

An NMR spectrum ( $C_6D_6$ ) of the orange residue only exhibited resonances for the corresponding *m*- and *p*-tolyl bromide complexes. The ratio of the integrated intensities of the tolyl methyl resonances (meta,  $\delta$  2.309, 69%; para,  $\delta$  2.279, 31%) was within the experimental limit of error of the ratio of the starting materials (67:33).

**Preparation of  $\alpha,\alpha,\alpha$ -Trideuterio-2-bromo-*p*-xylene.** The compound was prepared in 4 steps from methyl *p*-toluate and used for the preparation of **8a** as previously described.<sup>16</sup> Monobromination of methyl *p*-toluate (3.5 g) with  $AlCl_3/Br_2$ <sup>34</sup> gave methyl 3-bromotoluate (2.45 g, 46%) as a colorless liquid after Kugelrohr distillation (140 °C (10 mm)). Reduction of the ester (1.29 g) with lithium aluminum deuteride using standard procedures<sup>35</sup> afforded 2-methyl-5-hydroxymethyl- $d_2$ -bromobenzene in 84% yield (0.96 g) after Kugelrohr distillation (110 °C (10 mm)). Treatment of the deuterated alcohol (0.80 g) with  $PMe_3$  in  $CCl_4$ <sup>36</sup> followed by solvent removal, ether extraction, and concentration afforded 2-methyl-5-chloromethyl- $d_2$ -bromobenzene in 90% crude yield. Reduction of the crude alkyl chloride with lithium triethylborodeuteride in ether followed by a standard aqueous workup afforded the desired 2-bromo- $\alpha,\alpha,\alpha$ -trideuterio-*p*-xylene in 83% overall yield from the benzylic alcohol. The product was purified by preparative gas chromatography prior to use (6 ft  $\times$  1/4 in. 10% SE-30/Chromosorb WAW, 140 °C, 20 mL/min).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.351 (s, 3 H), 7.001 (dd,  $J$  = 7.7, 1.2 Hz, 1 H), 7.105 (d,  $J$  = 7.6 Hz, 1 H), 7.358 (d,  $J$  = 0.9 Hz, 1 H).

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loan of rhodium trichloride. We gratefully acknowledge valuable discussions with Prof. R. S. Eisenberg, Prof. J. A. Kampmeier, and Prof. G. McLendon concerning the thermodynamic considerations in this work.

**Registry No.** 1, 84624-01-1; 2, 81971-46-2; 2- $d_5$ , 88704-00-1; 2- $d_5$  (ortho isomer), 88704-33-0; 2- $d_5$  (meta isomer), 88704-34-1; 2- $d_5$  (para isomer), 88704-35-2; 2- $d_6$ , 84624-02-2; 3, 88704-01-2; 4, 84624-03-3; *p*-6, 81971-48-4; *m*-6, 81971-47-3; 7, 84624-04-4; 8a, 88704-02-3; 8b, 88704-03-4; 10, 88704-04-5;  $(C_5Me_5)Rh(PMe_3)(C\equiv CHCH_2CH_2CH_2)H$ , 88704-05-6;  $(C_5Me_5)Rh(PMe_3)(CH=CHCH_2CH_2CH_2)$ , 88704-06-7;  $(C_5Me_5)Rh(PMe_3)[2,5-C_6H_3(i-Pr)_2]H$ , 88704-07-8;  $(C_5Me_5)Rh(PMe_3)(3,5-C_6H_3Me_2)H$ , 88704-08-9;  $(C_5Me_5)Rh(PMe_3)(3,4-C_6H_3Me_2)H$ , 88704-09-0;  $(C_5Me_5)Rh(PMe_3)(p-C_6H_4CF_3)H$ , 88704-10-3;  $(C_5Me_5)Rh(PMe_3)(m-C_6H_4CF_3)H$ , 88704-11-4;  $(C_5Me_5)Rh(PMe_3)(m-C_6H_4OMe)H$ , 88704-12-5;  $(C_5Me_5)Rh(PMe_3)(p-C_6H_4OMe)H$ , 88704-13-6;  $(C_5Me_5)Rh(PMe_3)(o-C_6H_4OMe)H$ , 88704-14-7;  $[(C_5Me_5)Rh(PMe_3)(C_6H_5)(THF)]^+[PF_6]^-$ , 88704-16-9;  $[(C_5Me_5)Rh(PMe_3)(p-tolyl)(THF)]^+[PF_6]^-$ , 88704-17-0;  $[(C_5Me_5)Rh(PMe_3)(2,5-C_6H_3Me_2)(THF)]^+[PF_6]^-$ , 88704-19-2;  $[(C_5Me_5)Rh(PMe_3)(2-CH_3-5-CP_3-C_6H_3)(THF)]^+[PF_6]^-$ , 88704-21-6;  $[(C_5Me_5)Rh(PMe_3)(C_6D_5)(THF)]^+[PF_6]^-$ , 88704-23-8;  $[(C_5Me_5)Rh(PMe_3)(C\equiv CHCH_2CH_2CH_2)(THF)]^+[PF_6]^-$ , 88704-25-0;  $(C_5Me_5)Rh(PMe_3)Cl_2$ , 80298-79-9;  $(C_5Me_5)Rh(PMe_3)Br_2$ , 88704-26-1;  $(C_5Me_5)Rh(PMe_3)I_2$ , 88704-27-2;  $(C_5Me_5)Rh(PMe_3)(C_6H_5)Cl$ , 88704-28-3;  $(C_5Me_5)Rh(PMe_3)(C_6H_5)Br$ , 81971-44-0;  $(C_5Me_5)Rh(PMe_3)(C_6H_5)I$ , 88704-29-4;  $(C_5Me_5)Rh(PMe_3)(CH_3)Cl$ , 84623-98-3;  $(C_5Me_5)Rh(PMe_3)(p-tolyl)Br$ , 81971-45-1;  $(C_5Me_5)Rh(PMe_3)(2-CH_3-5-CD_3-C_6H_3)Br$ , 88704-30-7;  $(C_5Me_5)Rh(PMe_3)(C\equiv CH)$ , 88704-31-8;  $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ , 22722-98-1;  $Li^+[HBtEt_3]^-$ , 22560-16-3;  $Li^+[HB(sec-Bu)_3]^-$ , 38721-52-7;  $K^+[HB(O-i-Pr)_3]^-$ , 42278-67-1;  $AgPF_6$ , 26042-63-7;  $C_6D_5H$ , 13657-09-5; toluene, 108-88-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; propane, 74-98-6; cyclopentane, 287-92-3; 1,4-di-*tert*-butylbenzene, 1012-72-2; cyclopentene, 142-29-0;  $\alpha,\alpha,\alpha$ -trideuterio-2-bromo-*p*-xylene, 88704-32-9;  $C_6H_6$ , 71-43-2.

## Stepwise Reductive Acidolysis of $OsH_4(PMe_2Ph)_3$ . Mechanism of Hydrogen Elimination/Ligand Addition

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**Abstract:** The polyhydride  $OsH_4(PMe_2Ph)_3$  (**1**) reacts with either  $HBf_4 \cdot OEt_2$  or  $Ph_3CPF_6$  and  $CH_3CN$  to give [*fac*- $Os(PMe_2Ph)_3(CH_3CN)_3$ ] $X_2$  (**6**) ( $X = BF_4, PF_6$ ). The acidolysis reaction proceeds in stepwise fashion through several intermediate species. Using limiting reagent quantities (acid and  $CH_3CN$ ), it is possible to either isolate or spectrally characterize  $OsH_5(PMe_2Ph)_3^+$  (**2**),  $OsH_3(PMe_2Ph)_3(CH_3CN)^+$  (**3**), *mer,cis*- $OsH(PMe_2Ph)_3(CH_3CN)_2^+$  (**4**), and *mer*- $Os(PMe_2Ph)_3(CH_3CN)_3^{2+}$  (**5**) on the pathway to **6**. Additionally, kinetic and labeling studies indicate that  $H_2$  substitution by  $CH_3CN$  occurs via a preequilibrium  $H_2$  loss and subsequent trapping by  $CH_3CN$ . The X-ray diffraction structure of **6** ( $X = PF_6$ ) is also reported.

The syntheses and certain reaction pathways of transition-metal phosphine polyhydrides are becoming increasingly well developed. This is particularly true for compounds containing third-row transition metals, in addition to various  $MoH_4(PR_3)_4$  derivatives.<sup>1</sup> The polyhydrides are characterized by high formal metal oxidation states and coordination numbers, as well as a strong adherence to the 18-electron rule. This latter restriction, coupled with the relative kinetic inertness of third-row compounds, has led to diverse

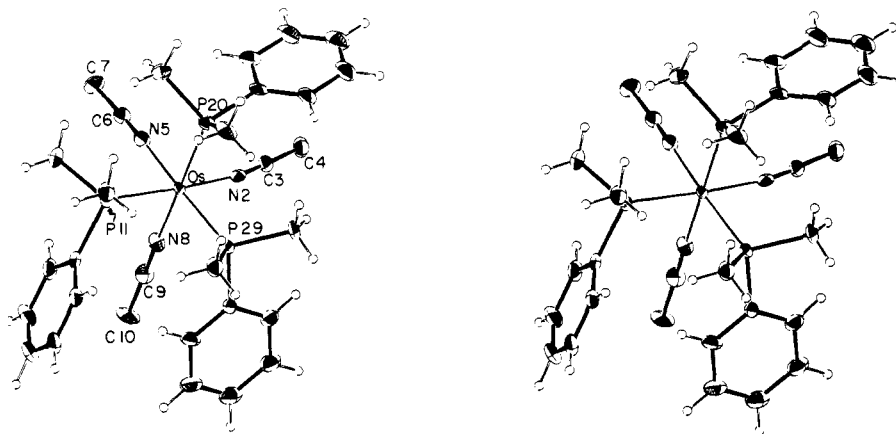
efforts aimed at activating polyhydrides for intermolecular processes. One approach has been complexation with Lewis acids in the hope of enhancing the susceptibility of the transition-metal center to nucleophilic attack;<sup>2-6</sup> it is not always clear that the

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**Figure 1.** ORTEP stereodrawing of *fac*-Os(NCMe)<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub><sup>2+</sup>, showing atom labeling for the inner coordination sphere. This view is down the idealized C<sub>3</sub> axis of the *fac*-OsN<sub>3</sub>P<sub>3</sub> unit.

resulting complex is more reactive than its precursor.<sup>5</sup>

More success has been realized in systems designed to create coordinatively unsaturated intermediate fragments. This process is thermally induced in the high-valent ReH<sub>7</sub>(PR<sub>3</sub>)<sub>2</sub>, which readily loses H<sub>2</sub> to give (initially) reactive [ReH<sub>5</sub>(PR<sub>3</sub>)<sub>2</sub>]<sup>7,8</sup> For thermally stable polyhydrides, photochemical activation often leads to efficient loss of either H<sub>2</sub><sup>9,10</sup> or coordinated phosphine.<sup>11,12</sup> The usefulness of these approaches has been amply demonstrated in C-H activation processes<sup>7b,c,11b,13-16</sup> and the transformations of unsaturated organics.<sup>7a,d,8</sup>

Two other, somewhat related, means of activating polyhydrides are oxidation<sup>17,18</sup> and acidolysis.<sup>18b,19-22</sup> Although added acid

**Table I.** Crystal Data for [Os(NCMe)<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>

empirical formula	OsCl <sub>2</sub> P <sub>3</sub> F <sub>12</sub> N <sub>3</sub> C <sub>31</sub> H <sub>35</sub>
color	colorless
crystal dimensions, mm	0.12 × 0.12 × 0.13
space group	<i>P</i> $\bar{1}$
cell dimensions (at -160 °C; 42 reflections)	
<i>a</i> , Å	19.653 (4)
<i>b</i> , Å	11.407 (1)
<i>c</i> , Å	10.201 (1)
$\alpha$ , deg	67.03 (1)
$\beta$ , deg	95.69 (1)
$\gamma$ , deg	94.96 (1)
molecules/cell	2
volume, Å <sup>3</sup>	2092.28
calcd density, g/cm <sup>3</sup>	1.736
wavelength, Å	0.71069
mol wt	1093.59
linear absorption coeff, cm <sup>-1</sup>	34.5
total no. of reflections collected (6° ≤ 2θ ≤ 45°)	5951
no. of unique intensities	5477
no. of <i>F</i> > 0.0	5302
no. with <i>F</i> > σ( <i>F</i> )	5185
no. with <i>F</i> > 2.33σ( <i>F</i> )	5023
final residuals	
<i>R</i> ( <i>F</i> )	0.0506
<i>R</i> <sub>w</sub> ( <i>F</i> )	0.0514
goodness of fit for the last cycle	1.489
maximum Δ/σ for last cycle	0.05

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(particularly acids with noncoordinating anions) can lead to simple protonation (eq 1),<sup>20a,22,23</sup> in most cases either oxidation or aci-



dolysis results in multiple loss of hydrides (presumably as H<sub>2</sub>) if suitable incc ning ligands are available.<sup>16,20,21</sup> As such, reactions of this type are mechanistically complex and seldom lend themselves to elucidation of discrete reaction steps. Herein we report our study of the acidolysis of OsH<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>,<sup>19a</sup> a system that contradicts the above generalizations only in the sense that it is amenable to detailed mechanistic inquiry. Specifically, we have observed and characterized (to varying extents) several of the intermediate species on the pathway to multiple hydride loss.

## Results and Discussion

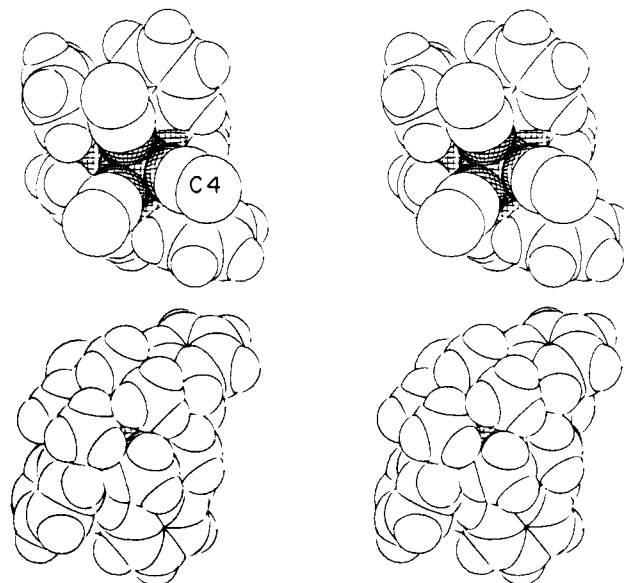
Addition of excess HBF<sub>4</sub>·OEt<sub>2</sub> to a CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN solution of OsH<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> (only sparingly soluble in neat CH<sub>3</sub>CN) results

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**Table II.** Fractional Coordinates and Isotropic Thermal Parameters for  $[\text{Os}(\text{NCMe})_3(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2 \cdot \text{CH}_2\text{Cl}_2$ 

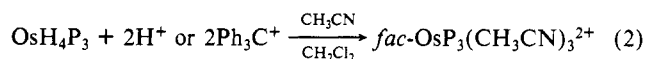
	$10^4x$	$10^4y$	$10^4z$	$10B_{\text{iso}}, \text{\AA}^2$
Os(1)	2369.1 (2)	1934.4 (3)	3209.7 (4)	11
N(2)	2156 (4)	3382 (7)	3867 (8)	15
C(3)	1979 (5)	4231 (9)	4065 (9)	17
C(4)	1734 (5)	5275 (10)	4310 (10)	23
N(5)	1798 (4)	3018 (7)	1341 (8)	19
C(6)	1533 (5)	3698 (9)	313 (10)	20
C(7)	1185 (5)	4535 (10)	-1034 (10)	26
N(8)	3194 (4)	3142 (7)	2270 (8)	18
C(9)	3669 (5)	3748 (9)	1813 (10)	21
C(10)	4296 (5)	4496 (11)	1204 (12)	29
P(11)	2585 (1)	546 (2)	2137 (2)	16
C(12)	2417 (5)	-1174 (9)	3042 (10)	21
C(13)	2096 (5)	854 (10)	416 (10)	24
C(14)	3465 (5)	665 (9)	1615 (9)	18
C(15)	3669 (5)	1732 (10)	433 (10)	22
C(16)	4341 (5)	1872 (10)	27 (11)	27
C(17)	4807 (5)	965 (11)	815 (11)	28
C(18)	4605 (5)	-103 (10)	1962 (11)	27
C(19)	3931 (5)	-244 (10)	2353 (10)	21
P(20)	1372 (1)	785 (2)	4149 (3)	17
C(21)	747 (5)	482 (11)	2859 (12)	28
C(22)	1392 (5)	-798 (10)	5582 (11)	25
C(23)	865 (4)	1664 (9)	4856 (11)	20
C(24)	495 (5)	2667 (10)	3911 (12)	26
C(25)	127 (5)	3385 (11)	4396 (13)	33
C(26)	124 (5)	3081 (11)	5849 (14)	33
C(27)	496 (5)	2081 (11)	6806 (13)	32
C(28)	865 (5)	1373 (10)	6325 (11)	24
P(29)	3050 (1)	1044 (2)	5308 (2)	14
C(30)	3286 (5)	-612 (9)	5991 (10)	22
C(31)	2726 (5)	1139 (10)	6892 (10)	21
C(32)	3894 (4)	1863 (8)	5254 (9)	15
C(33)	4032 (5)	2787 (9)	5837 (10)	21
C(34)	4665 (5)	3422 (10)	5768 (11)	27
C(35)	5168 (5)	3176 (11)	5057 (11)	29
C(36)	5044 (5)	2287 (10)	4452 (11)	26
C(37)	4402 (5)	1631 (10)	4535 (10)	22
Cl(38)	6619 (2)	3754 (3)	-2560 (3)	35
C(39)	7058 (6)	3238 (12)	-865 (12)	37
Cl(40)	6810 (2)	1675 (3)	188 (3)	51
P(41)	6892 (1)	4587 (2)	2591 (3)	21
F(42)	6225 (3)	5394 (6)	2228 (6)	34
F(43)	7559 (3)	3776 (6)	2975 (7)	35
F(44)	7336 (4)	5715 (7)	2857 (8)	43
F(45)	7058 (3)	5206 (6)	954 (6)	36
F(46)	6730 (3)	3946 (9)	4220 (6)	54
F(47)	6436 (4)	3477 (6)	2280 (8)	43
P(48)	808 (2)	7453 (4)	221 (3)	37
F(49)	435 (6)	7042 (12)	-995 (11)	101
F(50)	1178 (5)	7828 (7)	1458 (8)	67
F(51)	302 (8)	6679 (24)	1194 (20)	218
F(52)	1272 (6)	6331 (11)	655 (12)	95
F(53)	421 (9)	8669 (17)	-239 (18)	166
F(54)	1291 (11)	8349 (16)	-814 (16)	171

in moderate gas evolution. At 25 °C this continues for 45–60 min with no visible precipitate. Addition of  $\text{Et}_2\text{O}$  causes prompt precipitation of a colorless solid. The  $^{31}\text{P}$  NMR spectrum of this compound contains a singlet at -36.89 ppm. In addition to P–Ph and P–Me (18 H) resonances, the  $^1\text{H}$  NMR spectrum contains a singlet (9 H) at 2.32 ppm, attributed to  $\text{CH}_3\text{CN}$  ligands. These are also evident as two  $\nu(\text{C}\equiv\text{N})$  bands in the infrared spectrum. There is no evidence of metal-bound hydride anywhere in the  $^1\text{H}$  NMR spectrum. These data are consistent with the formulation  $\text{fac-Os}(\text{PMe}_2\text{Ph})_3(\text{CH}_3\text{CN})_3^{2+}$ , an 18-electron dication. We also found that treatment of  $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$  with  $\text{Ph}_3\text{CPF}_6$  (in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ ) yielded this same complex. In view of the simplicity of the NMR spectra, we sought crystallographic verification of the proposed structure. Suitable crystals (from a  $\text{Ph}_3\text{CPF}_6$  preparation) were obtained by cooling a solution of the compound in a mixture of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$ . The resulting structure corroborated the process shown in eq 2 ( $\text{P} \equiv \text{PMe}_2\text{Ph}$ ). During the course of this work Crabtree and co-workers reported

**Figure 2.** Space-filling model stereodrawings of  $\text{fac-Os}(\text{NCMe})_3(\text{PMe}_2\text{Ph})_3^{2+}$  from two perspectives. Upper: three MeCN ligands project toward viewer (methyl hydrogens not shown). Lower: three  $\text{PMe}_2\text{Ph}$  ligands project toward viewer.**Table III.** Bond Distances (Å) and Angles (deg) for  $[\text{Os}(\text{NCMe})_3(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2 \cdot \text{CH}_2\text{Cl}_2$ 

Distances			
Os–P(11)	2.334 (2)	N(2)–C(3)	1.150 (11)
Os–P(20)	2.329 (2)	N(5)–C(6)	1.139 (12)
Os–P(29)	2.318 (2)	N(8)–C(9)	1.137 (12)
Os–N(2)	2.096 (8)	C(3)–C(4)	1.439 (13)
Os–N(5)	2.097 (8)	C(6)–C(7)	1.473 (14)
Os–N(8)	2.081 (8)	C(9)–C(10)	1.479 (13)
Angles			
P(11)–Os–P(20)	93.3 (1)	P(29)–Os–N(8)	89.8 (2)
P(11)–Os–P(29)	98.3 (1)	N(2)–Os–N(5)	83.1 (3)
P(20)–Os–P(29)	94.7 (1)	N(2)–Os–N(8)	85.2 (3)
P(11)–Os–N(2)	171.6 (2)	N(5)–Os–N(8)	85.0 (3)
P(11)–Os–N(5)	89.3 (2)	Os(1)–N(2)–C(3)	170.7 (7)
P(11)–Os–N(8)	90.6 (2)	Os(1)–N(5)–C(6)	173.5 (8)
P(20)–Os–N(2)	90.3 (2)	Os(1)–N(8)–C(9)	175.9 (8)
P(20)–Os–N(5)	89.9 (2)	N(2)–C(3)–C(4)	178.1 (10)
P(20)–Os–N(8)	173.5 (2)	N(5)–C(6)–C(7)	177.8 (10)
P(29)–Os–N(2)	89.0 (2)	N(8)–C(9)–C(10)	177.8 (11)
P(29)–Os–N(5)	170.9 (2)		

their observation of this same acidolysis reaction;<sup>21b</sup> our results are in agreement with theirs.

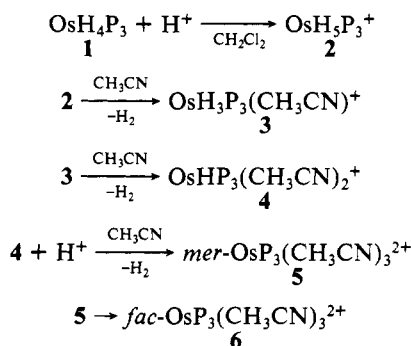


**Structure of  $[\text{fac-Os}(\text{PMe}_2\text{Ph})_3(\text{CH}_3\text{CN})_3](\text{PF}_6)_2$ .** The X-ray diffraction study confirms (Tables I–III and Figures 1 and 2) the facial octahedral geometry indicated by the  $^1\text{H}$  and  $^{31}\text{P}$  NMR data and the  $\text{C}\equiv\text{N}$  infrared data. The colorless crystals yield a lattice with 1 mol of  $\text{CH}_2\text{Cl}_2$  for each osmium, a result that was quantitatively confirmed by  $^1\text{H}$  NMR spectroscopy. The three Os–N distances are identical to within  $2\sigma$ , while the three Os–P distances differ by less than  $5\sigma$ . Among the acetonitrile ligands,  $\text{C}\equiv\text{N}$  and C–CH<sub>3</sub> bond lengths are identical to within  $1\text{--}3\sigma$ , and the  $\text{N}\equiv\text{C}$ –C angles differ insignificantly from  $180^\circ$ . Noteworthy is the manner in which the  $\text{fac-MX}_3\text{Y}_3$  unit deviates from orthogonality in a system where the X ligands are bulky and the Y ligands are slender. The P–Os–P angles predictably increase from  $3$  to  $8^\circ$  above  $90^\circ$ , while the N–Os–N angles decrease from  $5$  to  $7^\circ$  below  $90^\circ$ . However, these distortions occur in a manner such that all cis N–Os–P angles remain at  $90.0 \pm 1.0^\circ$ . The trigonal distortions thus occur so as to avoid any decrease in cis N...P distances.

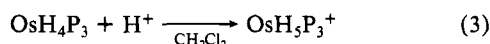
**Mechanism of Acidolysis.** In view of the multistep nature of the conversion of  $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$  to  $\text{fac-Os}(\text{PMe}_2\text{Ph})_3$ –

(CH<sub>3</sub>CN)<sub>3</sub><sup>2+</sup>, we sought information on the sequence of protonation (twice), H<sub>2</sub> elimination (three times), and CH<sub>3</sub>CN addition (three times) steps. The course of the acidolysis process is most conveniently studied via <sup>31</sup>P NMR. Hence, OsH<sub>4</sub>P<sub>3</sub> (<sup>31</sup>P = -28.8 ppm) was dissolved in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (50:50) in an NMR tube, and excess HBF<sub>4</sub>·OEt<sub>2</sub> was added to start the reaction. Initially one observes a singlet resonance at -33.96 ppm, which decays over 20–30 min at room temperature, giving rise to another singlet at -33.80 ppm. This signal also decays over 10–20 min, with a concurrent growth of a singlet at -36.89 ppm, due to formation of *fac*-OsP<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub><sup>2+</sup>. To simplify the discussion of this process we first present a proposed mechanistic pathway (Scheme I). Although the overall conversion of **1** to **6** is portrayed as passing through a large number of intermediates, we have successfully obtained spectroscopic characterization of each numbered species. All contain 18 valence electrons but display varying stabilities and lifetimes. We now present conditions that allowed characterization of the individual species.

Scheme I

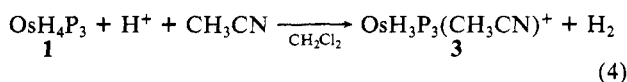


**Protonation of OsH<sub>4</sub>P<sub>3</sub> to [OsH<sub>5</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>](BF<sub>4</sub>) (2).** Douglas and Shaw<sup>19</sup> have presented conductometric evidence for the simple protonation of OsH<sub>4</sub>P<sub>3</sub> with HCl and CF<sub>3</sub>CO<sub>2</sub>H, but the presence of OsH<sub>5</sub>P<sub>3</sub><sup>+</sup> was not spectroscopically verified. Since subsequent chemistry (in Scheme I) seemed to involve CH<sub>3</sub>CN, we carried out the protonation of OsH<sub>4</sub>P<sub>3</sub> in neat CH<sub>2</sub>Cl<sub>2</sub> (eq 3). The <sup>31</sup>P



spectrum showed the transient singlet at -33.96 ppm detected previously in the experiment with excess acid, but it now showed no decay (i.e., in the absence of CH<sub>3</sub>CN). Selective coupling to metal-bound hydrides did lead to a broadened <sup>31</sup>P NMR signal, but the coupling was too small to resolve. At -60 °C, the <sup>31</sup>P{<sup>1</sup>H} spectrum showed a very broad signal, indicating a fluxional process was slowed but not frozen out. The <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 220 MHz) exhibited, in addition to P-Me and P-Ph resonances, a hydride signal at -7.02 ppm. At lower operating frequency (60 MHz) this was resolvable into a quartet with <sup>2</sup>J<sub>P-H</sub> = 4 Hz, consistent with an OsP<sub>3</sub>H<sub>x</sub><sup>+</sup> formulation. Theoretically the value of *x* could be determined by integration of the <sup>1</sup>H NMR spectrum, but we have observed inaccuracies in the integration of compounds like these.<sup>17b</sup> To show that *x* = 5, OsH<sub>4</sub>P<sub>3</sub> was protonated with excess HBF<sub>4</sub>·OEt<sub>2</sub>, and formation of OsP<sub>3</sub>H<sub>5</sub><sup>+</sup> (**2**) was confirmed by <sup>31</sup>P NMR spectroscopy. Excess NEt<sub>3</sub> was then added and another spectrum recorded, showing complete regeneration of OsH<sub>4</sub>P<sub>3</sub>. This was taken as evidence of simple protonation and thus establishes **2** as OsH<sub>5</sub>P<sub>3</sub><sup>+</sup>. Interestingly, if limiting quantities of acid are employed, both OsH<sub>4</sub>P<sub>3</sub> and OsH<sub>5</sub>P<sub>3</sub><sup>+</sup> are observed via <sup>31</sup>P NMR spectroscopy, indicating that this acid-base conjugate pair does not undergo rapid exchange under these conditions.

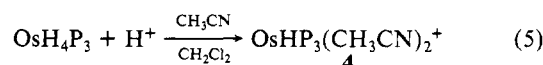
**Spectral Characterization of [OsH<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>(CH<sub>3</sub>CN)](BF<sub>4</sub>) (3).** Considering stoichiometry alone, the production of **3** (Scheme I) requires only 1 equiv each of acid and CH<sub>3</sub>CN. Hence, the reaction (eq 4) was carried out with 1 equiv of acid and only a



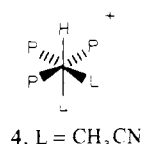
slight excess of CH<sub>3</sub>CN. Subsequent spectra confirmed that further reaction of **3** was negligible with this stoichiometry and at 25 °C.

At 25 °C the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3** displays a singlet at -33.80 ppm. Due to near overlap with the resonance of **2** (-33.96 ppm) a selectively hydride-coupled spectrum could not be obtained. Moreover, the <sup>1</sup>H NMR spectrum indicated the coupling constant (<sup>2</sup>J<sub>P-H</sub>) was very small (vide infra) and probably not resolvable in the <sup>31</sup>P NMR spectrum. The <sup>1</sup>H NMR spectrum showed the aforementioned resonances for **2**, as well as free CH<sub>3</sub>CN (1.97 ppm) and Et<sub>2</sub>O (3.49 (q), 1.15 (t)) from the HBF<sub>4</sub>·OEt<sub>2</sub>. The spectrum of **3** contains P-Ph and P-Me resonances at 7.51 and 1.83 ppm, an Os-H quartet (<sup>2</sup>J<sub>P-H</sub> = 4 Hz) at -10.02 ppm, and a singlet at 2.31 ppm for the CH<sub>3</sub>CN ligand. It should be noted that the facile fluxional process (rapid even at -35 °C) in **3** is entirely consistent with its formulation as a seven-coordinate species. For example, K<sup>+</sup>OsH<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub><sup>-</sup> and OsH<sub>4</sub>P<sub>3</sub> (**1**) are both 18-electron compounds with multiple hydride ligands; the former (six-coordinate) is conformationally rigid at 25 °C<sup>24</sup> while the latter is stereochemically nonrigid.

**Synthesis of [OsH(PMe<sub>2</sub>Ph)<sub>3</sub>(CH<sub>3</sub>CN)<sub>2</sub>](BF<sub>4</sub>) (4).** It is interesting to note that under conditions of excess acid and CH<sub>3</sub>CN, compound **4** (Scheme I) is never observed during the <sup>31</sup>P NMR monitoring of the conversion of **1** to **6**. Since **4** is a monocation and a likely intermediate in the process, we carried out the reaction shown in eq 5 with 1 equiv of HBF<sub>4</sub>·OEt<sub>2</sub> but a large excess of



CH<sub>3</sub>CN; under these conditions, the reaction is observed to proceed through species **2** and **3** (<sup>31</sup>P NMR) but never reaches compound **6**. The product (**4**) exhibits an A<sub>2</sub>B pattern with a doublet at -26.05 ppm and a triplet at -31.40 ppm (<sup>2</sup>J<sub>P-P</sub> = 21 Hz). Selective coupling to the hydride ligand converts the doublet to a doublet of doublets (<sup>2</sup>J<sub>P-H</sub> = 16 Hz) and the triplet to a virtual quartet in which <sup>2</sup>J<sub>P-H</sub> ≈ <sup>2</sup>J<sub>P-P</sub>. The <sup>1</sup>H NMR spectrum shows P-Ph at 7.2–7.6 ppm, P-Me at 1.59 (12 H) and 1.37 ppm (6 H), CH<sub>3</sub>CN at 2.51 and 1.95 ppm, and Os-H at -16.60 ppm (virtual quartet, *J*(apparent) ≈ 15 Hz). Although the A<sub>2</sub>B phosphine pattern could be consistent with either a facial or meridional arrangement of these nuclei, the similar (and somewhat small) P-H coupling constants indicated the hydride was *cis* to all three phosphines. This observation together with the presence of two inequivalent CH<sub>3</sub>CN ligands requires the *mer.cis* structure as shown.



These data are also consistent with data for *mer.cis*-RuH(ttp)(L)<sub>2</sub><sup>+</sup>, in which ttp is PhP(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> and L = CH<sub>3</sub>CN.<sup>25</sup> This compound exhibits a virtual quartet for the hydride with *J*<sub>P-H</sub> ≈ *J*<sub>P-P</sub> = 19 Hz. Further, *mer.cis*-RuH(PPh<sub>3</sub>)<sub>3</sub>(CH<sub>3</sub>CN)<sub>2</sub><sup>+</sup> has been prepared from RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> and Ph<sub>3</sub>CPF<sub>6</sub> in CH<sub>3</sub>CN.<sup>26</sup> We suspected that OsH<sub>4</sub>P<sub>3</sub> could likewise be converted to **4** with 1 equiv of Ph<sub>3</sub>CPF<sub>6</sub>; indeed the reaction proceeds cleanly in this manner, as verified by <sup>31</sup>P NMR spectroscopy.

Crabtree has shown that cationic hydrides of iridium with weakly bound ligands L (IrH<sub>2</sub>L<sub>2</sub>P<sub>2</sub><sup>+</sup>) are active in a wide range of interesting transformations of small organics.<sup>14</sup> However, no such activity was exhibited by **6** or by WH<sub>2</sub>(CH<sub>3</sub>CN)<sub>3</sub>P<sub>3</sub><sup>2+</sup>, ostensibly because the CH<sub>3</sub>CN ligand is too tightly bound.<sup>21</sup> In compound **4**, however, one CH<sub>3</sub>CN is *trans* to a hydride, and previous workers have observed facile dissociation under such

(24) Green, M. A.; Caulton, K. G., unpublished observations.

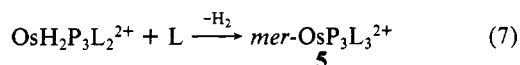
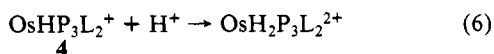
(25) (a) Mazanec, T. J.; Letts, J. B.; Meek, D. W. *J. Chem. Soc., Chem. Commun.* **1982**, 356–358. (b) Letts, J. B.; Mazanec, T. J.; Meek, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 3898–3905. (c) Letts, J. B.; Mazanec, T. J.; Meek, D. W. *Organometallics*, **1983**, *2*, 695–704.

(26) Sanders, J. R. *J. Chem. Soc., Dalton Trans.* **1973**, 743–747.

circumstances.<sup>25,27</sup> Indeed, addition of  $\text{CH}_3\text{CN}$  to an NMR solution of **4** ( $\text{CD}_2\text{Cl}_2$ ) results (within 5 min) in a decrease in the resonance at 2.51 ppm with a concurrent growth of a signal for free  $\text{CH}_3\text{CN}$  at 1.97 ppm, indicating facile exchange. This suggests that **4** may be reactive with other organic nucleophiles.

Finally, we sought evidence that **4** truly lies on the pathway to **6**. In an NMR tube, **4** (prepared with 1 equiv of  $\text{H}^+$ ) was dissolved in a mixture of  $\text{CD}_2\text{Cl}_2$  and  $\text{CD}_3\text{CN}$  and a spectrum recorded. Addition of a second equivalent of  $\text{HBF}_4\cdot\text{OEt}_2$  caused immediate disappearance of **4** ( $^{31}\text{P}$  NMR), ultimately giving **6**, as verified by  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectroscopy.

**Spectral Observation of 5.** When the acidification of **4** was carried out (as above) and monitored via  $^{31}\text{P}$  NMR, we observed an intermediate compound **5** with a lifetime of only a few minutes at room temperature. Like compound **4**, **5** is never observed when  $\text{OsH}_4\text{P}_3$  is converted to **6** with excess acid. Compound **5** exhibits an  $\text{A}_2\text{B}$  pattern in the  $^{31}\text{P}$  NMR spectrum (distinct from that of **4**) with a doublet at -30.5 ppm and a triplet at -40.8 ppm ( $^2J_{\text{P-P}} = 17$  Hz). Unfortunately, this compound is too short-lived for further spectroscopic characterization. Protonation of **4** and loss of  $\text{H}_2$  would presumably occur via two steps (eq 6 and 7). We

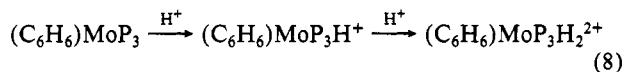


disfavor the identification of **5** as  $\text{OsH}_2\text{P}_3\text{L}_2^{2+}$  because the latter is seven-coordinate and would probably show equivalent phosphines due to rapid fluxionality. Rather, we suspect **5** is the meridional isomer of  $\text{OsP}_3(\text{CH}_3\text{CN})_3^{2+}$ , which rapidly isomerizes to facial **6**. It would appear that the conversions  $4 \rightarrow 5$  and  $5 \rightarrow 6$  proceed at comparable rates (with the former slightly faster) under the conditions employed, since **5** is only observed when large quantities of **4** are initially present.

### General Considerations

The present work exemplifies several interesting points related to polyhydride reaction patterns. First, it has been noted that although cationic dihydrides are somewhat common,<sup>14,28</sup> cationic  $\text{MH}_x\text{L}_y^+$  species with  $x \geq 3$  are relatively rare.<sup>21b</sup> In this work both **2** and **3** are observed, but both readily lose  $\text{H}_2$ , particularly in the presence of potential ligands ( $\text{CH}_3\text{CN}$ ). This reductive elimination is not unexpected in high-valent, highly coordinatively saturated compounds such as these. However, the fact that they proceed slowly enough to observe is a surprising consequence of the kinetic inertness of third-row transition metals. Further, the identification of **2** verifies that when metal d electrons are available, protonolysis seems to occur via a stepwise protonation-elimination sequence. The difference between this pathway and reaction with  $\text{Ph}_3\text{C}^+$  is that the latter appears to proceed via hydride abstraction (possibly via an electron transfer/H atom transfer sequence<sup>18,29</sup>). Thus, while acidolysis converts **1** to **3** via **2**,  $\text{Ph}_3\text{C}^+$  is thought to convert **1** directly to **3**, provided  $\text{CH}_3\text{CN}$  is present. If **1** is treated with  $\text{Ph}_3\text{C}^+$  in neat  $\text{CH}_2\text{Cl}_2$ , the result is a complex mixture of uncharacterized products.

The acidolysis of **1** to **6** involves two protonation steps and three  $\text{H}_2$  eliminations. Protonation of cationic  $\text{Rh}(\text{diphos})_2^+$  has been reported;<sup>30</sup> similarly, (arene) $\text{Mo}(\text{PR}_3)_3$  can be protonated once in dilute acid and twice in concentrated acid (eq 8).<sup>31</sup> In the



(27) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134-2143.

(28) (a) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2143-2147. (b) Schrock, R. R.; Osborn, J. A. *Ibid.* **1976**, *98*, 4450-4455. (c) Shapley, J. R.; Schrock, R. R.; Osborn, J. A. *Ibid.* **1969**, *91*, 2816-2817. (d) Schrock, R. R.; Osborn, J. A. *Ibid.* **1971**, *93*, 2397-2407.

(29) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570-5572.

(30) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055-8057.

Table IV. Kinetics of Reaction of **2** with  $\text{CH}_3\text{CN}^a$

solution	$[\text{CH}_3\text{CN}]$ , M	$k_{\text{obsd}}$ , $\text{s}^{-1}$
1	0.69	$(2.8 \pm 0.2) \times 10^{-4}$
2	3.5	$(3.1 \pm 0.2) \times 10^{-4}$

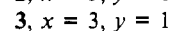
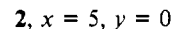
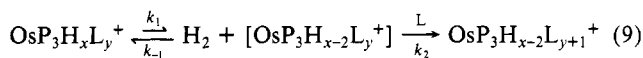
<sup>a</sup> Both solutions 0.093 M in **2**,  $\text{CH}_2\text{Cl}_2$  solvent, 20 °C.

<sup>b</sup> Determined from the least-squares slope of plots of  $\ln [(2)_0/(2)_t]$  vs. time. Errors are estimated uncertainties of slopes.

present system this sequence is clearly not operative. As shown in Scheme I, we observe single protonation to  $\text{OsH}_5\text{P}_3^+$  (**2**), which must then lose two molecules of  $\text{H}_2$  and gain two  $\text{CH}_3\text{CN}$  ligands before the second protonation occurs. The ready isolation of monocation **4** provides strong evidence for this. As such, we concur with the postulate that the  $\sigma$ -donor  $\text{CH}_3\text{CN}$  ligands in **4** are required to render the cationic osmium center basic enough for a second protonation.<sup>21b</sup>

A final point concerns the conversions  $2 \rightarrow 3$  and  $3 \rightarrow 4$ . As shown in Scheme I, both are thought to involve reaction with  $\text{CH}_3\text{CN}$ . Again, this is verified in the first case by the long lifetime of **2** in neat  $\text{CH}_2\text{Cl}_2$ . While it appears that incoming ligand serves to induce  $\text{H}_2$  elimination, the exact mechanism of this transformation is unclear. Since this is a reaction of fundamental importance in polyhydride chemistry, further mechanistic definition was desirable. We envisioned two likely pathways and chose to study the conversion of **2** to **3** since **2** is more readily available in pure form. One possible mechanism would be a  $\text{S}_{\text{N}}2$  process, first order in  $\text{CH}_3\text{CN}$ , proceeding through the transition state  $[\text{OsH}_5\text{P}_3(\text{CH}_3\text{CN})^+]^{\ddagger}$  of unspecified structure and bonding.

The second mechanistic alternative is depicted in eq 9 and



involves an equilibrium  $\text{H}_2$  loss to give a reduced osmium compound. This 16-electron transient is expected to be very reactive and the equilibrium should lie well to the left. Upon addition of L, the reduced species is trapped rapidly to give the resulting product. Any ability of  $\text{CH}_2\text{Cl}_2$  to stabilize the intermediate is expected to have little effect on the process since  $\text{CH}_3\text{CN}$  should displace  $\text{CH}_2\text{Cl}_2$  very readily.<sup>32</sup>

We have employed two probes to distinguish the mechanistic possibilities. Specifically, the  $\text{S}_{\text{N}}2$  process should exhibit a rate dependence on the concentrations of both **2** and  $\text{CH}_3\text{CN}$ , or overall second-order behavior. The mechanism in eq 9 should follow the rate equation in eq 10, derived by applying the steady-state ap-

$$-\frac{d[\mathbf{2}]}{dt} = k_1[\mathbf{2}] \left[ 1 - \frac{k_{-1}[\text{H}_2]}{k_2[\text{L}] + k_{-1}[\text{H}_2]} \right] \quad (10)$$

proximation to the 16-electron intermediate. In the limiting case where  $k_2[\text{L}] \gg k_{-1}[\text{H}_2]$ , eq 10 reduces to eq 11, indicating an

$$-d[\mathbf{2}]/dt = k_1[\mathbf{2}] \quad (11)$$

overall first-order process which is independent of  $\text{CH}_3\text{CN}$  concentration. Thus, the process in eq 9 reduces to a two-step reaction in which the first step is rate limiting. The above assumption is reasonable since the reaction is carried out under a  $\text{N}_2$  atmosphere at ambient pressure. Thus the concentration of  $\text{H}_2$  in solution is considerably lower than that of  $\text{CH}_3\text{CN}$ .

The kinetic order of the reaction (**2** with  $\text{CH}_3\text{CN}$ ) with respect to  $\text{CH}_3\text{CN}$  was determined at 20 °C. This was conveniently achieved by monitoring the disappearance of **2** (as well as the appearance of **3** and **6**) via  $^{31}\text{P}$  NMR spectroscopy. Rates were

(31) Green, M. L. H.; Mitchard, L. C.; Silverthorn, W. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1361-1363.

(32) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361-1366.

obtained with a 4.5- and 23-fold excess of  $\text{CH}_3\text{CN}$  (vs. **2**), and the resulting values of  $k_{\text{obsd}}$  are given in Table IV. Two observations are noteworthy. First, both reactions followed first-order kinetics over 2–3 half-lives, even though the first reaction did not involve pseudo-first-order conditions; i.e., there was not a large excess of  $\text{CH}_3\text{CN}$ . Second, the two rates are equal to within ca. 10%; a first-order dependence on  $\text{CH}_3\text{CN}$  would have resulted in a 5- to 6-fold difference in  $k_{\text{obsd}}$  for the two reactions. We assume that the small difference reflects the accuracy of the method and consider the reaction rate to be independent of  $\text{CH}_3\text{CN}$  concentration.

It is possible to augment the kinetic evidence for the pre-equilibrium mechanism in eq 9 by direct detection of the equilibrium itself. This equilibrium, if it exists, provides a mechanism for exchange of hydride ligands in  $\text{OsH}_3\text{P}_3^+$  with  $\text{D}_2$ , without requiring the presence of  $\text{CH}_3\text{CN}$ . Thus,  $\text{OsH}_4\text{P}_3$  (**1**) was protonated with  $\text{HBF}_4\cdot\text{OEt}_2$  (2.5 equiv) in  $\text{CH}_2\text{Cl}_2$  and stirred under 400 psi of  $\text{D}_2$  for 1 h. At that time excess  $\text{NEt}_3$  was added and the resulting **1** analyzed for deuterium content. The  $^2\text{D}$  NMR spectrum exhibited a signal at ca.  $-9.0$  ppm, indicative of Os–D. There was no evidence of deuterium in the phosphine ligands. The proton spectrum of **1** was then integrated to determine the approximate extent of D incorporation; this indicated a 70% loss of Os–H in favor of Os–D. Thus, both the kinetics and the deuterium labeling study favor eq 9 as the pathway from **2** to **3**.<sup>34</sup> Acetonitrile thus functions to trap the product of a dihydrogen reductive elimination equilibrium and does not actively displace  $\text{H}_2$ .

## Summary

The conversion of  $\text{OsH}_4\text{P}_3$  (**1**) to  $\text{fac-OsP}_3(\text{CH}_3\text{CN})_3^{2+}$  (**6**) is a multistep process involving several intermediates. This multiple loss of hydride ligands (as  $\text{H}_2$ ) appears to be a general reaction of polyhydrides, induced by acidolysis, hydride abstraction, or oxidation. Using combinations of limiting reagent concentrations and/or low temperatures we have been able to isolate or spectroscopically observe many of these intermediate species. From these studies several characteristics of osmium polyhydrides have been identified. First, although the overall conversion **1**  $\rightarrow$  **6** involves two protonations, these occur in separated (i.e., not consecutive) steps. The second protonation is only observed after formation of  $\text{OsHP}_3(\text{CH}_3\text{CN})_2^+$ , apparently facilitated by the electron-donating ability of  $\text{CH}_3\text{CN}$ . Also, osmium compounds with coordination number greater than six show a marked tendency toward fluxionality while six-coordinate complexes are rigid. Such rigidity may account for the stereospecificity of the acidolysis of **4** (mer,cis) to **5** (mer) rather than directly to **6** (fac). Further, the reactions observed here show a tendency toward achieving octahedral coordination (within the constraints of the 18-electron rule) when suitable reagent stoichiometries are provided. Finally, the favorable (i.e., sluggish) kinetics of this particular system have allowed elucidation of several reactivity patterns of polyhydrides. These may serve as an acceptable model for acidolysis reactions of more labile systems, as well as for fundamental polyhydride transformations other than acidolysis.

## Experimental Section

All manipulations were carried out under a  $\text{N}_2$  atmosphere by using standard Schlenk techniques. Solid transfers were accomplished in a Vacuum Atmospheres Corp. glovebox. Methylene chloride (Aldrich) and acetonitrile (Aldrich) were distilled (under  $\text{N}_2$ ) from  $\text{P}_2\text{O}_5$  and  $\text{CaH}_2$ , respectively, and stored over Linde 4A molecular sieves.  $\text{Ph}_3\text{CPF}_6$  (Aldrich) was recrystallized from  $\text{CH}_2\text{Cl}_2$  prior to use and stored under  $\text{N}_2$ .  $\text{HBF}_4\cdot\text{OEt}_2$  (Aldrich) was used as received and transferred under

a  $\text{N}_2$  purge.  $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$  was synthesized according to the literature method,<sup>19a</sup> starting from  $\text{OsO}_4$  (Johnson-Matthey).

$^{31}\text{P}$  NMR spectra were obtained on a Varian XL-100 instrument (FT, 40.5 MHz). Negative chemical shifts are upfield from external 85%  $\text{H}_3\text{PO}_4$ .  $^1\text{H}$  NMR spectra were obtained on a Varian instrument (CW, 220 MHz). IR spectra were recorded on a Perkin-Elmer 283 instrument.

**Synthesis of [*fac*-Os(PMe<sub>2</sub>Ph)<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub> (**6**).** In the glovebox, 200 mg (0.33 mmol) of  $\text{OsH}_4\text{P}_3$  was weighed into a Schlenk flask. On a Schlenk line, 5 mL each of  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  was added. Similarly, 75  $\mu\text{L}$  (0.12 g, 0.74 mmol) of  $\text{HBF}_4\cdot\text{OEt}_2$  was added, and the solution was stirred at room temperature. When gas evolution had ceased (ca. 20 min), 20 mL of diethyl ether was added slowly. The resulting colorless solid was filtered and washed with ether. IR (KBr):  $\nu(\text{CN})$  2292 (w), 2310 (w)  $\text{cm}^{-1}$ ,  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ):  $-36.89$  (s) ppm.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.26 (m, P–Ph), 2.32 (s, 9 H,  $\text{CH}_3\text{CN}$ ), 2.05 (d, 18 H, P–Me,  $J_{\text{PH}} = 8$  Hz). When **6** was prepared with  $\text{CD}_3\text{CN}$ , the singlet at  $\delta$  2.32 was absent.

Alternatively, **6** was prepared as the  $\text{PF}_6^-$  salt from  $\text{Ph}_3\text{CPF}_6$ . In a Schlenk flask was prepared a solution of 300 mg (0.8 mmol) of  $\text{Ph}_3\text{CPF}_6$  in 10 mL of  $\text{CH}_3\text{CN}$ . A second solution of 250 mg (0.41 mmol) of  $\text{OsH}_4\text{P}_3$  in 8 mL each of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  was added slowly via an addition funnel. Addition was stopped when the yellow color of  $\text{Ph}_3\text{CPF}_6$  disappeared. The resulting solution was stripped in vacuo and the residue washed with 10 mL of toluene (to remove  $\text{Ph}_3\text{CH}$  and unreacted  $\text{OsH}_4\text{P}_3$ ). Crystals for X-ray diffraction were obtained by slowly cooling ( $-20^\circ\text{C}$ ) a solution of **6** ( $\text{PF}_6^-$ ) in 90:10  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ . The compound prepared this way had spectral identical with that of the acidolysis product but also showed a  $\text{PF}_6^-$  resonance ( $-144.5$  ppm, septet,  $J_{\text{P-F}} = 708$  Hz).

**X-ray Crystallography.** A suitable sample was cleaved from a larger crystal and transferred to the goniostat by using standard inert-atmosphere techniques. A systematic search of a limited hemisphere of reciprocal space revealed no systematic absences or symmetry, indicating a triclinic lattice. Parameters of the data collection<sup>33</sup> are shown in Table I. No absorption correction was applied. The structure was solved by Patterson and Fourier techniques, followed by full-matrix refinement. A stoichiometric solvent ( $\text{CH}_2\text{Cl}_2$ ) of crystallization was present. A difference Fourier phased on all non-hydrogen atoms clearly revealed hydrogen atoms with the exception of those on the MeCN ligands. Final cycles included hydrogens (except those of MeCN) as fixed-atom contributors in idealized (C–H distance = 0.95 Å) positions. A final difference Fourier indicated hydrogen positions for one of the MeCN ligands and was otherwise featureless.

The results of the structural study are shown in Tables II and III and Figures 1 and 2. Further details (including peripheral ligand,  $\text{PF}_6^-$ , and  $\text{CH}_2\text{Cl}_2$  parameters) are available as Supplementary Material.

**Synthesis of [*mer,cis*-OsH(PMe<sub>2</sub>Ph)<sub>3</sub>(CH<sub>3</sub>CN)<sub>2</sub>](BF<sub>4</sub>) (**4**).** In the glovebox, 200 mg (0.33 mmol) of  $\text{OsH}_4\text{P}_3$  was added to a Schlenk flask. On the Schlenk line, 5 mL each of  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  was added, followed by 35  $\mu\text{L}$  (58 mg, 0.36 mmol) of  $\text{HBF}_4\cdot\text{OEt}_2$ . The solution was stirred at room temperature for 45 min and then stripped to dryness in vacuo. The residue was washed with 10 mL of ether, yielding a colorless oily solid. Although the solid was greater than 90% pure ( $^{31}\text{P}$  NMR), it was difficult to isolate **4** without traces of **3** and **6** present.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $-26.05$  (d),  $-31.40$  (t) ( $J_{\text{PP}} = 21$  Hz) ppm,  $^{31}\text{P}$  NMR (selectively coupled to hydrides) ( $\text{CD}_2\text{Cl}_2$ ):  $-26.05$  (d of d,  $J_{\text{PH}} = 16$  Hz),  $-31.40$  (virtual q, apparent  $J_{\text{P-H}} = 16$  Hz) ppm.  $^1\text{H}$  NMR:  $\delta$  7.2–7.6 (m, P–Ph), 2.51 (s, 3 H,  $\text{CH}_3\text{CN}$  trans to H), 1.95 (s, 3 H,  $\text{CH}_3\text{CN}$ ), 1.59 (d, 12 H, P–Me,  $J_{\text{PH}} = 11$  Hz), 1.37 (d, 6 H, P–Me,  $J_{\text{PH}} = 9$  Hz),  $-16.60$  (virtual q, 1 H, Os–H, apparent  $J = 16$  Hz). Addition of  $\text{CD}_3\text{CN}$  caused a decrease in the signal at 2.51 ppm, with evidence of free  $\text{CH}_3\text{CN}$  at 1.97 ppm. The resonance at 1.95 ppm was unaffected.

**Spectral Observation of [*OsH<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>](BF<sub>4</sub>)*** (**2**).  $\text{OsH}_4\text{P}_3$  (100 mg, 0.16 mmol) was added to an NMR tube and dissolved in  $\text{CD}_2\text{Cl}_2$ . To this solution was added 20  $\mu\text{L}$  (30 mg, 0.21 mmol) of  $\text{HBF}_4\cdot\text{OEt}_2$ . The resulting compound (formed quantitatively ( $^{31}\text{P}$ )) was stable in solution for hours.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $-33.96$  (s) ppm. Hydride coupling was not resolved but led to significant broadening of the observed singlet.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.47 (m, P–Ph), 1.78 (d, P–Me,  $J_{\text{PH}} = 8$  Hz),  $-7.02$  (q, Os–H,  $J_{\text{PH}} = 4$  Hz). Addition of excess  $\text{NEt}_3$  to this solution resulted in regeneration of  $\text{OsH}_4\text{P}_3$  ( $^{31}\text{P}$  =  $-28.80$ ) with no phosphorus-containing byproducts.

**Spectral Observation of [*OsH<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>(CH<sub>3</sub>CN)](BF<sub>4</sub>)*** (**3**).  $\text{OsH}_4\text{P}_3$  (60 mg, 0.10 mmol) was added to an NMR tube and dissolved in  $\text{CD}_2\text{Cl}_2$ . To this solution was added 15  $\mu\text{L}$  (25 mg, 0.15 mmol) of  $\text{HBF}_4\cdot\text{OEt}_2$ . The tube was immersed in a  $-78^\circ\text{C}$  slush bath, and 10  $\mu\text{L}$  of  $\text{CH}_3\text{CN}$  was added. The sample was immediately inserted into the NMR probe cooled to  $-35^\circ\text{C}$  for a  $^{31}\text{P}$  NMR spectrum. This showed overlapping singlets for **2** ( $-33.96$  ppm) and **3** ( $-33.80$  ppm). Subsequently  $^1\text{H}$  NMR data were obtained at  $25^\circ\text{C}$ . In addition to resonances

(33) Details of the data collection, processing, and refinement techniques are given in: Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

(34) A referee has suggested that the available data are consistent with a pre-equilibrium in eq 9 ( $x = 5$ ,  $y = 0$ ) with dissociation of  $\text{PMe}_2\text{Ph}$  instead of  $\text{H}_2$ . We are less attracted to this possibility since  $\text{PMe}_2\text{Ph}$ , once dissociated, would probably not be competitive with the 23-fold excess of MeCN for recoordination to osmium; the predicted bis(phosphine) complexes were never observed.

of **2**, free CH<sub>3</sub>CN (1.97 ppm), and Et<sub>2</sub>O (3.49 (q), 1.15 (t)), the resonances for **3** were observed. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.51 (m, P-Ph), 2.31 (s, CH<sub>3</sub>CN), 1.63 (d, P-Me, *J*<sub>PH</sub> = 8 Hz), -10.02 (q, Os-H, *J*<sub>PH</sub> = 4 Hz).

**Kinetic Studies.** In the glovebox, 225 mg (0.37 mmol) of OsH<sub>4</sub>P<sub>3</sub> was weighed and dissolved in 2.0 mL of CH<sub>2</sub>Cl<sub>2</sub> (0.19 M). Under N<sub>2</sub> purge, 80 μL of HBF<sub>4</sub>·OEt<sub>2</sub> (0.82 mmol) was added. The excess was employed to ensure production of only **3** and **6** (singlets in <sup>31</sup>P); the A<sub>2</sub>B pattern of **4** would be more difficult to integrate. The above solution was transferred to two NMR tubes (0.5 mL each). To the first was added 110 μL of a 4:1 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN solution (0.42 mmol of CH<sub>3</sub>CN, 0.69 M), and the reaction was monitored via <sup>31</sup>P{<sup>1</sup>H} NMR (20 °C). To the second tube was added 110 μL of neat CH<sub>3</sub>CN (2.12 mmol of CH<sub>3</sub>CN, 3.5 M), and the reaction was monitored similarly. Both reactions lasted 1–1.5 h, and spectra were recorded (15 s acquisition time) every 5–10 min. The rate of disappearance of **2** exhibited first-order behavior and the rate constant *k*<sub>obsd</sub> (= *k*<sub>1</sub>, eq 9) was determined as the slope of a plot

of ln [(2)<sub>0</sub>/(2)<sub>*t*</sub>] vs. time; data are given in Table IV.

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**Registry No.** **1**, 24228-57-7; **2** (BF<sub>4</sub>), 88703-91-7; **3** (BF<sub>4</sub>), 88703-93-9; **4** (BF<sub>4</sub>), 88703-95-1; **5**, 88764-07-2; **6** (PF<sub>6</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>, 88703-96-2; **6** (PF<sub>6</sub>)<sub>2</sub>, 88703-89-3; **6** (BF<sub>4</sub>)<sub>2</sub>, 88129-95-7; HBF<sub>4</sub>·OEt<sub>2</sub>, 67969-82-8; Ph<sub>3</sub>CPF<sub>6</sub>, 437-17-2; CH<sub>3</sub>CN, 75-05-8.

**Supplementary Material Available:** Anisotropic temperature factors, distances and angles within the PMe<sub>2</sub>Ph, PF<sub>6</sub><sup>−</sup>, and CH<sub>2</sub>Cl<sub>2</sub> moieties, and observed and calculated structure factors for [Os-(NCMe)<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (36 pages). Ordering information is given on any current masthead page.

## Structural Phase Transitions in Dihalo(*N,N'*-disubstituted-diazabutadiene)nickel Complexes. Structures of Bis[dibromo(*N,N'*-di-*tert*-butyldiazabutadiene)nickel] and Dibromo(*N,N'*-di-*tert*-butyldiazabutadiene)nickel

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**Abstract:** Violet tetrahedral complexes NiX<sub>2</sub>(dab) (X = Br, Cl; dab = *N,N'*-disubstituted-diazabutadienes) are formed when crystals of the yellow dimers [NiX<sub>2</sub>(dab)]<sub>2</sub> are heated. The structural transformation when X = Br and dab = *N,N'*-di-*tert*-butyldiazabutadiene is irreversible but topotactic—single crystallinity is largely preserved in the transformation. The yellow complex has been found by single-crystal X-ray structure analysis to be a distorted trigonal-bipyramidal centrosymmetric dimer: Ni—Br(terminal) = 2.457 (1) Å, Ni—Br(bridging) = 2.497 (1) and 2.583 Å, Ni—N = 2.042 (4) and 2.039 (4) Å, Br(terminal)—Ni—Br(bridging, long) = 165.79 (3)° (defines the pseudotrigonal axis), Br(bridging)—Ni—Br(bridging) = 83.11 (3)°, N—Ni—N = 80.8 (2)°. The monomer (structural analysis of a sample separately prepared at ~130 °C) has tetrahedral *D*<sub>2h</sub> symmetry: Ni—Br = 2.333 (2) and 2.343 (2) Å, Ni—N = 1.996 (7) and 2.002 (8) Å, Br—Ni—Br = 126.78 (6)°, N—Ni—N = 82.5 (3)°. The reaction mechanism involves cleavage of the long Ni—Br bond and concerted movement of NiBr<sub>2</sub>(dab) monomers with concomitant rearrangement to a tetrahedral *D*<sub>2d</sub> system such that centrosymmetrically related Ni centers, formerly 3.806 Å separated, become separated by 9.893 Å and related by a 2<sub>1</sub> screw axis. Movements of the monomeric NiBr<sub>2</sub>(dab) units of about 10 Å are observed, while crystallinity is largely preserved. Relevant crystal and refinement data are as follows. For [NiBr<sub>2</sub>(dab)]<sub>2</sub>: space group *C*<sub>2h</sub><sup>2</sup>-*C*<sub>2</sub>/c, *a* = 20.429 (5) Å, *b* = 7.156 (1) Å, *c* = 20.504 (5) Å, β = 98.50 (2)°, *V* = 2965 Å<sup>3</sup> at 22 °C, *Z* = 4 (dimers have  $\bar{1}$  symmetry), ρ<sub>calcd</sub> = 1.73, ρ<sub>obsd</sub> = 1.72 (1) g/cm<sup>3</sup>, 2560 reflections with *I* > 3σ<sub>*i*</sub> in the range 0.0246 < (sin θ)/λ < 0.7049 Å<sup>−1</sup> (graphite-monochromated Mo Kα radiation), *R* and *R*<sub>w</sub> on *F* 0.039 and 0.047. For NiBr<sub>2</sub>(dab): space group *C*<sub>2h</sub><sup>2</sup>-*P*2<sub>1</sub>/n, *a* = 7.125 (3) Å, *b* = 19.717 (10) Å, *c* = 10.396 (5) Å, β = 90.91 (2)°, *V* = 1459 Å<sup>3</sup> at −150 °C, *Z* = 4, ρ<sub>calcd</sub> = 1.67, ρ<sub>obsd</sub> = 1.66 (1) g/cm<sup>3</sup> (based upon room-temperature cell constants), 2300 reflections in the range 0.0246 < (sin θ)/λ < 0.5734 Å<sup>−1</sup>, *R* and *R*<sub>w</sub> on *F*<sup>2</sup> (all data including *F*<sup>2</sup> < 0 was used) 0.091 and 0.127, for the 1545 reflections with *I* > 3σ<sub>*i*</sub> *R* and *R*<sub>w</sub> on *F* 0.055 and 0.062.

The evaluation of kinetic parameters for solid-state reactions and structural phase transitions is conventionally based on analogy to the theory for processes occurring in homogeneous solution for lack of any better formulation.<sup>1</sup> Thus, when free mobility of particles can no longer occur, when temperature exchange between the reacting species and solvent is not relevant, and when physical meaning for the reaction order is absent, interpretation of kinetic parameters is hazardous. Nonetheless by taking a series of compounds of known structure and comparing the parameters derived, it should be possible to make some meaningful com-

parisons and interpretations. In order to relate kinetic and thermodynamic data to a *mechanism* for the solid-state reaction or structural transformation, these processes should occur topotactically.<sup>2,3</sup> For only with knowledge of the crystallographic

(1) (a) Sesták, J.; Satava, V.; Wendlandt, W. W. *Thermochim. Acta* **1973**, *7*, 333–352. (b) Behnisch, J.; Schaff, E.; Zimmermann, H. *J. Therm. Anal.* **1978**, *13*, 117–128. (c) Coats, A. W.; Redfern, J. P. *Nature (London)* **1964**, *201*, 68–69. (d) Satava, V. *Thermochim. Acta* **1971**, *2*, 423–428.

(2) Following Günter and Oswald,<sup>3a</sup> we define a reaction as topotactic if the solid product is formed in one or only several definite crystallographic orientations relative to the parent crystal as a consequence of a chemical reaction or solid-state structural transformation and if it can proceed throughout the entire volume of the parent crystal. This definition differs in words only from several others.

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