(X = Cl, Br, I). Our isolation and characterization of the redox pair $ReH(acac)_2(PPh_3)_2$ and $[ReH(acac)_2(PPh_3)_2]PF_6$ provides further important examples and the first complete structural characterization of such derivatives.

Acknowledgment. Support from the National Science Foundation, through Grant No. CHE88-07444 to R.A.W. and Grant No. CHE86-15556 for the purchase of the MicroVAX II computer and diffractometer, is gratefully acknowledged. We also acknowledge the National Institutes of Health (Grant No. RR-01077) and the National Science Foundation (Grant No. 87-14258) for funds for the purchase of the NMR spectrometers.

Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters for **1**-**3** (Table S1-S3), non-hydrogen positional parameters for **1**-**3** (Tables S4-S6), positional parameters for the hydrogen atoms of **1**-**3** (Tables S7-S9), anisotropic thermal parameters for **1** and **3** (Tables S10 and S11), and complete bond distances (Tables S12-S14) and bond angles (Tables S15-S17) for **1**-**3** and figures (Figures S1-S3) showing the full atomic numbering schemes for **1**-**3** (46 pages); tables of observed and calculated structure factors (91 pages). Ordering information is given on any current masthead page.

Contribution from the Sterling Chemistry Laboratory,
Yale University, New Haven, Connecticut 06511-8118

Planar Tricoordinate Oxygens in a Mixed Aqua(tetrahydrofuran)iridium Complex: X-ray Crystal and Molecular Structure of $[IrH_2(THF)(H_2O)(PPh_3)_2]SbF_6\cdot THF$

Xiao-Liang Luo, Gayle K. Schulte, and Robert H. Crabtree*

Received June 7, 1989

The hydrogenation of $[(cod)Ir(PPh_3)_2]SbF_6$ in tetrahydrofuran (THF) gives $[IrH_2(THF)_2(PPh_3)_2]SbF_6$ (**1**). $[IrH_2(THF)(H_2O)(PPh_3)_2]SbF_6$ (**2**) is formed on recrystallization of **1** from moist THF/hexane. The crystal structure of **2**·THF has been determined by a single-crystal X-ray diffraction study. This is one of the rare crystallographically characterized examples of THF and of water binding to a late d-block transition metal. **2**·THF crystallizes in the space group $P2_1/n$ with a = 10.745 (4) Å, b = 18.793 (8) Å, c = 22.425 (8) Å, β = 96.42 (3)°, V = 4500 (6) Å^3, Z = 4, and ρ_{calcd} = 1.64 g/cm^3. The structure was refined by full-matrix least-squares techniques to a final R factor of 0.039 for 3666 reflections. One THF and one H_2O molecule occupy two cis sites of the octahedron around the iridium(III) center. The phosphines are trans with Ir-P(av) of 2.298 (3) Å. The Ir-O bond distances are 2.305 (9) and 2.258 (9) Å, significantly longer than are expected in the absence of the trans influence of the hydride ligands. The coordinated THF ligand is reasonably well-defined and adopts an envelope conformation with C(3) on the flap atom; the tricoordinate oxygen atom is in a planar configuration, in contrast to the commonly observed pyramidal configuration. The aqua ligand is hydrogen-bonded to an F atom of the SbF_6 counterion and to the oxygen of the lattice THF. The approximate positions of the H atoms constituting the H-bonds were deduced from the heavy-atom positions by using the Ferraris-Franchini-Angela correlations. These are consistent with the H_2O ligand also having a planar rather than a pyramidal oxygen. Arguments about π-bonding and 2-e vs 4-e donor character for ligands of the R_2O type should therefore not be simply based on the distinction between planar and pyramidal geometries.

Introduction

Transition-metal solvento complexes, which contain weakly coordinated solvent molecules as ligands, are of great importance.[1] They have been proposed to be the intermediates in many homogeneous catalytic processes.[2] The facile dissociation of the labile solvent molecules can create vacant coordination sites required for substrate binding and activation. Indeed, many isolable solvento complexes have shown catalytic activity in a variety of reactions[3-8] including C-H activation.

In spite of its importance as a ligand, the structural chemistry of coordinated H_2O has received relatively little attention in organometallic, as opposed to coordination, compounds. These two classes of aqua complex may prove to have similar structural chemistries, but evidence has been lacking up to now. In coordination compounds, neutron diffraction has usually been necessary to allow secure conclusions to be drawn. It has been found[9] that coordinated H_2O retains the H-O-H angle of 107°, characteristic of the free molecule, showing that the sp^3 hybridization is retained on binding. Both protons on the H_2O often form H-bonds in the crystal. Surprisingly, metal ions coordinate apparently indiscriminantly in the plane of the lone pairs, so that both planar and pyramidal configurations are found for the three-coordinate oxygen of bound H_2O, as well as intermediate forms. In the planar form, neither of the lone pairs on oxygen is pointing directly at the metal, and the structure disobeys the Nyholm-Gillespie rules. A possible explanation for the common occurrence of the planar form is that the bonding in the structures which have been studied (e.g., $MnCl_2(H_2O)_4$, $Cu(H_2O)_5(SO_4)$) is predominantly ionic. The first question, therefore, is whether the tendency for oxygen to be planar is also manifested in 18-e organometallic species, where we expect more covalent character in the bond.

---

(1) (a) Davies, J. A.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 79. (b) Crabtree, R. H.; Demou, P. C.; 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.; Davis, M. W.; Mellea, M. F.; Mihelcic, J. M. *Inorg. Chim. Acta* **1983**, *72*, 223. (d) Crabtree, R. H.; Hlatky, G. G.; Parnell, B. E.; Segmuller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1984**, *23*, 354. (e) Rhodes, L. F.; Zubkowski, J. D.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1982**, *21*, 4185. (f) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663. (g) Allison, J. D.; Moehring, G. A.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1986**, 67. (h) Moehring, G. A.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1987**, 715.

(2) (a) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319. (b) Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11. (c) Backvall, J. E.; Akermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411. (d) Stille, J. K.; Divakaruni, R. *J. Organomet. Chem.* **1979**, *169*, 239.

(3) (a) Shapley, J. R.; Schrock, R. R.; Osborn, J. A. *J. Chem. Soc. Soc.* **1969**, *91*, 2816. (b) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134. (c) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2143. (d) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 4450.

(4) (a) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (b) Crabtree, R. H.; Parnell, C. P. *Organometallics* **1984**, *3*, 1727. (c) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816. (d) Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1987**, *6*, 696. (e) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527.

(5) (a) Davies, J. A.; Hartley, F. R.; Murray, S. G. *Inorg. Chem.* **1980**, *19*, 2299. (b) Davies, J. A.; Hartley, F. R.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2246. (c) Davies, J. A.; Hartley, F. R.; Murray, S. G. *J. Mol. Catal.* **1981**, *10*, 171.

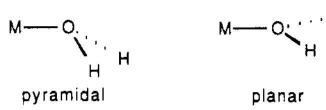
(6) Roper, M.; He, R.; Schieren, M. *J. Mol. Catal.* **1985**, *31*, 335.

(7) (a) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627. (b) Sen, A.; Lai, T.-W. *Organometallics* **1982**, *1*, 415. (c) Sen, A.; Thomas, R. R. *Organometallics* **1982**, 1251.

(8) Conelly, N. G.; Draggett, P. T.; Green, M. *J. Organomet. Chem.* **1977**, *140*, C10. Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902.

(9) Ferraris, G.; Franchini-Angela, M. *Acta Crystallgr.* **1972**, *B28*, 3572.

0020-1669/90/1329-0682$02.50/0 © 1990 American Chemical Society



What holds for water might be expected to hold for alcohols and ethers as ligands. In the case of ethers, such as tetrahydrofuran (THF), two heavy atoms are bound to the ligating oxygen and so X-ray structural methods should be adequate to define the structural features. As we shall see below, not only the coordinated H_2O but also the THF ligand of the title complex contain a planar oxygen. An alternative explanation of planarity of H_2O is that intramolecular H-bonds lock the H_2O in the planar conformation. A useful feature of the structure described below is that we also have a coordinated THF in the same molecule, which is also planar but is not affected by H-bonding.

Being a hard-donor ligand, THF tends to form complexes with hard Lewis acids. There are many crystallographically characterized examples of THF coordination in group IA–IIIA metals,[10-12] early d-block transition metals (groups IIIB–VIB),[13-16] and f-block transition metals.[17] By comparison, THF coordination rarely occurs in late d-block transition metals, which are generally considered as soft Lewis acids. Several platinum metal complexes of THF, mostly cationic, have been reported,[5b,18] but these were mainly studied in solution and no crystallographic data are available. There seem to be only three crystallographically characterized THF complexes of late d-block transition metals, i.e., $(2FeCl_2{\cdot}2THF)_2$,[19a] $Fe(TPP)(THF)_2$,[19b] and $Zn(TPP)(THF)_2$[19c] (TPP = tetraphenylporphyrinato); these complexes are only stable in the crystal lattice, and the weakly bound THF ligands dissociate readily in solution, or in the solid state upon standing.

Table I. Crystal Data for **2**·THF

empirical formula	$C_{44}H_{50}P_2IrSbF_6O_3$
fw	1116.77
crystal system	monoclinic
lattice parameters	a = 10.745 (4) Å b = 18.783 (8) Å c = 22.425 (8) Å β = 96.42 (3)°
space group	$P2_1/n$ (No. 14)
Z value	4
ρ_{calcd}	1.64 g/cm^3
F_{000}	2184
μ(Mo Kα)	36.78 cm^{-1}
diffractometer	Enraf-Nonius CAD4
radiation	Mo Kα (λ = 0.71069 Å), graphite monochromated
scan rate	10–2.5°/min
temp	23 °C
$2\theta_{max}$	50.0°
no. of observns ($I > 3\sigma(I)$)	3668
no. of variables	514
residuals: R; R_w	0.039; 0.045
goodness-of-fit indicator	1.22
max shift in final cycle	0.20
largest peak in final diff map	1.88 e/Å^3

Table II. Selected Intramolecular Distances (Å) and Angles (deg) for **2**·THF

Ir–O(1)(THF)	2.308 (8)	Ir–O(2)···F(1)	140.26 (10)
Ir–O(2)(H_2O)	2.258 (9)	Ir–O(1)–C(1)	121.6 (8)
O(2)···F(1)[a]	2.92 (1)	Ir–O(1)–C(4)	132 (1)
Ir–P(1)	2.300 (3)	O(1)–Ir–O(2)	90.6 (3)
Ir–P(2)	2.297 (3)	P(2)–Ir–P(1)	168.3 (1)
Sb–F(2–6)(av)	1.834 (10)	O(2)–Ir–P(2)	95.0 (2)
Sb–F(1)	1.871 (9)	O(2)–Ir–P(1)	92.0 (2)
O(1)–C(4)	1.38 (2)	O(1)–Ir–P(2)	95.2 (2)
P–C(av)	1.83 (1)	O(1)–Ir–P(1)	94.1 (2)
O(2)···O(3)[a]	2.70 (2)	Ir–O(2)···O(3)	123.44 (10)
O(1)–C(1)	1.47 (1)	O(3)···O(2)···F(1)	90.51 (10)
		Sb–F(1)–O(2)	117.55 (10)

[a] These are the H-bonding interactions.

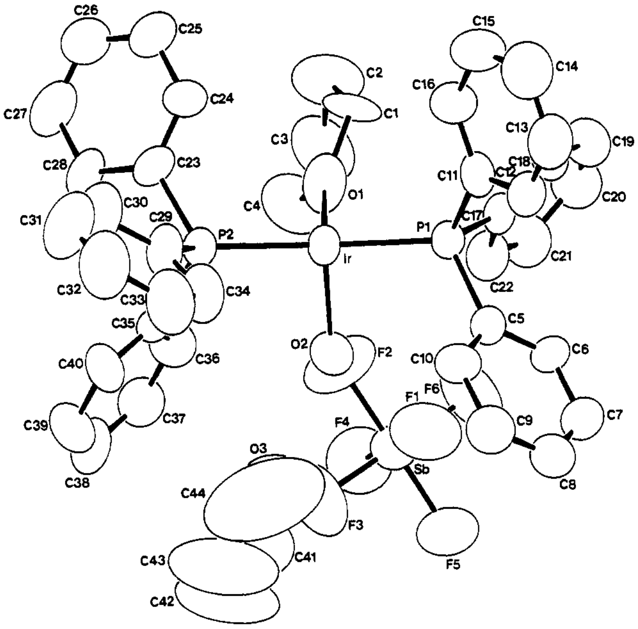


Figure 1. Labeled ORTEP diagram of the structure of **2**·THF.

An unusually wide range of solvento complexes of the type *cis,cis,trans*-$[IrH_2S_2L_2]SbF_6$ (S = solvent; L = PPh_3) can be prepared by hydrogenation of $[Ir(cod)L_2]SbF_6$ (cod = 1,5-cyclooctadiene) in an appropriate solvent.[1b-d,3a] Both hard and soft S ligands can be bound in this system. It has been suggested that this is because the positive charge of the complex encourages binding of hard ligands, while the high trans effect of the hydride ligands can stabilize soft ligand binding.[1c] These solvento com-

---

(10) (a) Brauer, D. J.; Stucky, G. D. *J. Organomet. Chem.* **1972**, *37*, 217. (b) Krausse, J.; Marx, G.; Schodl, G. *J. Organomet. Chem.* **1970**, *21*, 159. (c) Brauer, D. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 3956. (d) Secaur, C. A.; Day, V. W.; Ernst, R. D.; Kennelly, W. J.; Marks, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 3713.

(11) (a) Toney, T.; Stucky, G. D. *J. Organomet. Chem.* **1971**, *28*, 5. (b) Perucaud, M. C.; Le Bihan, M. T. *Acta Crystallogr.* **1968**, *B24*, 1502. (c) Vallino, M. *J. Organomet. Chem.* **1969**, *20*, 1.

(12) (a) Hoberg, H.; Gotor, V.; Milchereit, A.; Kruger, C.; Sekutowski, J. K. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 539. (b) Cowley, A. H.; Cusher, M. C.; Davis, R. E.; Riley, P. E. *Inorg. Chem.* **1981**, *20*, 1179.

(13) (a) Atwood, J. L.; Smith, K. D. *J. Chem. Soc., Dalton Trans.* **1974**, 921. (b) Segal, B. G.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 844. (c) Rogers, R. D.; Atwood, J. L.; Emad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383.

(14) (a) Brauer, D. J.; Kruger, C. *J. Organomet. Chem.* **1972**, *42*, 129. (b) Brauer, D. J.; Kruger, C. *Inorg. Chem.* **1975**, *14*, 3053. (c) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

(15) Oumous, H.; Lecomte, C.; Protas, J.; Poncet, J. L.; Barbe, J. M.; Guilard, R. *J. Chem. Soc., Dalton Trans.* **1984**, 2677.

(16) (a) Schubert, U.; Friedrich, P.; Orama, O. *J. Organomet. Chem.* **1978**, *144*, 175. (b) Edelman, F.; Trotter, J. *J. Organomet. Chem.* **1977**, *131*, 65. (c) Daly, J. J.; Sneeden, R. P. A. *J. Chem. Soc. A* **1967**, 736. (d) Bott, S. G.; Clark, D. L.; Green, M. L. H.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1989**, 418. (e) Chisholm, M. H.; Eichhorn, B. W.; Folting, E. K.; Huffman, J. C.; Ontiveros, C. D.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1987**, *26*, 3182.

(17) (a) Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1972**, *11*, 171. (b) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Organomet. Chem.* **1980**, *192*, 65. (c) Day, C. S.; Day, V. W.; Ernst, R. D.; Vollmer, S. H. *Organonmetallics* **1982**, *1*, 998. (d) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 292. (e) Ernst, R. D.; Kennelly, W. J.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2656. (f) Rietz, R. R.; Edelstein, N. M.; Ruben, H. W.; Templeton, D. H. *Inorg. Chem.* **1978**, *17*, 658. (g) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1989**, *111*, 3329 and references therein.

(18) (a) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. (b) Dehand, J.; Pfeffer, M.; Zinsius, M. *J. Organomet. Chem.* **1976**, *118*, C62. (c) Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 797. (d) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (e) Linn, D. E., Jr.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2969. (f) Rhodes, L. F.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 259.

(19) (a) Bel'skii, V. K.; Ishchenko, V. M.; Bulychev, B. M.; Protskii, A. N. *Inorg. Chim. Acta* **1985**, *96*, 123. (b) Reed, C. A.; Mashiko, T.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1980**, *102*, 2302. (c) Schauer, C. K.; Anderson, O. P.; Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1985**, *24*, 4082.

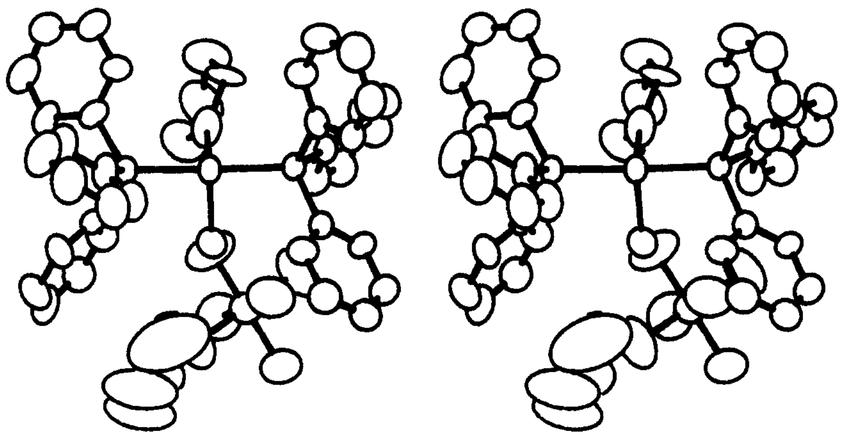


Figure 2. Stereodiagram of **2**·THF, showing the contacts between the SbF_6^- ion and lattice THF with the phosphine ligands.

plexes have been employed as precursors to reactive ligand-deficient species for the stoichiometric or catalytic activation of alkanes and silanes under mild conditions.[4]

We report here the X-ray crystal structure of a mixed solvento complex $[IrH_2(THF)(H_2O)(PPh_3)_2]SbF_6{\cdot}THF$ (**2**·THF), which is stable both in solution and in the solid state.

Results and Discussion

Synthesis. Treatment of $[Ir(cod)L_2]SbF_6$ (cod = 1,5-cyclooctadiene) with H_2 at 0 °C in tetrahydrofuran (eq 1) gave

$$[Ir(cod)(PPh_3)_2]SbF_6 + H_2 \xrightarrow{\text{THF, 0 °C}} \underset{\mathbf{1}}{[IrH_2(THF)_2(PPh_3)_2]SbF_6} \quad (1)$$

$[IrH_2(THF)_2(PPh_3)_2]SbF_6$ (**1**). The product can be obtained as an off-white solid by precipitation with hexane. The ^1H NMR spectrum of **1**[20] in CD_2Cl_2 shows a broad singlet hydride resonance at δ −28.6. The broadening is probably due to exchange between the THF ligands and trace of H_2O present in the solvent. A similar phenomenon has previously been observed in some related halocarbon complexes.[21] The resonances due to the coordinated THF appear as two broad singlets at δ 1.5 and 3.4. Upon cooling of the sample to 223 K, the hydride resonance becomes a broad triplet ($^2J_{PH}$ = 16 Hz).

Although **1** is quite stable both in solution and in the solid state, the coordinated THF is extremely labile and can be displaced by a variety of other ligands.[1b] On recrystallization of **1** from THF/hexane (1:10 v/v), a trace of H_2O in the solvent mixture replaced one THF to form a mixed solvento complex $[IrH_2(THF)(H_2O)(PPh_3)_2]SbF_6$ (**2**) (eq 2).

$$\underset{\mathbf{1}}{[IrH_2(THF)_2(PPh_3)_2]SbF_6} \xrightarrow{\text{moist THF/hexane}} \underset{\mathbf{2}}{[IrH_2(THF)(H_2O)(PPh_3)_2]SbF_6} + THF \quad (2)$$

X-ray Crystallography. **2** crystallizes from a THF/hexane bilayer as a THF solvate. The crystal structure of **2**·THF has been determined by a single-crystal X-ray diffraction study. The crystallographic data appear in Tables I–III, a labeled ORTEP diagram is shown in Figure 1, and a stereoview is shown in Figure 2. The structure consists of an $[IrH_2(THF)(H_2O)(PPh_3)_2]^+$ cation hydrogen-bonded to a lattice THF and a fluoride of the SbF_6^- anion, and a stereoview of the hydrogen-bonded groups is also included (Figure 3).

Two hard ligands, one THF and one H_2O, are directly bound to a relatively soft metal, iridium. The two hydride ligands could not be located in the X-ray analysis because of the usual difficulties

Table III. Positional Parameters and *B*(eq) for **2**·THF

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ir	0.403784 (47)	0.201528 (24)	0.768713 (17)	3.66 (2)
Sb	0.848863 (91)	0.048537 (53)	0.679962 (40)	5.73 (5)
P(1)	0.35846 (29)	0.23466 (16)	0.66992 (11)	3.6 (1)
P(2)	0.43010 (28)	0.19000 (15)	0.57131 (11)	3.6 (1)
F(1)	0.76541 (86)	0.13558 (49)	0.66769 (46)	10.3 (6)
F(2)	0.7236 (10)	0.02110 (65)	0.72288 (51)	12.9 (8)
F(3)	0.9317 (11)	0.08278 (60)	0.74872 (41)	12.2 (7)
F(4)	0.92720 (95)	−0.03870 (47)	0.69422 (44)	10.1 (6)
F(5)	0.97575 (86)	0.07818 (53)	0.63740 (42)	9.9 (6)
F(6)	0.7630 (10)	0.01471 (57)	0.61044 (42)	11.7 (7)
O(1)	0.36308 (95)	0.08270 (40)	0.74992 (36)	6.0 (5)
O(2)	0.60787 (78)	0.18464 (48)	0.75746 (34)	6.2 (5)
C(1)	0.2382 (13)	0.05788 (76)	0.72486 (63)	6.4 (8)
C(2)	0.2396 (0)	−0.1902 (97)	0.73012 (96)	11 (1)
C(3)	0.3760 (21)	−0.04030 (87)	0.73187 (81)	10 (1)
C(4)	0.4349 (16)	0.02241 (82)	0.763032 (75)	8 (1)
C(5)	0.4725 (10)	0.29491 (64)	0.644032 (42)	4.1 (5)
C(6)	0.5238 (12)	0.28591 (65)	0.59014 (49)	4.9 (6)
C(7)	0.6046 (13)	0.33560 (85)	0.57034 (55)	6.1 (7)
C(8)	0.6391 (13)	0.39372 (81)	0.60440 (63)	6.1 (8)
C(9)	0.5935 (14)	0.40356 (71)	0.65817 (62)	6.6 (8)
C(10)	0.5104 (12)	0.35453 (70)	0.67808 (51)	5.4 (7)
C(11)	0.2096 (12)	0.28138 (64)	0.65418 (44)	4.6 (6)
C(12)	0.1983 (12)	0.34520 (72)	0.62353 (52)	5.2 (7)
C(13)	0.0845 (17)	0.37730 (81)	0.61018 (62)	7.0 (9)
C(14)	−0.0200 (17)	0.3458 (11)	0.62624 (72)	8 (1)
C(15)	−0.0122 (14)	0.28169 (88)	0.65600 (71)	7 (1)
C(16)	0.1008 (14)	0.25126 (68)	0.67002 (54)	5.4 (7)
C(17)	0.3478 (11)	0.16200 (59)	0.61453 (42)	3.9 (5)
C(18)	0.2480 (12)	0.15261 (66)	0.57200 (49)	5.1 (6)
C(19)	0.2485 (16)	0.09558 (80)	0.53132 (58)	6.6 (8)
C(20)	0.3463 (17)	0.05068 (86)	0.53260 (65)	7 (1)
C(21)	0.4492 (15)	0.06008 (79)	0.57362 (63)	6.9 (8)
C(22)	0.4480 (13)	0.11523 (75)	0.61525 (50)	5.6 (7)
C(23)	0.3318 (11)	0.12010 (57)	0.90065 (46)	3.9 (6)
C(24)	0.2134 (12)	0.11065 (71)	0.87516 (49)	5.1 (7)
C(25)	0.1340 (14)	0.05939 (81)	0.89515 (61)	6.4 (8)
C(26)	0.1794 (16)	0.01919 (72)	0.94345 (68)	6.2 (8)
C(27)	0.2968 (17)	0.02760 (71)	0.97033 (61)	6.2 (8)
C(28)	0.3749 (12)	0.07814 (64)	0.95011 (51)	5.0 (6)
C(29)	0.3948 (13)	0.26851 (65)	0.91426 (47)	4.9 (6)
C(30)	0.3474 (17)	0.26247 (72)	0.96933 (58)	7.9 (9)
C(31)	0.3324 (19)	0.32287 (91)	1.00368 (65)	9 (1)
C(32)	0.3594 (18)	0.38891 (84)	0.98386 (70)	8 (1)
C(33)	0.4093 (18)	0.39571 (71)	0.93081 (65)	8 (1)
C(34)	0.4257 (15)	0.33645 (70)	0.89447 (52)	6.4 (8)
C(35)	0.5890 (10)	0.16849 (58)	0.90437 (44)	3.7 (5)
C(36)	0.6535 (13)	0.11382 (69)	0.88002 (54)	5.5 (7)
C(37)	0.7698 (15)	0.09607 (68)	0.90092 (63)	5.8 (8)
C(38)	0.8311 (14)	0.13269 (94)	0.94875 (66)	7.1 (9)
C(39)	0.7709 (14)	0.18589 (95)	0.97396 (57)	7.5 (9)
C(40)	0.6500 (13)	0.20520 (79)	0.95166 (49)	6.2 (7)
O(3)	0.7975 (16)	0.26545 (95)	0.80943 (75)	14 (1)
C(41)	0.9237 (28)	0.2446 (13)	0.8210 (10)	12 (2)
C(42)	0.9906 (27)	0.2946 (16)	0.8582 (17)	16 (2)
C(43)	0.9018 (40)	0.3463 (20)	0.8700 (21)	20 (3)
C(44)	0.7764 (42)	0.3315 (15)	0.8283 (25)	24 (3)

---

(20) The previously reported ^1H NMR spectrum of $[IrH_2(THF)_2(PPh_3)_2]BF_4$[1b] is incorrect as a result of the formation of $[IrH_2(THF)(H_2O)(PPh_3)_2]BF_4$ upon recrystallization.

(21) (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.

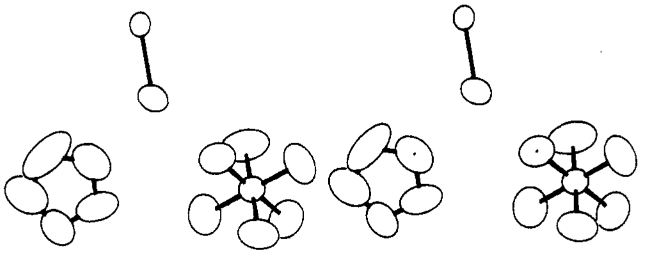


Figure 3. Stereodiagram of **2**·THF, showing the hydrogen-bonded groups. For the cation, only Ir and O(2) of the bound water are shown. The other ligands have been omitted for clarity. F(1) of the SbF_6 counterion and O(3) of the lattice THF are labeled with a dot. The key distances and angles are shown in Table II.

of detecting hydrogen atoms in the presence of heavy atoms.[22] However, the arrangement of the other donor atoms surrounding the iridium atom suggests that the coordination polyhedron is an octahedron, with the two unobserved hydride ligands occupying the two cis sites trans to the THF and H_2O ligands. The O(1)–Ir–O(2) angle (90.6 (3)°) is nearly ideal for an octahedral configuration. The bond angle P(1)–Ir–P(2) is 168.3 (1)° so that P(1) and P(2) are bent away from the THF and H_2O ligands toward the smaller hydride ligands. The phenyl groups on P(1) are staggered with respect to those on P(2).

The Ir–O(THF) and Ir–O(H_2O) distances are 2.305 (8) and 2.258 (9) Å, respectively. The absorption problems associated with the presence of Ir and Sb may mean that the true errors in these distances are larger than shown. They are unusually long for Ir–O coordinate bonds, and the lengthening may be a result of the unusually high trans influence of the hydride ligands. In the absence of the trans influence, the "expected" Ir–O bond length has been estimated to be 2.02 Å in an Ir aqua complex.[23] Alternatively, the expected Ir–O distance can be derived from the average Ir–P distance (2.30 Å) in the structure, with allowance made for the difference in the covalent radii of oxygen and phosphorus; this gives 1.94 Å. The lengthening in the Ir–O bond in **2** is at least 0.25–0.28 Å, or 13–14% of the expected bond length. A similar but slightly smaller Ir–O bond elongation has also been observed in the related complexes $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$[1d] and $[IrH(H_2O)(bq)(PPh_3)_2]SbF_6$[24] (bq = 7,8-benzoquinolato). The great lengthening of the Ir–O bonds due to the trans influence the hydride ligands is consistent with the rather weak iridium–oxygen interactions, as reflected by the high reactivity of these complexes.[4]

As shown by far-infrared[25] and microwave[26] spectroscopy, free THF can have either a twist conformation with C_2 symmetry or an envelope conformation with C_s symmetry, the latter being slightly lower in energy. The interconversion barrier is extremely low because of the facile pseudorotation for the ring-flexing process.[27] Both conformations have been observed in crystallographically characterized THF complexes,[10-17] with the envelope conformation being more common. As a result of the ease of ring flexing, disorder of the THF ligand seems to be common, however, and good structural parameters have rarely been obtained.

The crystal structure of **2**·THF shows a reasonably well-defined geometry for the coordinated THF, but the THF trapped in the crystal lattice is somewhat less well-defined. The lattice THF adopts a twist conformation, but the coordinated THF assumes an envelope conformation with C(3) as the flap atom; the dihedral angle formed by the C(2), C(3), C(4) plane with the least-squares best plane defined by C(2), C(1), O(1), C(4) is 30.7°. The average C–C and C–O bond lengths are 1.47 (4) and 1.39 (2) Å, respectively, for the lattice THF; these values differ from those (C–C = 1.535 Å, C–O = 1.426 Å) reported for the twist form in an electron diffraction study[27e] of gaseous THF, and the relatively large deviations are probably due to disorder of the lattice THF. The average C–C and C–O bond lengths in the coordinated THF are 1.49 (2) and 1.41 (2) Å, slightly different from those (C–C = 1.538 Å, C–O = 1.430 Å) found for the envelope form in the gas phase,[27e] and the changes in the bond lengths are likely caused by coordination. The C(1)–O(1)–C(4) angle (107 (1)°) is essentially unchanged from the gas-phase value.

Planar Configuration of the Three-Coordinate Oxygens in 2·THF. In VSEPR (valence-shell electron-pair repulsion) theory, three-coordinate oxygen should have a pyramidal configuration. A literature survey shows that this pyramidal configuration is found in almost all previous crystallographically characterized transition-metal THF complexes. An exception is $V(OEP)(THF)_2$ (OEP = octaethylporphyrinato),[15] where the oxygen atoms of the THF ligands seems to be bonded in a trigonal-planar configuration, although no comment about this was made by the authors. The planarity would normally be considered as implying that the THF ligands are acting as 4-e donors to the otherwise 15-e vanadium center. The crystal structure of an alkali-metal complex of THF, $[Na(THF)_2]_2[Al(CH_3)_2C_{14}H_{10}]_2$,[10a] also seems to indicate a trigonal-planar coordination geometry for the oxygen atoms. The planarity has been rationalized on the basis of ion-dipole interactions between THF and Na^+ in a predominantly ionic bond. In both structures, the THF is somewhat disordered, and so the reliability of the structural assignment is somewhat reduced.

To our surprise, the crystal structure of **2**·THF shows that the oxygen atom of the bound THF ligand adopts an essentially planar configuration. The Ir, O(1), C(1), and C(4) atoms deviate little from planarity, because O(1) is only 0.05 Å out of the Ir, C(1), C(4) plane. This cannot be ascribed to the ligand acting as a 4-e donor, because **2** is a clear-cut example of an 18-e complex, and in any case, the Ir–O(THF) bond is not unusually short.

Both protons of the coordinated water take part in hydrogen bonding, as shown in Figure 2. The O(2)···F(1) and O(2)···O(3) distances are 2.92 (1) and 2.70 (2) Å, indicating a hydrogen-bonding interaction between the H_2O and both the SbF_6^- counterion and the lattice THF. Thanks to these hydrogen bonds, we can also say something about the geometry of the bound H_2O, even though the protons were not located by the X-ray analysis. The data in an exhaustive survey of neutron diffraction studies on H_2O complexes by Ferraris and Franchini-Angela[9] (FFA) shows that the O–H–X angle in such systems is close to 180°, and so the positions of the protons can be inferred from the heavy-atom positions. In **2**·THF, these are consistent with planar, rather than pyramidal, H_2O because O(2) is only 0.31 Å out of the Ir–O(3)–F(1) plane and the sum of the angles about O(2) (354.2°) is close to 360°. This suggests that the tricoordinate oxygen atoms in both the THF and the H_2O ligands of **2** are bound in an essentially planar configuration.

The O(2)–H–F(1) H-bond shows evidence of of some strain. The Ir–O(2)–F(1) angle of 140.26° and O···F distance of 2.91 Å are at the high end of the ranges found by FFA. The Sb–F(1)–O(2) angle of 117.55° suggests that F(1) is oriented so that its more basic $p\pi$ lone pair is directed toward the proton. This brings F(2) and F(6) into contact with the phosphine ligands. The O(2)–H–O(3) H-bond is slightly shorter than the FFA average, and the Ir–O(2)–O(3) angle (123.44°) is normal. This strain may bend the O(2)–H–F(1) H-bond and may account for some of the deviation of O(2) from the Ir–F(1)–O(3) plane.

We do not fully understand why planar tricoordinate oxygen is found in **2**. Probably, the Ir–O bonding is rather ionic. Certainly, the more covalent $M–SR_2$ system is always pyramidal.[28] Alternatively, both lone pairs might be able to overlap satisfactorily

---

(22) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

(23) Shustorovich, E. M.; Porai-Koshits, M. A.; Buslaev, Y. A. *Coord. Chem. Rev.* **1975**, *17*, 1.

(24) Lavin, M.; Holt, E. M.; Crabtree, R. H. *Organometallics* **1989**, *8*, 99.

(25) (a) Lafferty, W. J.; Robinson, D. W.; Louis, R. V. St.; Russell, J. W.; Strauss, H. L. *J. Chem. Phys.* **1965**, *42*, 2915. (b) Greenhouse, J. A.; Strauss, H. L. *J. Chem. Phys.* **1969**, *50*, 124.

(26) Engerholm, G. C.; Luntz, A. C.; Gwinn, W. D.; Harris, D. O. *J. Chem. Phys.* **1969**, *50*, 2446.

(27) (a) Kilpatrick, J. E.; Pitzer, K. S.; Spitzer, R. *J. Am. Chem. Soc.* **1947**, *69*, 2483. (b) Pitzer, K. S. *J. Am. Chem. Soc.* **1958**, *80*, 6697. (c) Pitzer, K. S.; Donath, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 3213. (d) Engerholm, G. C.; Tolman, C. A.; Luntz, A. C.; Keller, R. A.; Kim, H.; Gwinn, W. D. *J. Chem. Phys.* **1969**, *50*, 2438. (e) Geise, H. J.; Adams, W. J.; Bartell, L. S. *Tetrahedron* **1969**, *25*, 3045.

(28) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.

with the empty orbital on the metal. Rehybridization of the ligating oxygen from sp^3 to $sp^2 + p$ would direct a lone pair toward the metal, but this seems inconsistent with the normal C–O–C angle for the coordinated THF.

Conclusion

The essentially planar configuration of the tricoordinate oxygen in bound H_2O often seen in coordination complexes is now found in an 18-e organometallic aqua complex (**2**), where the H_2O is a 2-e donor. Planar tricoordinate oxygen is also found for the coordinated THF. It may be that the H-bonds enforce planarity for water, especially where a long Ir–O bond is present, as here, but the same cannot be true for THF, which is also planar. Arguments about π-bonding and 2-e vs 4-e donor character for ligands of the R_2O type should therefore not be based solely on the distinction between planar and pyramidal geometries. The great lengthening of the Ir–O bonds found in **2**·THF due to the trans influence of the hydride ligands is consistent with the lability of the O-donor ligands and the unusual activity of the complex in a number of stoichiometric and catalytic reactions.

Experimental Section

All manipulations were performed under an atmosphere of purified nitrogen with use of standard Schlenk-tube techniques. ^1H NMR spectra were recorded on a Bruker WM 250 spectrometer, and IR spectra, on a Nicolet 5-SX FT-IR spectrometer. THF and hexane were distilled from Na/Ph_2CO and stored under nitrogen over 4-Å molecular sieves $[(cod)Ir(PPh_3)_2]SbF_6$ was synthesized by a method similar to that for the BF_4^- salt[29] and recrystallized before use.

Dihydridobis(tetrahydrofuran)bis(triphenylphosphine)iridium(III) Hexafluoroantimonate (1). A red solution of $[(cod)Ir(PPh_3)_2]SbF_6$ (1.0 g) in THF (10 mL) was cooled to 0 °C. Hydrogen was bubbled gently through the solution for 10–15 min until the solution turned pale yellow. The volume of the solution was then reduced to ca. 4 mL in vacuo. Hexane (40 mL) was added carefully to form a separate layer on top of the THF solution. After 24 h in a refrigerator, the resulting white crystalline product was filtered out, washed with hexane (4 × 10 mL), and dried in vacuo. Yield: 0.79 g (76%). Anal. Calcd for $C_{44}H_{48}F_6IrO_2P_2Sb$: C, 48.10; H, 4.40. Found: C, 47.92; H, 4.29. IR (Nujol): ν_{Ir-H} 2290 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 7.1–7.4 (c, 30 H, Ph), 3.4 (br s, 8 H, CH_2), 1.5 (br s, 8 H, CH_2), −28.6 (br s, 2 H, Ir–H).

Preparation of $[IrH_2(THF)(H_2O)(PPh_3)_2]SbF_6$·THF (2·THF) for Crystallography. $[IrH_2(THF)_2(PPh_3)_2]SbF_6$ (**1**) (70 mg) was dissolved in 2 mL of slightly moist THF in a small vial that was then submerged in 30 mL of hexane in a Schlenk tube. After several days in a cold room (4 °C), white crystals of **2**·THF were formed.

X-ray Crystallography of 2·THF. A suitable crystal (0.50 mm × 0.25 mm × 0.20 mm) of **2**·THF was sealed in a thin-walled glass capillary that was mounted on an Enraf-Nonius CAD-4 fully automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and variable scan speed (2.5–10°/min). The unit cell (see Table I) was determined and refined from 25 randomly selected reflections. The space group, based on the systematic absences observed in the data, was uniquely assigned as $P2_1/n$, with one molecule of $C_{44}H_{50}IrP_2O_3SbF_6$ forming the asymmetric unit. The absorption coefficient was μ(Mo Kα) = 36.78 cm^{-1} and an empirical absorption correction, based on azimuthal scans of three reflections (−2,−7,−2; −2,−7,−1; −2,−7,−3), was applied. The data were also corrected for Lorentz and polarization effects.

The structure was solved by a combination of Patterson and difference Fourier syntheses.[30] The position of the iridium atom was obtained from the Patterson synthesis. The remaining non-hydrogen atoms were obtained by iterative use of the WFOURIER option in DIRDIF.[31] All hydrogen atoms were calculated and input at their idealized positions. The full-matrix refinement of the non-hydrogen atoms and input of the hydrogen scattering factors resulted in convergence of the crystallographic reliability factor to an unweighted residual of 0.039 and a weighted residual of 0.045. The (101) reflection, having a $\Delta(F)/\sigma(F)$ value of 10.18 was ignored in the refinement. The final difference Fourier showed two electron density maxima close to the Ir atom at 0.2994, 0.1995, 0.7769, and 0.5099, 0.1989, 0.7653 with electron densities of 1.9 and 1.8 e/Å^3, respectively.

Acknowledgment. We thank the National Science Foundation for support, Professor J. W. Faller and a referee for crystallographic suggestions, and Dr. Marc Zimmer for discussions.

Supplementary Material Available: Tables of further bond distances and angles, torsion angles, calculated H atom positions, and thermal parameters for **2**·THF (10 pages); a listing of F_o vs F_c values for **2**·THF (25 pages). Ordering information is given on any current masthead page.

---

(29) Haines, L. M.; Singelton, E. *J. Chem. Soc., Dalton Trans.* **1972**, 1891.

(30) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corp: Woodlands, TX, 1985.

(31) Beurskens, P. T. DIRDIF: Direct Methods for Difference Structure—an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed, Nijmegen, The Netherlands.

Contribution from the Department of Chemistry,
University of Rochester, Rochester, New York 14627

Hydride Abstraction. The Reaction of IrX(CO)(dppe) with Cp_2TaH_3

Paul P. Deutsch, John A. Maguire, William D. Jones,* and Richard Eisenberg*

Received March 21, 1989

The reaction of IrX(CO)(dppe) (X = Br, I; dppe = 1,2-bis(diphenylphosphino)ethane) with Cp_2TaH_3 (Cp = η^5-cyclopentadienyl) is extremely rapid and leads to clean formation of *fac*-IrH_3(CO)(dppe) and Cp_2TaX, or Cp_2TaXL (L = CO, C_2H_4, $C_3H_7C\equiv CC_3H_7$) in the presence of added ligand. Trapping and isotope-labeling experiments indicate that the reaction does not proceed through production of free IrH_2X(CO)(dppe), [IrH(CO)(dppe)], or [Cp_2TaH]. the results are consistent with formation of unstable hydride and halide-bridged binuclear intermediates, in which transfer of all hydride and halide ligands occurs before fragmentation into mononuclear species.

Introduction

It has been shown that the reaction of H_2 with IrX(CO)(dppe) (**1**) (**1a**, X = Br; **1b**, X = I; dppe = 1,2-bis(diphenylphosphino)ethane) leads to rapid and reversible formation of an isomer of IrH_2X(CO)(dppe) (**2**) as the kinetically favored reaction product (eq 1).[1] With time, **2** disappears and another isomer of IrH_2X(CO)(dppe) (**3**) grows in as the thermodynamically favored product. A detailed kinetic study of the conversion of **2a** into **3a** by Kunin et al.[2] showed that the rate of conversion was

---

(1) (a) Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772. (b) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148.

0020-1669/90/1329-0686$02.50/0 © 1990 American Chemical Society