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Protonation of Chloride in $Os(H)_2Cl_2(P^iPr_3)_2$: Synthesis of $[(P^iPr_3)_2H_2Os(\mu\text{-}Cl)_3OsH_2(P^iPr_3)_2]CF_3SO_3$

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Protonation (CF_3SO_3H) of $Os(H)_2Cl_2L_2$ (L = P^iPr_3) in Et_2O or CH_2Cl_2 yields $Os_2(H)_4(\mu\text{-}Cl)_3L_4^+$, characterized by IR, ^1H NMR, and ^{31}P NMR spectroscopy, elemental analysis, and X-ray diffraction. The reaction thus involves selectivity for protonation at chloride (*vs* H or Os) and eliminates HCl. The dimetal cation reacts with $[NBu_4]Cl$ to regenerate $Os(H)_2Cl_2L_2$. Crystal data (−169 °C) for $[Os_2(H)_4Cl_3(P^iPr_3)_4]CF_3SO_3\cdot CH_2Cl_2$: $a = 16.859(4)$ Å, $b = 18.719(5)$ Å, $c = 18.488(5)$ Å, $\beta = 113.85(1)°$ with $Z = 4$ in space group $P2_1/a$.

Introduction

Protonation of transition metal complexes has been generally practiced only on 18-electron reagents.[1] When applied to a metal hydride reagent, it is one of the most general routes to an H_2 complex (eq 1).[2] Protonation reactions have generally been

$$L_nMH + H^+ \rightarrow L_nM(H_2)^+ \text{ or } L_nM(H)_2^+ \qquad (1)$$

carried out on compounds lacking ligands with a lone pair on the α-ligand atom (e.g., halides and pseudohalides), in part to avoid the question of selectivity of the site of proton transfer. Nevertheless, protonation of metal hydride halides has produced dihydrogen complexes in a few cases,[3] and other examples exist of cationic halide− (or pseudohalide−) dihydrogen complexes.[4] Our own interest in the dihydride species $Os(H)_2(Cl)_2L_2$,[5] **1** (L = P^iPr_3), which has only a 16-valence-electron count in the absence of any Cl→Os π-donation, was to protonate this molecule in an effort to synthesize a rare example of an unsaturated dihydrogen complex: $Os(H)(H_2)(Cl)_2L_2^+$. This would be the first six-coordinate unsaturated dihydrogen complex.[6] We now report the very different consequence of such a protonation, which reveals *selectivity* for protonation at halide rather than hydride. The operational unsaturation of the metal plays a large role in the course of the reaction.

Experimental Section

All manipulations were performed under inert atmosphere or *in vacuo* using standard Schlenk and glovebox techniques. All glassware was flame-dried under vacuum prior to use. Solvents were distilled from drying agents and stored in bulbs with Teflon valves. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. NMR spectra were recorded on either a Nicolet 360 MHz or a Varian 300 MHz instrument, with chemical shifts in ppm referenced to residual solvent peaks (^1H) or external H_3PO_4 (neat, ^{31}P). $OsH_2Cl_2(P^iPr_3)_2$ was synthesized according to the literature. Triflic acid and trimethylsilyl triflate (Aldrich) were degassed and stored in glass containers with Teflon closures. Tetrabutylammonium salts were dried *in vacuo* with heating and stored in a drybox.

$[(P^iPr_3)_2(H)_2Os(\mu\text{-}Cl)_3Os(H)_2(P^iPr_3)_2]CF_3SO_3$, 2. A Schlenk flask was charged with $Os(H)_2Cl_2(P^iPr_3)_2$ (200 mg, 0.34 mmol). Ether (15 mL) was added, and this suspension was stirred, as a solution of triflic acid (200 mL, 2.3 mmol) in ether (10 mL) was added. After 30 min, the light brown color of **1** had disappeared, and a pale yellow solid remained. The ether was decanted via cannula. The solid was washed with ether (3 × 10 mL) and dried *in vacuo*. The same product is obtained in a reaction of **1** with Me_3SiOT_f (1:1 equiv). Yield: 150 mg (0.117 mmol, 69%) $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): 25.5 (s). ^1H NMR ($CDCl_3$, 20 °C): 2.32 (mult, 12H), 1.28 (dd, J_{HP} = 15.6, J_{HH} = 7.3, 72H), −15.99 (t, J_{HP} = 35.3, 4H). ^1H NMR (CD_2Cl_2, −100 °C): −14.32 (t, J_{HP} = 37), −14.48 (t, J_{HP} = 33), −14.83 (t, J_{HP} = 33), −14.94 (t, J_{HP} = 28), −16.84 (t, J_{HP} = 36). The integrated intensity of the first four signals, compared to the fifth, is 4:5. IR (KBr): ν_{Os-H} = 2202, 2182 cm^{-1}. Anal. Calc: C, 34.70; H, 6.93. Found: C, 34.40; H, 6.88. Crystals were grown by layering a solution of **2** in CH_2Cl_2 with ether.

Search for Intermediates by Low-Temperature Protonation of $OsH_2Cl_2(P^iPr_3)_2$. An extended NMR tube was charged with **1** (10 mg, 0.017 mmol). In a small vial, triflic acid (100 μL, 1.1 mmol) was dissolved in CD_2Cl_2. The solution was added to the tube; the tube was fitted with a Schlenk adaptor, quickly (4 min) removed from the drybox, and cooled to −196 °C. It was then degassed by three freeze−pump−thaw cycles and sealed under vacuum. The tube was stored in a Dewar flask at −196 °C, until transferring it to a precooled NMR probe at −70 °C. The initial spectrum showed a mixture containing predominantly **2** with some **1** remaining, which was completely converted to **2** upon warming to −50 °C for 10 min. No other species were observed in this experiment.

Reaction of 2 with Bu_4NX. In an NMR tube, **2** (10 mg, 0.0078 mmol) and Bu_4NCl (10 mg, 27.1 mmol) were dissolved in $CDCl_3$. The color immediately changed from pale yellow to light brown, and quantitative conversion to **1** was observed (^{31}P NMR) in the time required to obtain the spectrum (~15 min).

Similarly, reaction with Bu_4NI immediately produced a purple color, and ^1H NMR showed a mixture of $OsH_2I_2L_2$, OsH_2IClL_2, and **1** (1.2:1.3:1 after 15 min).[7] After 1 week, almost complete conversion to $OsH_2I_2L_2$ was observed (^1H NMR).

Structure Determination. A crystal of suitable size was mounted in a nitrogen atmosphere glovebag using silicone grease. The crystal was then transferred to a goniostat where it was cooled to −169 °C

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[1] For the protonation of the *operationally* unsaturated agostic complex $(W(CO)_3(PCy_3)_2)$, see: Van Der Sluys, L. S.; Kubat-Martin, K. A.; Kubas, G. J.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 306.

[2] Heinekey, O. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

[3] Mezzetti, A.; Del Zotto, A.; Rigo, P.; Farnetti, E. *J. Chem. Soc., Dalton Trans.* **1991**, 1525.

[4] (a) Craw, J. S.; Bacskay, G. B.; Hash, N. S. *J. Am. Chem. Soc.* **1994**, *116*, 5937. (b) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946. (c) Albéniz, M. J.; Buil, M. L.; Esteruelas, M. A.; Lopez, A. M.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 3746.

[5] Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288.

[6] $RuHX(H_2)(PR_3)_2$ is currently the only unsaturated dihydrogen complex. See: Chaudret, B.; Chung, G.; Eisenstein, O.; Jackson, S. A.; Lahoz, F. J.; Lopez, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2314. Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1994**, *13*, 3800.

[7] These compounds have been previously reported and are easily identified by the chemical shifts of the hydride signals. See ref 15.

0020-1669/95/1334-1788$09.00/0

Table 1. Crystallographic Data for $[Os_2Cl_3H_4L_4]CF_3SO_3{\cdot}CH_2Cl_2$

chem formula	$C_{37}H_{84}Cl_3F_3O_3Os_2P_4S{\cdot}CH_2Cl_2$	space group	$P2_1/a$
a, Å	16.859(4)	T, °C	−169
b, Å	18.719(5)	λ, Å	0.710 69
c, Å	18.488(5)	ϱ_{calcd}, g cm^{-3}	1.695
β, deg	113.85(1)	μ(Mo Kα), cm^{-1}	52.1
V, Å^3	5336.22	R^a	0.0598
Z	4	$R_w{}^b$	0.0566
fw	1361.71		

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

for characterization (Table 1) and data collection ($6° < 2\theta < 45°$). A selective search of a limited hemisphere of reciprocal space revealed a primitive monoclinic cell. Following complete intensity data collection, the conditions $h = 2n$ for $h0l$ and $k = 2n$ for $0k0$ uniquely determined space group $P2_1/a$. The data were corrected for absorption, and four standards (measured every 300 data) showed no significant trends. The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. The positions of the osmium atoms were obtained from an initial E map. The positions of the remaining non-hydrogen atoms were obtained from subsequent iterations of a least-squares refinement and a difference Fourier calculation. In addition to the cation of interest, the asymmetric unit contained a triflate anion which was disordered and a molecule of CH_2Cl_2. The occupancies of the 12 partial atoms of the disordered triflate were then varied with fixed thermal parameters; they refined to a total occupancy of 8.2 (compare C, S, 3F, and 3O). The occupancies were then fixed for the remainder of the structure refinement. Hydrogens not attached to Os were included in fixed calculated positions with thermal parameters fixed at 1 plus the isotropic thermal parameter of the atom to which they were bonded. In the final cycles of refinement, the non-hydrogen atoms in the cation and the solvent molecule were varied with anisotropic thermal parameters. The disordered atoms of the triflate anion were varied with isotropic thermal parameters to give a final $R(F) = 0.060$ for the 4882 total variables using all of the unique data. Data having $F < 3\sigma(F)$ were given zero weight. The largest peak in the final difference map was an osmium residual of 2.3, and the deepest hole was −1.7 e/Å^3.

Results

When $Os(H)_2Cl_2L_2$ (**1**) (L = P^iPr_3) is treated with excess CF_3SO_3H in a diethyl ether slurry, there is a visible color change from light brown to pale yellow after about 10 min. Washing the product with ether to remove acids gives a single product (69% yield). Surprisingly, the product contains only classical hydrides (T_{1min} = 207 ms, −77 °C/300 MHz) characterized by a triplet at 25 °C and a *triplet* ($^2J_{PH}$ = 35.3 Hz) in selectively hydride-coupled ^{31}P NMR. This information indicates that the hydrides are "untouched" by the protonation: there remain two classical hydrides per L_2Os unit. These observations suggest that the site of protonation may be chloride, rather than hydride.

X-ray Structure of $Os_2Cl_3H_4L_4{}^+CF_3SO_3{}^-$ (2). Protonation of halide is supported by a single-crystal X-ray structure of the final product. The molecular formula, $Os_2Cl_3H_4L_4{}^+CF_3SO_3{}^-$ (**2**), indicates loss of HCl from "$OsH_3Cl_3L_2{}^+$", and coordination of a second molecule of **1**. In the solid state, **2** exists as discrete cation and anion, with no evidence for interaction of the triflate with the cation.[8] The cation consists of two OsH_2L_2 moieties linked by three bridging chlorides. The two P−Os−P planes intersect at a 78° angle. The atoms Os1, P6, P16, and Cl3 are nearly coplanar, as are Os2, P26, P36, and Cl4. An idealized C_2 axis passes through Cl5 and the midpoint between Os1 and Os2. The phosphines are nearly *cis*, with a remarkably small P−Os−P angle (110.2(1)°), considering their steric bulk. The hydrides on Os were not located crystallographically, but the molecular mechanics program XHYDEX[9] yielded terminal positions[10] with H−Os−H angles of 140°. In fact, the L_2H_2Os substructure is almost exactly the same as that found for **1**.[5] All Os−Cl distances within **2** are practically identical (average Os−Cl = 2.501 Å).[11] While face-sharing bioctahedra are well-known for group 8 bimetallic complexes, this is an unusual example of a *seven*-coordinate bimetallic compound with three bridging halides.[12]

The ^1H NMR spectrum of **2** in CD_2Cl_2 decoalesces in the hydride region below −70 °C and (at −97 °C) resolves into triplets (all with J_{PH} = 33 ± 3 Hz), but the number of triplets (5) demands the presence of more than one structure. The pseudo-C_2 axis present in the crystal structure of **2** relates P6/P26, P16/P36, H1/H4, and H2/H3. The only molecular motion required for the observation of a single ^{31}P (or ^1H) NMR resonance is a slight (∼12°) twist of P36−Os2−P26 with respect to P6−Os−P16 (Figure 2), creating a plane of symmetry through Os1, Os2, Cl3, P6, P16, H3, and H4. It seems unlikely that such a twist would be slow on the NMR time scale even at −70 °C. The fact that four of the triplets have equal intensity, while the fifth (at −16.8 ppm) has a much larger intensity (about 1.3 times the total intensity of the 1:1:1:1 triplets), suggests unequal populations of two species. This conclusion is reinforced by the $^{31}P\{^1H\}$ NMR spectrum at −97 °C in CD_2Cl_2 (Figure 3), which also shows five signals, of approximate intensity 1:1:2:1:1. These we assign to two isomers, one without symmetry (the 1:1:1:1 lines) and one symmetric (four equivalent P).[13] We attribute this complex spectral behavior to low-temperature decoalescence of two conformers which differ by rotation about Os−P and P−C bonds.[14] Due to the large number of possible rotamers involved, we do not speculate in additional detail.

Complex **2** is unreactive with H_2 and stable in $CDCl_3$ and CD_2Cl_2. Remarkably, **2** can be quantitatively converted back to **1** by addition of Bu_4NCl at room temperature. Facile bridge splitting is unusual at such a crowded and saturated metal center especially when the product is unsaturated. It also reacts with Bu_4NI to form first an $OsH_2I_2L_2/OsH_2IClL_2/\mathbf{1}$ mixture and eventually only $OsH_2I_2L_2$.

Discussion

The course of the reaction observed here permits the conclusion that *chloride* is the site of protonation. Protonation at the metal or at a hydride ligand can only lead to the observed product by some intuitively unattractive and/or non-least-motion processes. Perhaps the high metal oxidation state makes protonation (following ion oxidative addition) of Os^{IV} unfavorable. Accepting $Os(H)_2(HCl)ClL_2{}^+$ as the primary product of proton transfer,[12] this must lose HCl either in a spontaneous fashion or (since it is unsaturated) by a nucleophilic displace-

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(8) A distance of 3.16 Å between the CH_2Cl_2 carbon and one triflate oxygen (C54−O47) is consistent with weak triflate hydrogen bonding to the CH_2Cl_2 hydrogen.

(9) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

(10) Attempts at placing hydrides in bridging positions using XHYDEX led to unreasonable values for potential energy.

(11) For the compound $[Os_2(\mu\text{-}Cl)_3(PEt_3)_6]PF_6$, the average Os−Cl distance is 2.496 Å: Fanwick, P. E.; Fraser, I. F.; Tetrick, S. M.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 3786.

(12) Some examples of seven-coordinate dimetal species exist. See: He, Z.; Nefedou, S.; Lugan, N.; Neibecker, D.; Mathieu, R. *Organometallics* **1993**, *12*, 3837. Dawson, D. M.; Henderson, R. A.; Hills, A.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1972**, 973.

(13) No two of these lines have identical spacing (thus no AB patterns) nor any pattern that we can recognize as AB_2M etc.

(14) For similar phenomena, see: Notheis, J. U.; Heyn, R. H.; Caulton, K. G. *Inorg. Chim. Acta*, in press.

Table 2. Fractional Coordinates and Isotropic Thermal Parameters[a] for $[Os_2Cl_3H_4L_4]CF_3SO_3{\cdot}CH_2Cl_2$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2		10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Os1	4967.5(3)	2898.3(3)	7739.3(3)	12	C31	6426(10)	4617(8)	6180(8)	25
Os2	5024.3(3)	4754.2(3)	7390.6(3)	13	C32	5688(9)	5789(7)	5814(8)	20
Cl3	5092(2)	4002(2)	8543(2)	15	C33	6277(9)	6350(7)	7650(8)	20
Cl4	5947(2)	3697(2)	7413(2)	16	C34	6914(9)	6822(8)	7418(9)	25
Cl5	3956(2)	3776(2)	6781(2)	18	C35	6396(9)	6507(8)	8482(8)	25
P6	5165(2)	2302(2)	8884(2)	15	P36	3880(2)	5533(2)	7256(2)	19
C7	6011(8)	2747(7)	9761(7)	15	C37	4091(8)	6501(8)	7169(9)	23
C8	6855(9)	2924(8)	9670(8)	22	C38	4064(10)	6706(8)	6355(9)	27
C9	6220(9)	2364(8)	10548(9)	25	C39	3501(11)	7034(8)	7375(9)	34
C10	4217(8)	2298(7)	9158(8)	17	C40	3555(10)	5517(8)	8090(8)	27
C11	3911(10)	3028(8)	9298(9)	28	C41	4317(10)	5696(8)	8879(9)	28
C12	3428(9)	1891(9)	8561(9)	28	C42	3100(10)	4830(9)	8155(9)	33
C13	5441(9)	1340(7)	8908(8)	21	C43	2856(9)	5269(8)	6404(8)	24
C14	5243(10)	859(8)	9503(9)	26	C44	2938(9)	5206(8)	5608(8)	23
C15	6400(9)	1200(7)	9027(8)	19	C45	2074(11)	5742(10)	6320(11)	41
P16	4806(2)	2083(2)	6728(2)	15	S46	10967(4)	6276(3)	7913(3)	32(1)
C17	5716(13)	1406(10)	6971(10)	46	O47	10448(10)	6872(8)	7427(9)	30(3)
C18	5544(13)	834(10)	6320(10)	49	O48	11906(7)	6402(6)	8287(6)	34(2)
C19	6629(10)	1738(10)	7263(11)	47	O49	10767(9)	5553(8)	7621(8)	44(3)
C20	3841(12)	1516(11)	6353(12)	47	C50	10666(14)	6287(11)	8745(13)	32(4)
C21	2991(10)	2026(10)	6125(9)	37	F51	9846(9)	6130(7)	8533(8)	45(3)
C22	3842(10)	883(8)	6902(9)	28	F52	10830(7)	6929(6)	9111(6)	41(2)
C23	4775(13)	2573(10)	5815(11)	45	F53	11145(9)	5803(8)	9308(8)	42(3)
C24	4160(13)	2211(9)	5025(11)	42	C54	6222(12)	1122(9)	3854(11)	39
C25	5604(10)	2725(8)	5765(9)	27	Cl55	7271(3)	1494(3)	4311(3)	43
P26	6222(2)	5386(2)	7415(2)	16	Cl56	5766(4)	905(4)	4497(4)	79
C27	7270(8)	4987(8)	8130(8)	21	S57	11334(29)	5922(25)	8383(27)	33(8)
C28	8086(8)	5383(8)	8220(8)	22	O58	11650(29)	5575(24)	9021(26)	56(9)
C29	7270(9)	4829(8)	8938(9)	24	C59	10354(11)	6519(9)	8301(11)	30(3)
C30	6376(9)	5370(8)	6470(8)	21	F60	10160(26)	6951(22)	7634(24)	37(9)

[a] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table 3. Selected Bond Distances (Å) and Angles (°) for $[Os_2Cl_3H_4L_4]CF_3SO_4$

Os1-Os2	3.5385(11)	Os2−Cl3	2.516(3)
Os1−Cl3	2.513(3)	Os2−Cl4	2.508(3)
Os1−Cl4	2.468(3)	Os2−Cl5	2.496(3)
Os1−Cl5	2.503(3)	Os2−P26	2.325(4)
Os1−P6	2.309(3)	Os2−P36	2.349(4)
Os1−P16	2.330(3)		
Cl3−Os1−Cl4	75.02(10)	Cl3−Os2−P26	121.74(12)
Cl3−Os1−Cl5	75.42(11)	Cl3−Os2−P36	101.01(12)
Cl3−Os1−P6	84.25(12)	Cl4−Os2−Cl5	75.98(11)
Cl3−Os1−P16	165.59(11)	Cl4−Os2−P26	82.69(12)
Cl4−Os1−Cl5	76.56(11)	Cl4−Os2−P36	165.66(12)
Cl4−Os1−P6	130.69(12)	Cl5−Os2−P26	147.63(12)
Cl4−Os1−P16	94.69(11)	Cl5−Os2−P36	89.75(12)
Cl5−Os1−P6	140.18(12)	P26−Os2−P36	110.88(13)
Cl5−Os1−P16	92.55(12)	Os1−Cl3−Os2	89.43(10)
P6−Os1−P16	110.16(13)	Os1−Cl4−Os2	90.65(10)
Cl3−Os2−Cl4	74.28(10)	Os1−Cl5−Os2	90.13(11)
Cl3−Os2−Cl5	75.50(11)		

ment process involving $Os(H)_2Cl_2L_2$ as the nucleophile. We have been unable to observe any intermediate in the reaction, even when the protonation is done in an NMR tube at −70 °C. It is interesting that this nucleophile has diminished electron density at chlorine due to Cl→Os π-donation,[15] yet it is nucleophilic toward the electrophile $Os(H)_2(HCl)ClL_2^+$ or $Os(H)_2ClL_2^+$. Although Cl→Os π-donation can diminish the Brønsted basicity of the chloride in $Os(H)_2Cl_2L_2$, the high acid strength of triflic acid is evidently sufficient to effect protonation. Finally, it is interesting that this reaction is carried out with excess acid (>3 H^+/Os), yet the reaction mechanism seemingly requires unprotonated $Os(H)_2Cl_2L_2$, and the reaction stoichiometry (eq 2) requires only 0.5 H^+/Os.

$$2Os(H)_2Cl_2L_2 + H^+ \rightarrow Os_2(H)_4Cl_3L_4^+ + HCl \qquad (2)$$

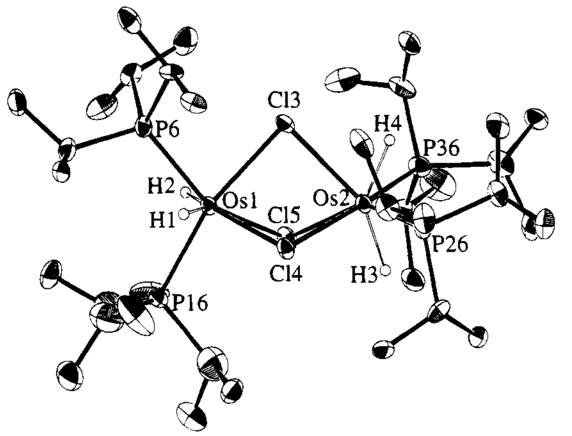

Figure 1. ORTEP drawing of $Os_2H_4Cl_3(P^iPr_3)_4^+$ (organic hydrogens are deleted) showing selected atom labeling.

Protonation of a metal halide in the presence of a metal hydride is quite surprising considering the relative basicity anticipated for hydride *vs* halide.[16] This reaction contrasts especially sharply with that recently reported,[17] where treatment of $OsHCl(CO)_2(PR_3)_2$ with triflic acid yields products derived from protonation of hydride and loss of H_2.

The reaction proceeds to a product which is coordinatively saturated without any metal−metal bonding. This is presumably a significant factor in making the thermodynamics favorable. Halide bridging is responsible for the otherwise paradoxical consequence that electrophilic attack (H^+) causes an unsaturated

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(15) Gusev, D. G.; Kuhlman, R.; Rambo, J. R.; Berke, H.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 281.

(16) A similar phenomenon has been observed by this research group for L_2PtHCl: *J. Am. Chem. Soc.*, submitted for publication.

(17) Cheng, T.-Y.; Ponce, A.; Rheingold, A. L.; Hillhouse, G. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 657.

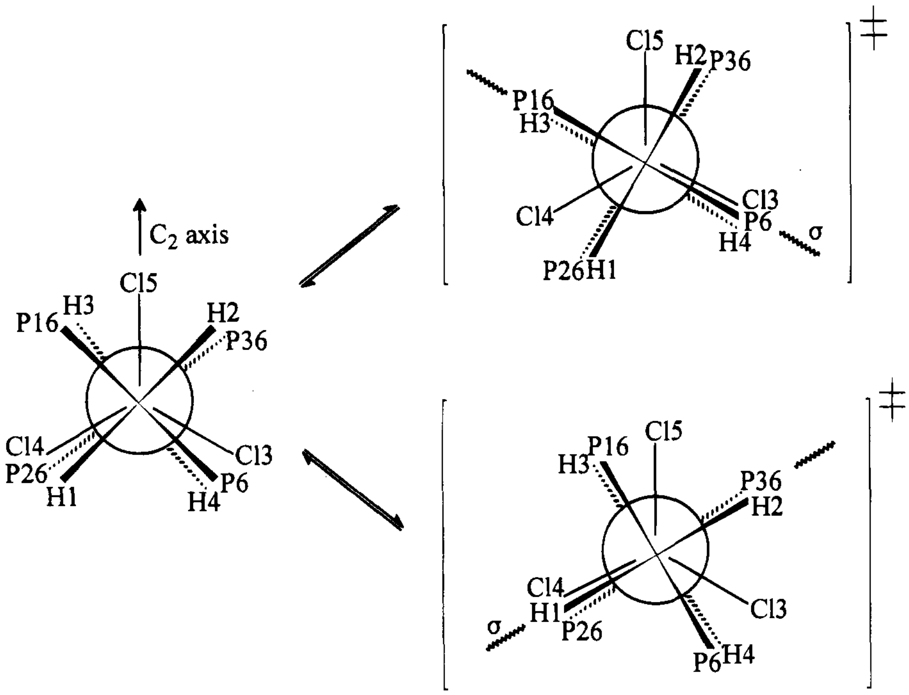

Figure 2. View down the Os/Os vector, demonstrating the fluxional process which equates the four phosphorus nuclei and also equates the four hydrides, spectroscopically.

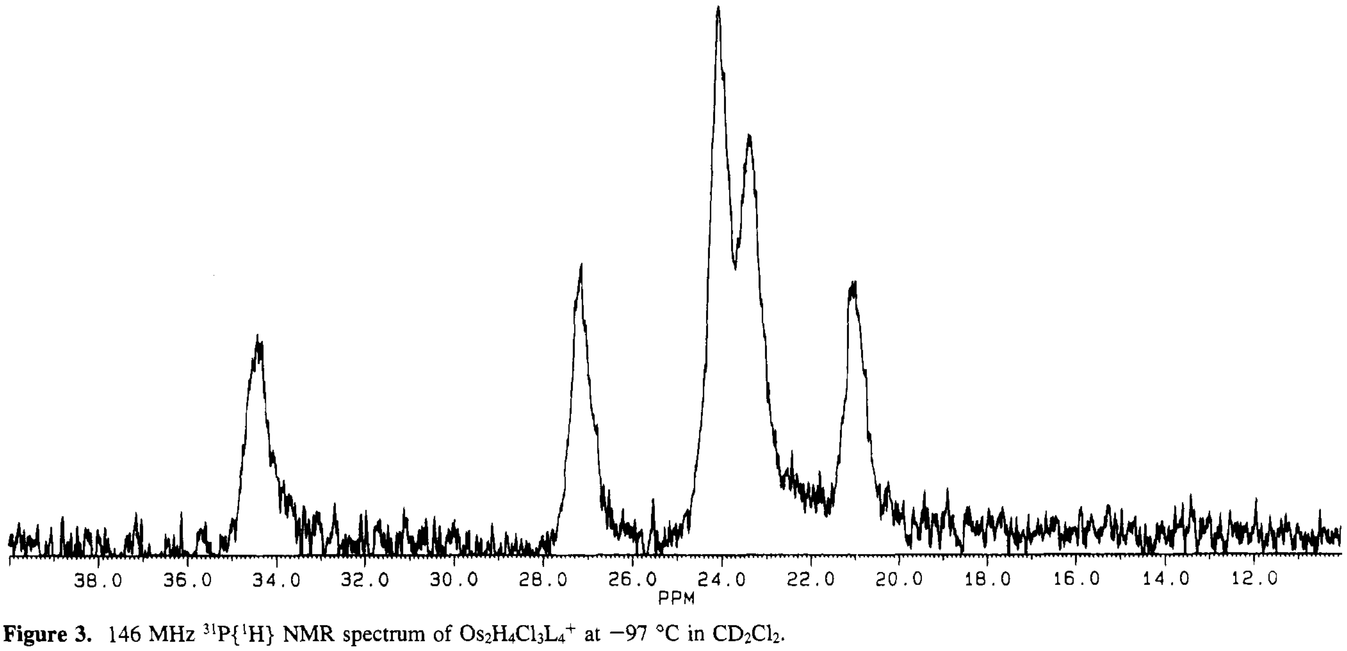

Figure 3. 146 MHz $^{31}P\{^1H\}$ NMR spectrum of $Os_2H_4Cl_3L_4^+$ at −97 °C in CD_2Cl_2.

species to become saturated. Although the product has the $M_2(\mu\text{-Cl})_3$ core structure common for Ru^{II} and Os^{II}, the higher metal oxidation state here (IV) and the consequent higher coordination number (7 *vs.* 6 for Os^{II}) make $Os_2(H)_4Cl_3L_4^+$ an unusual dimetal species.

Seven-coordinate Os^{IV} dihydride is especially interesting, when one compares **2** with the known complexes[18] $(P^iPr_3)_2OsLCl_2(H_2)$ (L = pyrazole), and $(P^iPr_3)_2OsLCl(H_2)^+$ (L = 2,2′-biimidazole). Complex **2** is similar in molecular composition to these complexes, with "L = $(P^iPr_3)_2OsH_2Cl^+$", yet contains *classical* hydrides. One may have guessed that the structure of **2** may instead have been $(H_2)(P^iPr_3)_2Os(\mu\text{-Cl})_3Os(P^iPr_3)_2(H_2)^+$, with octahedral coordination at each Os^{II} center.[19] In fact, electronic considerations seem to favor η^2-H_2 since **2** is cationic and therefore $Os\rightarrow H_2$ π-back-bonding should be diminished relative to $(P^iPr_3)_2OsLCl_2(H_2)$. However, the constraints of three bridging chloride ligands impose a steric frustration for octahedral coordination of Os. This geometry would demand P−Os−P angles of about 90°, while the angle is 110.2° in **2**. Also, in two octahedral Os centers, there would be eight P−Os−Cl angles of about 90° (four phosphines *cis* to two chlorines apiece), whereas in the observed structure of **2**, there are only six P−Os−Cl angles of less than 102°. Thus, the steric demands of the bulky phosphines may be the main influence in the preferred structure for **2**.

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[19] A related diruthenium complex contains η^2-H_2 on six-coordinate Ru: Hampton, C.; Cullen, W. R.; James, B. R.; Charland, J.-P. *J. Am. Chem. Soc.* **1988**, *110*, 6918.

Halide abstraction from a transition metal halide is normally effected with Ag^+ or Tl^+ and also, more recently, TMSOTf.[20] Use of a non-metal electrophile to abstract halide is known using CH_3^+ sources (e.g., Me_3O^+) as in eq 3,[21] and it is known that a transition metal electrophile (e.g., $CpFe(CO)_2^+$) can attach itself to a halide ligand (eq 4) to give an analog of the $Os(H)_2Cl(HCl)L_2^+$ intermediate implicated here. Alkyl halide complexes[22] are likewise analogs of our postulated intermediate HCl complex of Os(IV).

$$PtCl_2L_2 + Me_3O^+ \rightarrow PtClL_2^+ + MeCl + Me_2O \quad (3)$$

$$CpFe(CO)_2^+ + CpFe(CO)_2I \rightarrow [CpFe(CO)_2]_2(\mu\text{-}I)^+ \quad (4)$$

Conclusions

Electrophilic abstraction of halide from a metal complex can be achieved by protonation, even in the presence of hydride ligands. The site of protonation in metal hydride halides is variable and may perhaps be influenced by further reaction pathways available to the complex.

Seven-coordinate Os^{IV} is favored in **2** over the alternative six-coordinate Os^{II} containing η^2-H_2 ligands. This is probably a result of steric repulsion between the bulky phosphines and μ-Cl ligands.

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Supplementary Material Available: Tables of full crystallographic details and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

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