. (f) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527.

[31] (a) Alcock, N. W.; Howarth, O. W.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1979**, 1160. (b) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1982**, 541.

dppf (**2**)) can be readily synthesized from the reaction of $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ with $ReH_7(PPh_3)_2$ or ReH_7(dppf). The spectroscopic data for compounds **1** and **2** indicate that they contain three bridging hydride ligands as in the diiridium complexes $[L_2HIr(\mu\text{-}H)_3IrHL_2]^+$, not four as in the dirhenium species $L_2H_2Re(\mu\text{-}H)_4ReH_2L_2$. The coordination polyhedron about rhenium is a dodecahedron and that about iridium is an octahedron; the two polyhedra are fused by sharing a face containing the three bridging hydride ligands, which is an equilateral (E) triangular face of the dodecahedron and a triangular face of the octahedron. Compounds **1** and **2** are most likely produced by a formal dinuclear H_2 elimination mechanism, which involves initial displacement of the labile acetone ligands from $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ by the hydride ligands of ReH_7L_2 to give a transient hydride-bridged dinuclear $\eta^2\text{-}H_2$ species which subsequently undergoes facile H_2 elimination.

Bimetallic compounds with three bridging hydride ligands are common because many transition-metal complexes adopt a coordination polyhedron with triangular faces which are suitable for formation of an $M(\mu\text{-}H)_3M'$ arrangement without unduly distorting the normal geometries of the both metal centers. The $M(\mu\text{-}H)_4M'$ arrangement is relatively rare because only the square antiprism in eight-coordination and the four-legged piano stool in $(\eta^5\text{-}C_5R_5)MH_4$ have square faces suitable for this arrangement. Bimetallic compounds with five bridging hydride ligands are unknown because no transition-metal complexes adopt a coordination polyhedron with a pentagonal face suitable for forming an $M(\mu\text{-}H)_5M'$ arrangement.

Experimental Section

General Procedures. All manipulations were performed under a dry N_2 atmosphere by standard Schlenk-tube techniques. Diethyl ether, hexane, and tetrahydrofuran were distilled from Na/Ph_2CO; dichloromethane was distilled from CaH_2. All solvents were stored under N_2 over 4-Å molecular sieves. $ReH_7(PPh_3)_2$,[9] ReH_7(dppf),[10] and $[IrH_2S_2(PPh_3)_2]SbF_6$ (S = Me_2CO, MeCN, 2,2′-bipyridyl)[11] were prepared according to the literature methods.

^1H and ^{31}P NMR spectra were recorded on Bruker WM 250 and WM 500 spectrometers; ^1H chemical shifts were measured with the residual solvent resonance as reference; ^{31}P chemical shifts were measured with external 85% H_3PO_4 as reference. ^1H NMR T_1 measurements were carried out at 250 MHz by the inversion-recovery method using a standard 180°–τ–90° pulse sequence. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer. Microanalyses were carried out by Desert Analytics Co., Tucson, AZ.

$[(PPh_3)_2H_3Re(\mu\text{-}H)_3IrH(PPh_3)_2]SbF_6$ (1). To a solution of $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ (145 mg, 0.135 mmol) in CH_2Cl_2 (5 mL) was added $ReH_7(PPh_3)_2$ (101 mg, 0.141 mmol). Gas evolution occurred immediately. The resulting red solution was concentrated in vacuo to ca. 0.5 mL. Addition of Et_2O (15 mL) resulted in the precipitation of $[(PPh_3)_2H_3Re(\mu\text{-}H)_3IrH(PPh_3)_2]SbF_6$ (**1**) as a red solid, which was filtered off, washed with benzene (3 × 4 mL) and Et_2O (3 × 10 mL), and dried in vacuo. Yield: 208 mg (92%). Anal. Calcd for $C_{72}H_{67}F_6IrP_4ReSb$: C, 51.77; H, 4.04. Found: C, 51.61; H, 4.14. IR (Nujol): ν_{Ir-H} 2166 cm^{-1}; ν_{Re-H} 1999, 1902, 1818 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 7.0–7.4 (c, 60 H, Ph), –5.46 (br s, 6 H, Re–H and μ-H), –18.13 (t, $^2J_{PH}$ = 21.8 Hz, 1 H, Ir–H). ^1H NMR (CD_2Cl_2, 183 K): δ 7.0–7.5 (c, 60 H, Ph), –3.61 (br s, 1 H, μ-H), –4.35 (br s, 3 H, Re–H), –6.60 (br d, $^2J_{PH}$ = 65.0 Hz, 2 H, μ-H), –16.77 (t, $^2J_{PH}$ = 21.8 Hz, 1 H, Ir–H). ^{31}P NMR (CD_2Cl_2, 298 K): δ 34.1 (s, 2 P, Re–P), 18.8 (s, 2 P, Ir–P). ^{31}P NMR (CD_2Cl_2, 183 K): δ 37.3 (s, 1 P, Re–P), 33.02 (s, 1 P, Re–P), 18.5 (s, 2 P, Ir–P).

$[(dppf)H_3Re(\mu\text{-}H)_3IrH(PPh_3)_2]SbF_6$ (2). This complex was prepared analogously to **1** by using $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ (132 mg, 0.123 mmol) and ReH_7(dppf) (96 mg, 0.128 mmol) and was isolated as a green solid. Yield: 194 mg (93%). Anal. Calcd for $C_{70}H_{65}F_6FeIrP_4ReSb$: C, 49.45; H, 3.85. Found: C, 49.59; H, 3.99. IR (Nujol): ν_{Ir-H} 2169 cm^{-1}; ν_{Re-H} 2024, 1910, 1810 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 7.1–7.6 (c, 50 H, Ph), 4.31 (s, 4 H, Cp), 4.00 (s, 4 H, Cp), –4.85 (br s, 6 H, Re–H and μ-H), –16.81 (t, $^2J_{PH}$ = 21.3 Hz, 1 H, Ir–H). ^1H NMR (CD_2Cl_2, 183 K): δ 7.2–7.8 (c, 50 H, Ph), 4.38 (br s, 4 H, Cp), 4.10 (br s, 4 H, Cp), –2.50 (br s, 1 H), –4.20 (br s, 2 H), –5.74 (br s, 1 H), –6.66 (br s, 1 H), –7.49 (br d, $^2J_{PH}$ = 74.5 Hz, 1 H), –16.27 (br s, 1 H, Ir–H). ^{31}P NMR (CD_2Cl_2, 298 K): δ 27.56 (s, 2 P, Re–P), 21.18 (s, 2 P, Ir–P). ^{31}P NMR (CD_2Cl_2, 183 K): δ 30.3 (s, 1 P, Re–P), 25.8 (s, 1 P, Re–P), 22.9 (s, 1 P, Ir–P), 20.7 (s, 1 P, Ir–P).

Acknowledgment. We thank Yale University and the National Science Foundation for funding and Drs. Gregory J. Kubas and Carol J. Burns for valuable discussions.