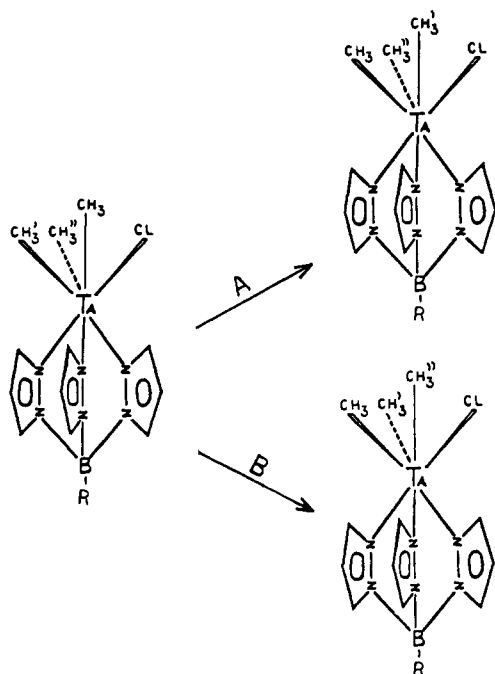


Scheme I



octahedron, rendering the pz rings nonequivalent. Thus, as observed, no changes are expected in the low-field part of the spectrum from this dynamic behavior. Above 65 °C, the Cl ligand must start to exchange with the methyl ligands so as to interconvert isomers A and B. Again, this process could take place by a simple exchange with the capping methyl ligand or a rotation of one of the triangular faces that these two atoms form with either of the two remaining methyl lig-

ands. This process now equilibrates the pz rings in isomer A with each other and with the pz rings of isomer B. The noncoordinated pz ring does not exchange with coordinated pz rings at any temperature studied.

It is interesting to compare the dynamic processes observed for these seven-coordinate Ta molecules with the six-coordinate $[\text{RB}(\text{pz})_3]\text{Zr}(\text{O}-t\text{-Bu})\text{Cl}_2$ complexes studied earlier.⁴ For the six-coordinate molecules, the three pz rings exchange at room temperature by a trigonal-twist rotation of the poly(pyrazolyl)borate ligand about the Zr-B axis. This process can be quenched below 0 °C. Clearly for isomer A, in which the pz rings are similarly nonequivalent, this type of rotation does not take place up to 65 °C. This can be simply explained by an increased steric barrier to the rotation in these seven-coordinate molecules. A similar steric argument was used to explain the fact that $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]\text{Zr}(\text{O}-t\text{-Bu})\text{Cl}_2$ is static up to 140 °C.

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Registry No. $[\text{HB}(\text{pz})_3]\text{Ta}(\text{CH}_3)_3\text{Cl}$ (isomer A), 88181-28-6; $[\text{HB}(\text{pz})_3]\text{Ta}(\text{CH}_3)_3\text{Cl}$ (isomer B), 88243-98-5; $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]\text{Ta}(\text{CH}_3)_3\text{Cl}$, 88181-29-7; $[\text{B}(\text{pz})_4]\text{Ta}(\text{CH}_3)_3\text{Cl}$ (isomer A), 88181-30-0; $[\text{B}(\text{pz})_4]\text{Ta}(\text{CH}_3)_3\text{Cl}$ (isomer B), 88243-97-4; TaMe_3Cl_2 , 3020-02-8.

Supplementary Material Available: Tables of fractional coordinates for H atoms, anisotropic thermal parameters, and structure factor amplitudes for $[\text{HB}(\text{pz})_3]\text{TaMe}_3\text{Cl}$ (9 pages). Ordering information is given on any current masthead page.

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Solvento Complexes of Tungsten, Rhenium, Osmium, and Iridium and the X-ray Crystal Structure of $[\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$

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$[\text{WH}_5(\text{PMe}_2\text{Ph})_3]$, $[\text{ReH}_5(\text{PMe}_2\text{Ph})_3]$, $[\text{ReH}_7(\text{PPh}_3)_2]$, $[\text{OsH}_4(\text{PMe}_2\text{Ph})_3]$, and $[\text{IrH}_5(\text{PPh}_3)_2]$ react with HBF_4 in MeCN (=S) to give $[\text{WH}_2\text{S}_3(\text{PMe}_2\text{Ph})_3]^{2+}$, $[\text{ReHS}_3(\text{PMe}_2\text{Ph})_3]^{2+}$, $[\text{ReHS}_4(\text{PPh}_3)_2]^{2+}$, $[\text{OsS}_3(\text{PMe}_2\text{Ph})_3]^{2+}$, and $[\text{IrH}_2\text{S}_2(\text{PPh}_3)_2]^{2+}$ as the BF_4 salts. The reaction mechanism and evidence for the initial protonation of some of the d^0 polyhydrides at an M-H bond is discussed. In all but the iridium case, MeOH and Me_2CO failed to give analogous complexes and no alkane or alkene dehydrogenation reactions were ever observed with the acetonitrile complexes. In the iridium case a variety of solvento complexes can be obtained. Where S = Me_2CO , these are active in alkene and alkane dehydrogenation, and in this case a single-crystal X-ray diffraction study was performed: monoclinic unit cell; $a = 10.565$ (2) Å; $b = 25.315$ (7) Å; $c = 15.460$ (4) Å; $\beta = 95.74$ (2)°; $V = 4114$ (4) Å³; space group $P2_1/c$; $Z = 4$; $R = 5.6\%$. The trans influence of the hydride ligands on the O-bound acetone groups was pronounced: Ir-O = 2.228 (5) Å (av), ca. 10% longer than the expected 2.02 Å. This is consistent with the high reactivity of the acetone complex.

We have been studying solvento complexes of the transition metals¹ as possible precursors to reactive, ligand-deficient species for the catalytic and stoichiometric activation of normally unreactive substrates, such as alkanes. For example we found that $[\text{IrH}_2\text{S}_2(\text{PPh}_3)_2]\text{BF}_4$ (**1**) is active for alkane dehydrogenation² where S = Me_2CO (**1a**) but not where S

= MeCN (**1b**) and that **1** can be obtained by acidolysis of $\text{IrH}_5(\text{PPh}_3)_2$ with HBF_4 in the solvent S.³ We therefore decided to attempt the preparation of a variety of similar solvento complexes of other metals. While this work was in progress, Caulton et al.^{4a} showed that acidolysis of MoH_4 -

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Table I. Colors and Spectral Data for the Complexes

complex ^a	color	¹ H NMR ^b			³¹ P NMR ^c PR ₃	IR ^d	ref
		MH	PMe	MeCN			
[WH ₂ S ₃ (PMe ₂ Ph) ₃] ²⁺	yellow	-0.30 (q, 52.8)	1.81 (d, 8.5)	2.24 (s)	+3.45 (tt, 7, 165 ^e)	2280 m, 2260 m	
[ReHS ₃ (PMe ₂ Ph) ₃] ²⁺	off-white	-6.82 (q, 55)	1.72 (d, 11)	2.36 (s)	-15.98 (d, 16)	2290 w, 2260 w	
[ReHS ₄ (PPh ₃) ₂] ²⁺	yellow-green	-4.48 (t, 63)		2.36 (s)	+24.41 (d, 17)	2290 m, 2260 m, 2240 s	4b
[OsS ₃ (PMe ₂ Ph) ₃] ²⁺	white		1.95 (d, 11)	2.14 (s)	-33.78	2280 sh, 2275 m, 2270 m	9b
[IrH ₂ S ₂ (PPh ₃) ₂] ⁺	white	-20.63 (t, 15)		2.13 (s)	+21.49 (t, 5.5)	2260 m, 2240 m, 2200 s	

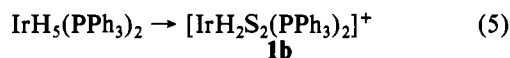
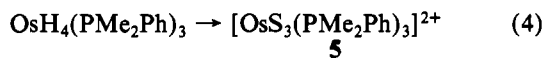
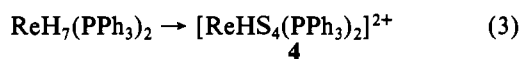
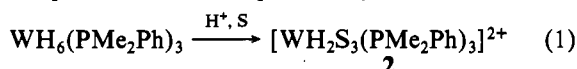
^a S = MeCN. ^b In CD₂Cl₂ at 25 °C relative to Me₄Si reported as position (δ), with the multiplicity and coupling constant (Hz) in parentheses. An aromatic multiplet at δ 7.1–7.5 appears in all cases. ^c In CD₃CN at 25 °C relative to external 85% H₃PO₄. Values are as for ¹H NMR. ^d KBr pellet, position in cm⁻¹. ^e ¹J(W,P).

(PMe₂Ph)₄ and MoH₄(PMePh₂)₄ with HBF₄ in MeCN (=S) gave [MoH₂S₂(PMe₂Ph)₄]²⁺ and [MoH₂S₃(PMePh₂)₃]²⁺, respectively; our own results on these complexes are in full agreement. More recently, Allison and Walton^{4b} described complex **4**, formed by eq 3.

Acidolysis of polyhydrides using coordinating acids is well-known and leads to a variety of complexes in which the counterion is coordinated to the metal.⁵ Even HBF₄ is not immune in this respect since we have shown that MoH₄(PMePh₂)₄ reacts with HBF₄ in THF to give [Mo₂(μ-F)₃H₄L₆]⁺ by F⁻ abstraction from the BF₄⁻ ion,^{6a} and BF₄⁻ can also directly coordinate^{6b} in some cases.

Results and Discussion

A variety of polyhydrides react with HBF₄ in MeCN (S) to give the products shown in eq 1–5 as crystalline fluoroborate



salts. These salts were characterized by microanalytical and spectral methods. In particular all the hydridic products **1–4** showed a binomial multiplet in the high-field region of the ¹H NMR spectrum (Table I) due to coupling with the phosphines. Coordinated acetonitrile was also observed between δ 2.13 and 2.36 (free nitrile: δ 1.93).

The ³¹P NMR spectrum (Table I) was particularly useful in assigning the number of hydrides by selective decoupling techniques.⁷ Irradiation at a frequency corresponding to the ligand phenyl protons decoupled these and effectively removed coupling due to the aliphatic protons as well, by off-resonance effects. Only the coupling to the hydride protons can be detected in the cases of **1**, **3**, and **4**. In the tungsten case, **2**, additional coupling to tungsten was observed (¹⁸³W, *I* = 1/2, 14.4%, ¹J(W,P) = 165 Hz).

The IR spectrum shows bands of medium intensity due to ν(CN) and ν(MH) (Table I). As expected,⁸ these are at higher wavenumber than in free acetonitrile, the σ-donor orbital on

nitrogen being CN antibonding.

The configuration of the complexes could be deduced in some cases. For example a single-crystal X-ray structure (vide infra) shows that **1a**, and by extension **1b**, has the cis,cis,trans stereochemistry.

The other octahedral product, the osmium complex **5**, is most probably *fac* since only one ³¹P and one ¹H MeCN resonance is observed in the NMR spectra. We previously found that the analogous ruthenium complexes, which have a similar IR spectrum, are certainly *fac*.⁹

Without a crystal structure, one cannot be sure of the precise structures of the eight-coordinate complex **2** and seven-coordinate **3** and **4**. [MoH₂S₂(PMe₂Ph)₄][BF₄]₂ is dodecahedral,⁴ resembling [MoH₄(PMePh₂)₄].¹⁰ A similar structure is likely for [WH₂S₃(PMe₂Ph)₃]²⁺ (**2**). The likeliest geometry for **3** is a capped octahedron, but [ReHS₄(PPh₃)₂]²⁺ (**4**) might be a pentagonal bipyramid, since it has two bulky PPh₃ groups and five relatively small H or S groups.

Several mechanistic points of interest arise from these reactions. Two of the starting complexes: WH₆(PMe₂Ph)₃ and ReH₇(PPh₃)₂ are d⁰ systems and therefore would not be expected to protonate at the metal. Neither complex reacts with MeCN under the conditions of protolysis, so reductive elimination of H₂ is not fast. The most likely site of protonation is at the M–H bond to give either a linear or bent M–H–H⁺ system. Bridged M–H–H–X systems may be involved in H₂ (X = H)¹¹ or C–H (X = C)¹² additions to metals; several examples of the latter have been observed crystallographically.¹³

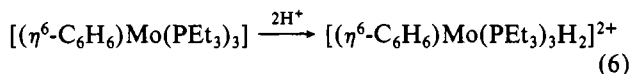
Among the dⁿ hydrides where n ≥ 2, protonation at the metal is allowed. This is a reasonable first step for the osmium tetrahydride and iridium and rhenium pentahydrides. [WH₅(PMePh₂)₄][BF₄], formed by protonation of the tetrahydride, is isolable.^{5c} Conductimetric evidence for the existence of the adducts OsH₅(PMe₂Ph)₃⁺ and ReH₆(PMe₂Ph)₃⁺ has been put forward.^{5c,14} We have observed by ¹H NMR that IrH₅(P(Cy)₃)₂ reacts with HBF₄ at –80 °C in CD₂Cl₂ without loss of H₂ and that the addition of NEt₃ regenerates the original pentahydride.¹⁵ Repeated efforts to characterize these and related intermediates by selective proton decoupling of the ³¹P NMR spectra of these species at –80 °C failed because of instrumental difficulties. There is also indirect evidence for the existence of [MoH₅(PMePh₂)₄]⁺ at –60 °C in solutions of [MoH₄(PMePh₂)₄] in CD₂Cl₂ containing CF₃SO₃H. At –60 °C the eight-coordinate neutral complex no longer shows fluxional behavior, as the static structure begins to be frozen

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out. We find that on adding acid there is a downfield shift from δ -2.65 to -1.89 and a pure binomial coupling to phosphorus reappears. This suggests either that proton exchange with free acid or that fluxionality within a new polyhydride species is fast at -60 °C. In view of the fact that the observed resonance position shifts significantly on protonation and that nine-coordinate complexes are known¹⁶ to have particularly low rearrangement barriers, we prefer the latter explanation. If this is true, then IrH_6L_2^+ is a unique example of an Ir(VII) species and MoH_5L_4^+ an unusual example of a Mo(VI) hydride.

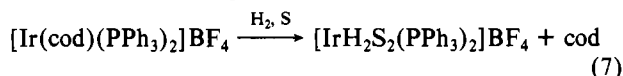
The protonated adducts are unstable at room temperature and lose H_2 . It is reasonable to suppose that the resulting empty sites are filled by solvent. In most of the cases, a 2+ cation results. This implies that the acetonitriles are sufficiently good donors to render the metal species basic enough to protonate again. This is rare although it has even been observed when no other change in the coordination sphere takes place:¹⁷



The formation of the monohydrides **3** and **4** and of $\text{OsS}_3\text{-}(\text{PMe}_2\text{Ph})_3^{2+}$ can be rationalized on the basis of the loss of the maximum number of hydrides as H_2 together with binding of S and the second protonation. $[\text{WH}_2\text{S}_3(\text{PMe}_2\text{Ph})_3]^{2+}$ (**2**) and $[\text{IrH}_2\text{S}_2(\text{PPh}_3)_2]^+$ (**1**) do not lose the final H_2 . Dicationic metal hydrides are relatively rare, and we are examining their chemistry further to see if they have any unusual properties.¹⁸ So far they have proved rather inert to a variety of reagents.

The formal oxidation states of the resulting complexes show an irregular trend by group: Mo(IV) and W(IV), Re(III), Os(II), and Ir(III). This order broadly reflects the most common organometallic oxidation states in each case.

Attempts to obtain solvento complexes with other solvents, such as Me_2CO or MeOH , in all but one case were uniformly unsuccessful. These could not even be detected in situ by selective proton-decoupled ³¹P NMR spectroscopy. In the iridium case, however, a range of solvento complexes having different S groups were formed: e.g., H_2O , Me_2CO , and MeOH . We do not understand the reason for this difference in behavior. The iridium complexes were also formed by treatment of $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{BF}_4$ (cod = 1,5-cyclooctadiene) in S as solvent with H_2 ¹⁹



or by treatment of $[\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$ with S.²⁰ In general the last two were more useful as preparative methods and with them a number of exotic solvento complexes have been prepared, e.g., S = *i*-PrOH,¹⁹ *t*-BuOH,¹⁹ or MeI²⁰ or S_2 = *o*-C₆H₄I₂,²⁰ PhNO₂,²¹ or cod.¹

Of particular importance is the case S = Me_2CO , because we were able to observe alkane dehydrogenation² (eq 8). We

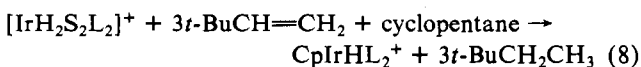


Table II. Experimental Data for the X-ray Diffraction Study of $[\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$

(A) Crystal Parameters at 26 (2) °C	
space group: $P2_1/c$	$V = 4114$ (4) Å ³
$a = 10.565$ (2) Å	$M_x = 921.77$
$b = 25.315$ (7) Å	$Z = 4$
$c = 15.460$ (4) Å	ρ (calcd) = 1.48 g/cm ³
$\beta = 95.74$ (2) Å	
(B) Measurement of Intensities	
radiation	Mo K α (0.710 73 Å)
monochromator	graphite
detector aperture, mm	horizontal, $A + B \tan \theta$ ($A = 3.0$, $B = 1.0$); vertical, 4
reflens measd	$h, k, \pm l$
2θ (max), deg	46
scan type	moving crystal-stationary counter
ω scan rate, deg/min	max, 10; min, 1.5
ω scan width, deg	1.0
bkgd	one-fourth additional scan at each end of scan
std reflens	3 measd after each 90 min, showing only random fluctuations
reflens measd	6161
reflens used ($F^2 > 3\sigma(F^2)$)	2235
(C) Treatment of Data	
abs coeff, μ , cm ⁻¹	33.585
ρ factor	0.010
final residuals R, R_w	0.056, 0.050
esd of unit wt	3.290
largest error on final cycle	0.17
largest peak in final diff Fourier	1.51

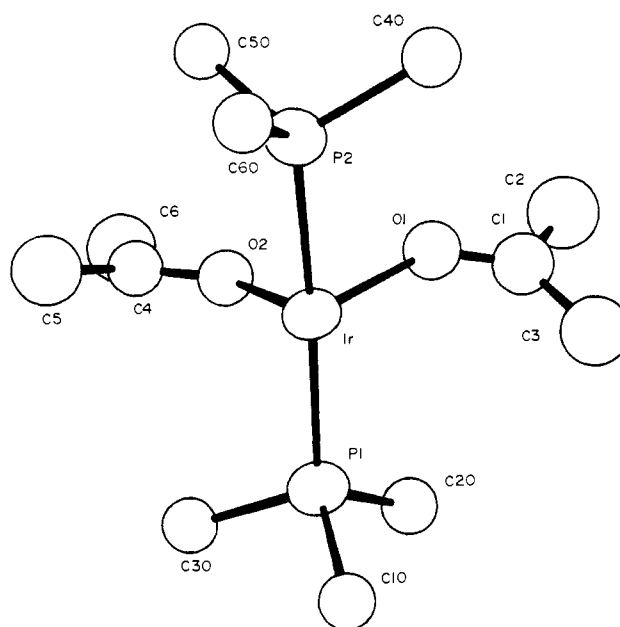


Figure 1. ORTEP diagram of the core of the $[\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$ cation. The carbon atoms of the C_6H_5 groups not directly bound to phosphorus were omitted for clarity.

therefore carefully examined the reactions of the other solvento complexes **2-5** with cyclopentene, cyclohexene, and cyclopentane/*t*-BuCH=CH₂. In no case were tractable products isolated, although further efforts are in progress. Most likely, the acetonitrile ligands were too strongly held, especially in these 2+ cations, for reaction with hydrocarbons to occur.

We decided to look at one case crystallographically in order to learn something about the details of the structure. The most interesting complex of the series is, of course, **1a**, and we were fortunately able to grow suitable crystals from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at 4 °C. The details of the structure are given in Tables II-V and Tables 1-4 (supplementary material), the methods used are described in the Experimental Section, and a diagram of

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Table III. Positional and Thermal Parameters for $[\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4^a$

atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ir	0.09409 (5)	-0.11806 (2)	-0.23126 (4)	2.51 (2)	5.28 (3)	3.28 (2)	-0.14 (3)	0.38 (2)	-0.21 (3)
P1	0.2281 (3)	-0.1090 (2)	-0.1044 (2)	3.2 (1)	5.6 (2)	3.8 (2)	-0.4 (2)	0.5 (1)	0.0 (2)
P2	-0.0527 (3)	-0.1377 (1)	-0.3488 (2)	2.7 (1)	5.1 (2)	3.9 (2)	-0.0 (1)	0.5 (1)	0.3 (2)

atom	x/a	y/b	z/c	$B, \text{\AA}^2$	atom	x/a	y/b	z/c	$B, \text{\AA}^2$
F1	0.509 (1)	0.1410 (5)	-0.2679 (8)	13.2 (4)	C31	0.363 (1)	-0.2037 (6)	-0.0956 (10)	6.2 (4)
F2	0.525 (1)	0.1231 (5)	-0.4075 (8)	12.8 (4)	C32	0.463 (2)	-0.2385 (7)	-0.1062 (11)	7.4 (5)
F3	0.430 (1)	0.0652 (5)	-0.3288 (8)	11.5 (3)	C33	0.573 (1)	-0.2160 (6)	-0.1297 (10)	6.7 (4)
F4	0.343 (1)	0.1428 (5)	-0.3633 (8)	13.7 (4)	C34	0.587 (2)	-0.1652 (7)	-0.1420 (11)	7.3 (4)
O1	0.0920 (8)	-0.0337 (3)	-0.2739 (6)	4.7 (2)	C35	0.486 (1)	-0.1296 (5)	-0.1326 (9)	5.4 (4)
O2	0.2635 (7)	-0.1116 (3)	-0.3048 (5)	4.4 (2)	C40	-0.168 (1)	-0.0841 (5)	-0.3779 (8)	4.0 (3)
C1	0.055 (1)	0.0075 (6)	-0.2450 (9)	5.3 (4)	C41	-0.203 (1)	-0.0688 (6)	-0.4624 (10)	5.8 (4)
C2	0.080 (2)	0.0575 (7)	-0.2935 (11)	7.9 (5)	C42	-0.290 (1)	-0.0281 (6)	-0.4806 (10)	6.8 (4)
C3	-0.008 (1)	0.0132 (6)	-0.1667 (10)	6.4 (4)	C43	-0.342 (1)	-0.0041 (6)	-0.4145 (10)	6.3 (4)
C4	0.332 (1)	-0.1448 (5)	-0.3367 (8)	4.5 (3)	C44	-0.313 (1)	-0.0188 (6)	-0.3307 (9)	5.7 (4)
C5	0.313 (1)	-0.2004 (6)	-0.3390 (10)	6.8 (4)	C45	-0.222 (1)	-0.0580 (6)	-0.3104 (9)	5.3 (4)
C6	0.440 (2)	-0.1220 (7)	-0.3804 (11)	7.7 (4)	C50	0.020 (1)	-0.1511 (5)	-0.4493 (8)	3.8 (3)
C10	0.169 (1)	-0.1313 (5)	-0.0045 (8)	3.9 (3)	C51	0.097 (1)	-0.1113 (5)	-0.4800 (8)	4.3 (3)
C11	0.042 (1)	-0.1423 (5)	0.0021 (8)	4.6 (3)	C52	0.611 (1)	-0.1227 (6)	-0.5510 (9)	5.4 (3)
C12	-0.001 (1)	-0.1582 (6)	0.0802 (9)	5.4 (4)	C53	0.153 (1)	-0.1700 (6)	-0.5893 (9)	5.5 (4)
C13	0.085 (1)	-0.1667 (6)	0.1531 (10)	6.0 (4)	C54	0.078 (1)	-0.2097 (6)	-0.5627 (9)	5.3 (4)
C14	0.211 (1)	-0.1554 (6)	0.1475 (10)	6.5 (4)	C55	0.011 (1)	-0.1994 (5)	-0.4906 (9)	4.5 (3)
C15	0.256 (1)	-0.1389 (6)	0.0702 (9)	5.4 (4)	C60	-0.155 (1)	-0.1945 (5)	-0.3355 (8)	3.6 (3)
C20	0.284 (1)	-0.0418 (5)	-0.0802 (8)	4.5 (3)	C61	-0.130 (1)	-0.2310 (5)	-0.2693 (8)	4.4 (3)
C21	0.268 (1)	-0.0168 (6)	-0.0006 (10)	6.0 (4)	C62	-0.208 (1)	-0.2756 (6)	-0.2642 (10)	5.9 (4)
C22	0.301 (2)	0.0356 (7)	0.0124 (11)	7.2 (4)	C63	-0.308 (1)	-0.2835 (6)	-0.3272 (10)	6.0 (4)
C23	0.350 (2)	0.0634 (7)	-0.0521 (11)	7.3 (4)	C64	-0.336 (1)	-0.2485 (6)	-0.3910 (9)	5.6 (4)
C24	0.370 (1)	0.0396 (6)	-0.1293 (10)	6.4 (4)	C65	-0.261 (1)	-0.2038 (6)	-0.3993 (10)	5.8 (4)
C25	0.336 (1)	-0.0121 (6)	-0.1438 (9)	5.0 (3)	B1	0.455 (3)	0.115 (1)	-0.333 (2)	12.6 (9)
C30	0.373 (1)	-0.1508 (5)	-0.1084 (8)	4.3 (3)					

^a The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$.

Table IV. Selected Bond Lengths (Å) for $[\text{IrH}_2(\text{Me}_2\text{CO})(\text{PPh}_3)_2]\text{BF}_4$

Ir-P(1)	2.313 (2)	O(2)-C(4)	1.242 (8)
Ir-P(2)	2.321 (2)	C(1)-C(2)	1.51 (1)
Ir-O(1)	2.235 (5)	C(1)-C(3)	1.44 (1)
Ir-O(2)	2.220 (5)	C(4)-C(5)	1.42 (1)
O(1)-C(1)	1.216 (8)	C(4)-C(6)	1.50 (1)

Table V. Selected Bond Angles (deg) for $[\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$

P(1)-Ir-P(2)	171.63 (8)	O(1)-C(1)-C(3)	125.9 (8)
P(1)-Ir-O(1)	98.2 (1)	C(2)-C(1)-C(3)	116.9 (8)
P(1)-Ir-O(2)	88.3 (1)	O(2)-C(4)-C(5)	126.6 (8)
P(2)-Ir-O(1)	89.3 (1)	O(2)-C(4)-C(6)	114.6 (8)
P(2)-Ir-O(2)	97.2 (1)	C(5)-C(4)-C(6)	118.7 (8)
O(1)-C(1)-C(2)	117.2 (8)		

the cation is shown in Figure 1. Solvento complexes of this type have been reported several times since 1963^{22a} although they were sometimes formulated as $[\text{IrH}_2(\text{PPh}_3)_2]^+$.^{22b} Shapley, Schrock, and Osborn reported several members of the series.²³ Hartley and Davies²⁴ state that the isolation of acetone complexes of the low-valent platinum metals is usually unsuccessful because the solvent is so weakly bound that even H_2O can usually displace it. Here, acetone is more strongly bound than water and the complex is quite stable.¹⁹

The structure consists of discrete BF_4^- anions and $[\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2]^+$ cations with no unusually close contacts. The most interesting feature is the pair of coordinated acetone molecules. The Ir-O distances (2.220 (5)-2.235 (5) Å) are extremely long.

The "expected" length of an Ir-O single bond in an aquo complex is said to be 2.02 Å.²⁵ The sp^2 O of a ketone would,

if anything, give a slightly shorter distance. An independent method of deriving the expected distance is to calculate it from the Ir-P distance observed in this structure, 2.32 Å (av), with allowance made for the difference in the covalent radii²⁶ of oxygen and phosphorus; this gives 1.96 Å, very close to the literature estimate. Conservatively, therefore, the lengthening is at least 0.21 Å or just over 10% of the expected distance. In the only other structurally characterized acetone complex known,²⁷ in which the trans ligand is mesitylene, the Ru-O distance of 2.11 Å is only 3% longer than the expected 2.05 Å. A comparable lengthening occurs in $[\text{RhH}(\text{NH}_3)_5]^{2+}$,²⁸ where the unique Ru-N distance is 8% longer than the average of the others and 9% longer than the expected²⁵ distance.

The high reactivity of the complex, known to be due to acetone dissociation,²⁹ is therefore probably associated with the high trans effect of the hydrides, as is reflected in the structural data.

Another feature of interest is the high value for the Ir-O=C angle in the acetone groups (133.1 (5) and 134.9 (6)°). This suggests that the endo methyl groups C(3) and C(5) of each acetone may be subject to the steric repulsion of the IrL_2 group. As might be expected if this were true, the other angles involving this methyl group are also distorted: C(5)-C(4)-O(2) = 126.6 (8)° and C(3)-C(1)-C(1) = 125.9 (8)° are more open and C(3)-C(1)-C(2) = 116.9 (8)°, C(5)-C(4)-O(6) = 118.7 (8)°, C(2)-C(1)-O(1) = 117.2 (8)°, and C(6)-C(4)-O(2) = 114.6 (8)° are more compressed than might be expected. The CO bond lengths are similar to that in acetone itself (1.20 Å).³⁰ The σ -bound acetone ligands in **1a**

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contrast with the π -bound groups formed only for electron-acceptor ketones as in the complex³¹ [Pt(PPh₃)₂(η^2 -(CF₃)₂CO)].

The heavy atoms of each acetone group are very close to a plane. For example, C(2) and C(3) are -0.089 (17) and 0.025 (16) Å, respectively, from a plane (plane 1) defined by Ir, O(1), and C(1); C(5) and C(6) are 0.088 (15) and -0.025 (16) Å, respectively, from a plane (plane 2) defined by Ir, O(2), and C(4). Plane 1 and plane 2 make a dihedral angle of 29.6° to one another. The O(1)-Ir-O(2) angle 76.3 (2)° is somewhat more acute than we expected. The hydride ligands, not detected in the X-ray analysis, must lie in the empty coordination positions trans to the acetone groups. The PPh₃ groups are bent away from the acetone groups (P(1)-Ir-P(2) = 171.63 (8)°) slightly less than is the case in our structure of the closely related complex [IrH₂(*o*-C₆H₄I₂)(PPh₃)₂]BF₄ (P(1)-Ir-P(2) = 166.5 (2)°). The PPh₃ groups are otherwise perfectly normal. Thermal parameters for the anion are large; disorder may be present.

Conclusion

Following up our earlier observation³ and paralleling the work of Allison and Walton^{4b} and Caulton et al.,^{4a,9b} we find that acidolysis of polyhydride complexes with a noncoordinating acid in the presence of MeCN gives a variety of unusual cationic solvento complexes. The type of complex obtained depends on the particular case considered: we found examples of six-, seven-, and eight-coordination (eq 1-5). Only in the iridium case were a range of solvento complexes obtained with different solvents, e.g., S = Me₂CO, MeOH.

The case of [IrH₂(Me₂CO)₂(PPh₃)₂]BF₄ is of unusual interest in view of its activity for alkane dehydrogenation. Crystallographically, we find a great lengthening of the Ir-O bond, due to the trans influence of the IrH groups. This is consistent with a weak metal-acetone bond, as is reflected in the extensive dissociative chemistry of this species²⁹ and in the high activity for alkane dehydrogenation.

Experimental Section

All reactions were run under an atmosphere of prepurified argon with use of standard Schlenk-tube techniques. Solvents were distilled as follows under N₂ but stored over molecular sieves under Ar: THF (Na/Ph₂CO), MeOH (NaBH₄/NaOMe), CH₃CN (CaH₂). ¹H NMR spectra were recorded on a JEOL FX-900 or a Bruker HX-270 spectrometer and ³¹P NMR spectra on a Varian CFT-20 spectrometer. IR spectra were recorded on a Beckman 4250 Series IR spectrometer. Reagents were obtained from Aldrich or Alfa. WH₆(PMe₂Ph)₃,³² ReH₂(PMe₂Ph)₃,¹⁴ ReH₂(PPh₃)₂,³³ OsH₄(PMe₂Ph)₃,^{5c} and IrH₅(PPh₃)₂³⁴ were prepared by literature procedures.

Reactions of Tetrafluoroboric Acid with the Polyhydride Complexes. Excess HBF₄·Et₂O (:10 mol equiv) was added to WH₆(PMe₂Ph)₃ (384 mg, 0.63 mmol) in MeCN (30 mL). The white suspension immediately turned clear orange, and a gas was evolved. After 30 min of stirring at room temperature the solvent was removed in vacuo and MeOH (15 mL) and then Et₂O (15 mL) were added to precipitate yellow crystals. These were filtered, washed with Et₂O (2 × 5 mL), and dried. The complex was recrystallized from MeCN/Et₂O (yield 504 mg, 86%). Anal. Calcd for C₃₀H₄₄F₈N₃P₃B₂W: C, 40.17; H, 4.94; P, 10.36. Found: C, 40.24; H, 4.95; P, 10.42.

The other MeCN complexes were prepared in a similar manner, except for the iridium complexes, which were prepared in CH₃CN,

MeOH, or Me₂CO to give the corresponding solvento complexes, which were recrystallized from CH₂Cl₂/Et₂O and identified by comparison with authentic samples prepared by the method of ref 19. The new complexes were fully characterized (Table I) and gave the following yields and microanalytical data.

[ReH(CH₃CN)₃(PMe₂Ph)₃][BF₄]₂ (yield 80%): Anal. Calcd for C₃₀H₄₃F₈N₃P₃B₂Re: C, 40.11; H, 4.82; P, 10.34. Found: C, 40.03; H, 4.82; P, 10.15. [ReH(CH₃CN)₄(PPh₃)₂][BF₄]₂ (yield 18%): Anal. Calcd for C₄₄H₄₃F₃N₄P₂B₂Re: C, 50.35; H, 4.13; P, 5.90. Found: C, 50.14; H, 4.34; P, 5.79. [Os(CH₃CN)₃(PMe₂Ph)₃][BF₄]₂ (yield 68%): Anal. Calcd for C₃₀H₄₂F₈N₃P₃B₂Os: C, 39.97; H, 4.70; P, 10.31. Found: C, 39.87; H, 4.49; P, 10.15. [IrH₂(CH₃CN)₂(PPh₃)₂][BF₄]₂ (yield 81%): Anal. Calcd for C₄₀H₃₈F₄N₂P₂B₂Ir: C, 54.12; H, 4.31; P, 6.98. Found: C, 54.05; H, 4.40; P, 7.03.

Preparation of Dihydrido(bis(acetone)bis(triphenylphosphine)iridium(III) Tetrafluoroborate for Crystallography.² A red solution containing [Ir(cod)(PPh₃)₂]BF₄ (310 mg, 0.34 mmol) dissolved in 6 mL of acetone was cooled to 0 °C. Hydrogen was then bubbled through the solution slowly for 45 min to give a slightly yellow solution. A white solid obtained after the addition of 50 mL of diethyl ether was filtered, washed with Et₂O (3 × 10 mL), and dried in vacuo; yield 283 mg (92%).

Crystals were obtained by dissolving 50 mg of the product in CH₂Cl₂ (1 mL), slowly adding Et₂O (10 mL) to form an upper layer, and placing the test tube in a cold room (4 °C) for several days.

Collection and Reduction of the X-ray Data. A suitable crystal (0.4 mm × 0.4 mm × 0.25 mm) was mounted in a thin-walled glass capillary. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo K α radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines.

The space group P2₁/c was established from the systematic absences observed in the data. Crystal data and data collection parameters are listed in Table II. No absorption correction was made. All data processing was performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library (Version 18). Neutral-atom scattering factors were calculated by the standard procedures.^{35a} Anomalous dispersion corrections were applied to all non-hydrogen atoms.^{35b} Full-matrix least-squares refinements minimized the functions $\sum hkl |w(|F_{\text{obsd}}| - |F_{\text{calcd}}|)|^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_{\text{obsd}}^2)/2F_{\text{obsd}}$, and $\sigma(F_{\text{obsd}}^2) = [\sigma(I_{\text{raw}})^2 + (PF_{\text{obsd}}^2)^2]^{1/2}/Lp$.

The structure was solved by a combination of Patterson and difference Fourier syntheses. The position of iridium was obtained from the Patterson synthesis while the remaining atoms were obtained from difference Fourier syntheses.

Tables IV and V list interatomic distances and angles. Estimated standard deviations were obtained with use of the inverse matrix obtained on the final cycle of refinement for each structure. The final residuals were $R = 0.056$ and $R_w = 0.05$. Hydrogen atom positions were calculated and included in the structure factors, but no attempt was made to detect or refine them. The results are shown in Figure 1, Tables II-V, and Tables 1-4 (supplementary data).

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Registry No. 1a, 82582-67-0; 1b, 83730-47-6; 2, 84430-76-2; 3, 88129-93-5; 4, 86664-82-6; 5, 88129-95-7; [Ir(cod)(PPh₃)₂]BF₄, 38834-40-1; ReH₂(PMe₂Ph)₃, 65816-70-8; ReH₂(PPh₃)₂, 12103-40-1; OsH₄(PMe₂Ph)₃, 24228-57-7; IrH₅(PPh₃)₂, 53470-69-2; WH₆(PMe₂Ph)₃, 20540-07-2; H₂, 1333-74-0.

Supplementary Material Available: A listing of observed and calculated structure factors, tables of further bond lengths and angles and molecular planes, and an ORTEP projection of the unit cell (19 pages). Ordering information is given on any current masthead page.

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