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# $OsH_5(PMe_2Ph)_3^+$: Structure, Reactivity, and Its Use as a Catalyst Precursor for Olefin Hydrogenation and Hydroformylation

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$OsH_5L_3^+$ (as its $BF_4^-$ salt; L = $PMe_2Ph$) is characterized by neutron diffraction as a dodecahedral pentahydride. However, the H/H separations are as short as 1.49(4) Å. Crystal data (11 K): $a = 53.35(2)$ Å, $b = 24.378(5)$ Å, $c = 8.422(3)$ Å with $Z = 16$ in space group *Fdd*2. This cation exchanges OsH with $D_2$ and is converted by CO to $OsH(CO)_2L_3^+$. This cation hydrogenates ethylene (<1 h) at 25 °C to generate *cis,mer*-$OsH(C_2H_4)_2L_3^+$, which was characterized by variable-temperature $^{31}P$, $^1H$, and $^{13}C$ NMR spectroscopy and X-ray diffraction. Crystal data (−155 °C): $a = 13.134(7)$ Å, $b = 13.300(8)$ Å, $c = 11.011(7)$ Å, $\alpha = 111.25(2)°$, $\beta = 113.15(3)°$, and $\gamma = 89.26(3)°$ with $Z = 2$ in space group $P\bar{1}$. The orientation of the olefins in this compound is explained using extended Hückel methods, as is the lack of a structural *trans* influence on Os−C bond lengths and the reversed kinetic *trans* effect. Studies with Os/D and $C_2D_4$ labeling, as well as trapping of transients with CO and with 1,5-cyclooctadiene, serve to define a reaction mechanism for ethylene hydrogenation, and the pentahydride cation also hydrogenates cyclohexene. In spite of the mutual *trans* stereochemistry of hydride and ethylene in $OsH(CO)(C_2H_4)L_3^+$, CO converts this molecule first to *cis,mer*-$Os(Et)(CO)_2L_3^+$and then more slowly to *cis,mer*-$Os[C(O)Et](CO)_2L_3^+$. A variety of isotopic labeling studies prove that the first of these reactions does not involve preequilibrium dissociation of CO, $PMe_2Ph$, or $C_2H_4$, nor does it involve bimolecular proton transfer to form the ethyl group. Intramolecular hydrogen migration to bring H *cis* to $C_2H_4$ is consistent with all observations. The carbonyl ligands in $OsH(CO)_2L_3^+$ are susceptible to nucleophilic attack by solvent in water, to effect the water gas shift reaction. In the presence of water and 1-hexene, Reppe hydroformylation ($H_2O$ + 2CO + olefin → aldehyde + $CO_2$) is catalyzed by $OsH(CO)(L')L_3^+$ (L′ = CO or $C_2H_4$) and by $Os(Et)(CO)_2L_3^+$.

## Introduction

We reported previously[1] that $OsH_5L_3^+$ (L = $PMe_2Ph$), the product of protonation of the tetra*hydride* $OsH_4L_3$, is in fact a dihydrogen ($H_2$) complex. We also communicated its stoichiometric hydrogenation of ethylene and its use as a catalyst to hydrogenate cyclohexene. We report here a re-evaluation of the structure of $OsH_5L_3^+$ and a more complete determination of the participants in what is quite a complex reaction network for ethylene hydrogenation. The mechanistic insights obtained by a variety of isotopic labeling experiments give a more detailed view of how polyhydride compounds can effect hydrogen transfer under conditions (25 °C, 1 atm pressure) quite mild for osmium.[2]

The compound $OsH(CO)(C_2H_4)(PMe_2Ph)_3^+$, in which H is *trans* to $C_2H_4$, reacts with CO to form an ethyl group. Mechanistic studies trace this unusual *trans* $\beta$-hydrogen migration to an intramolecular rearrangement. This cation contains the groups appropriate for hydroformylation, and it in fact serves as a catalyst for that reaction. Since the CO in this cation is subject to nucleophilic attack, the hydroformylation can be run with $H_2O$, not $H_2$, as the source of hydrogen (i.e., Reppe hydroformylation).

## Experimental Section

**General Methods.** All manipulations were carried out under an $N_2$ atmosphere using standard Schlenk techniques. Solid transfers were accomplished in a Vacuum Atmospheres Corp. glovebox. Methylene chloride and diethyl ether were distilled under nitrogen from $P_2O_5$ and NaK/benzophenone, respectively. $CD_2Cl_2$ was dried over $P_2O_5$ prior to use and stored in the glovebox. $HBF_4{\cdot}OEt_2$ (Aldrich 85%) was used as received. $^{13}C_2H_4$ (99%), $C_2D_4$ (99%), $C_2H_4$, $D_2$, $H_2$, $^{13}CO$ (99%), 1-hexene, and CO were used as received. $OsH_4(PMe_2Ph)_3$ was synthesized according to the literature[3] method, starting from $OsO_4$.

$^1H$ (360 MHz), $^2H$ (55 MHz), $^{31}P$ (146 MHz), and $^{13}C$ (90 MHz) NMR were obtained on a Nicolet NT-360 instrument. Negative $^{31}P$ chemical shifts are upfield from external 85% $H_3PO_4$. Certain $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker instrument at 125.4 MHz. Two-dimensional $^1H$, $^{13}C$ heteronuclear COSY spectra were obtained on a Bruker 500 instrument. IR spectra were recorded on a 510P Nicolet FTIR instrument.

**$[OsH_5L_3]BF_4$ (1).** To $OsH_4L_3$ (100 mg, 0.164 mmol) dissolved into 50 mL of diethyl ether was added 60 $\mu$L (0.492 mmol) of 85% $HBF_4{\cdot}OEt_2$. Yellow powder precipitated upon addition of the acid. This heterogeneous reaction mixture was allowed to stir for 15 min at 25 °C, and excess solvent was removed using a cannula. The yellow powder was dried *in vacuo*. $^1H$ NMR (24 °C, $CD_2Cl_2$): $\delta$ 7.47 (m, P−Ph), 1.78 (d, P−Me, $J_{PH}$ = 8 Hz), −7.02 (q, Os−H, $J_{PH}$ = 4 Hz).

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**Table 1.** Experimental Data for the Neutron Diffraction Study of $[OsH_5(PMe_2Ph)_3]BF_4$

| | |
|---|---|
| formula | $C_{24}H_{38}BF_4OsP_3$ |
| mol wt | 696.53 |
| crystal dimens, mm | 2.0 × 1.5 × 0.8 |
| data collcn *T*, K | 11.0 ± 0.5 |
| cryst syst | orthorhombic |
| space group | *Fdd*2 (No. 92) |
| *a*, Å | 53.35(2) |
| *b*, Å | 24.378(5) |
| *c*, Å | 8.422(3) |
| *V*, Å$^3$ | 10,953(3) |
| *Z* | 16 |
| $\varrho_{calcd}$, g cm$^{-3}$ | 1.689 |
| range of calcd transm factors | 0.65–0.78 |
| radiation, $\lambda$ (Å) | neutrons, 1.046 32<br>(Be, 002 reflect plane) |
| meas reflcns | $\pm h,+k,-l$ |
| $\theta$ range, deg | $3 \le \theta \le 41$ |
| no. of data collcd | 6159 |
| no. of indpdt data | 2985 |
| no. of data used ($n_o$) | 2935 |
| no. of params ($n_v$) | 414 |
| $R_{av}$ (agreement on averaging)$^a$ | 0.087 |
| $R(F^2)^b$ | 0.207 |
| $R_w(F^2)^c$ | 0.216 |
| $R(F)^d$ | 0.092 |
| gof $(S)^e$ | 1.254 |

[a] $R_{av} = \sum(\sum_i^{n'}|F_o^2 - (F_o^2)_i|)/\sum n'|F_o^2|$. [b] $R(F^2) = \sum|F_o^2 - (1/k^2)F_c^2|/\sum|F_o^2|$. [c] $R_w(F^2) = [\sum w(F_o^2 - (1/k^2)F_c^2)^2/\sum wF_o^4]^{1/2}$. [d] $R(F) = \sum||F_o| - (1/k)F_c||/\sum|F_o|$. [e] $S = [\sum w(F_o^2 - (1/k^2)F_c^2)^2/(n_o - n_v)]^{1/2}$.

$^{31}P\{^1H\}$ NMR (24 °C, $CD_2Cl_2$): −34.0 (s) ppm. IR: $\nu$(OsH) = 2044, 1973, 1867 cm$^{-1}$. Anal. Calcd for $C_{24}H_{38}BF_4P_3Os$: C, 41.39; H, 5.50. Found: C, 41.14; H, 5.45.

**Neutron Diffraction Structure Determination of $[OsH_5(PMe_2Ph)_3]BF_4$.** A colorless, approximately prismatic crystal with a volume of 2.4 mm$^3$ was mounted on an Al pin approximately along the 001 direction using halocarbon grease. The mount was sealed under a He atmosphere in an Al can attached to a closed-cycle He refrigerator,[4] which was placed on a four-circle diffractometer[5,6] at the Brookhaven High Flux Beam Reactor. The measurements were carried out at 11 K. Calibration of the Be (002)-monochromated neutron beam was carried out with a KBr crystal ($a_o$ = 6.6000 Å at 298 K)[7] yielding a value of $\lambda$ = 1.046 32 Å. A least-squares fit of the $\sin^2 \theta$ values of 22 reflections with 15 ° ≤ $\theta$ ≤ 32.5° gave the unit cell parameters listed in Table 1.

Intensities were collected in the $\omega/2\theta$ step scan mode. Data collection and other experimental parameters are listed in Table 1. The variable scan width for the high-angle region ($\theta$ > 30°) was determined by the dispersion relation $\Delta 2\theta$ (deg) = −0.85 + 6.82 tan $\theta$. The time for each step was about 5 s and depended on a constant monitor count of the incident beam. Two reference intensities were measured every 52 reflections. Analysis[8] of these intensities showed no significant variation. Backgrounds were computed on the basis of counts recorded for 10% of the steps at either end of each scan, and the resulting integrated intensities were corrected for Lorentz and absorption effects. The absorption correction employed a numerical integration over a Gaussian grid of 16 × 12 × 8 points relative to the reciprocal cell vectors. Averaging of equivalent reflections yielded a set of 2985 unique $F_o^2$ of which 50 were judged to be contaminated by scattering from the Al cryostat and omitted from the refinement. Starting values for the coordinates were taken from an X-ray structure determination.[9] All hydrogens were located in a series of difference Fourier syntheses and refined using a differential synthesis program.[10]

**Table 2.** Selected Bond Distances (Å) and Bond Angles (deg) for $[Os(H)_5(PMe_2Ph)_3]BF_4$

| | | | |
|---|---|---|---|
| Os−H1 | 1.65(2) | H2−H4 | 1.99(3) |
| Os−H2 | 1.64(2) | H2−H5 | 3.11(4) |
| Os−H3 | 1.65(2) | H3−H4 | 1.49(4) |
| Os−H4 | 1.62(3) | H3−H5 | 1.98(4) |
| Os−H5 | 1.65(2) | H4−H5 | 2.93(3) |
| H1−H2 | 1.75(3) | Os−P | 2.39(1) |
| H1−H3 | 2.85(4) | Os−P11 | 2.34(1) |
| H1−H4 | 1.90(4) | Os−P20 | 2.40(1) |
| H1−H5 | 3.15(4) | P−C$^a$ | 1.83(2) |
| H1−H3 | 2.81(3) | B−F$^a$ | 1.38(3) |
| H2−H4 | 1.99(3) | | |

| | | | |
|---|---|---|---|
| H1−Os−H2 | 64.2(1.0) | H2−Os−P11 | 70.5(8) |
| H1−Os−H4 | 71.2(1.5) | H2−Os−P20 | 140.1(9) |
| H1−Os−H3 | 119.5(1.4) | H3−Os−P | 156.3(1.1) |
| H1−Os−H5 | 145.7(1.3) | H3−Os−P11 | 75.1(1.0) |
| H2−Os−H3 | 116.9(1.3) | H3−Os−P20 | 76.2(1.0) |
| H2−Os−H4 | 75.2(1.3) | H4−Os−P | 149.4(1.0) |
| H2−Os−H5 | 141.8(1.3) | H4−Os−P11 | 91.0(1.3) |
| H3−Os−H4 | 54.1(1.4) | H4−Os−P20 | 86.4(1.2) |
| H3−Os−H5 | 73.7(1.4) | H5−Os−P | 82.6(1.2) |
| H4−Os−H5 | 127.7(1.4) | H5−Os−P11 | 78.3(1.0) |
| H1−Os−P | 80.5(1.1) | H5−Os−P20 | 76.9(1.0) |
| H1−Os−P11 | 134.1(9) | P−Os−P11 | 100.6(5) |
| H1−Os−P20 | 76.4(8) | P−Os−P20 | 98.5(5) |
| H2−Os−P | 82.2(1.0) | P11−Os−P20 | 146.2(5) |

[a] Mean value; esd's calculated as $\sigma(\bar{X}) = [\sum(X_i - \bar{X})^2/n(n - 1)]^{1/2}$; $n$ = number of observations.

The complete structure model was then refined by full-matrix least squares, using all data except for the 50 contaminated data mentioned above. Anisotropic thermal parameters were used for the hydride atoms and the $BF_4^-$ counterion; all other atoms were treated isotropically. A refinement including a type I isotropic extinction correction[11] resulted in a negative value of the extinction parameter. Effects of extinction were thus judged to be negligible, and the extinction correction was therefore omitted in the final refinement. The quantity minimized was $\sum w(F_o^2 - (1/k^2)F_c^2)^2$, with weights $w = \sigma^2(F_o^2)^{-1}$ and $\sigma^2(F_o^2) = [\sigma_{count}^2(F_o^2) + (0.03\ F_o^2)^2]$. At the end of the refinement, all parameter shift/error values were 0.1 or less. In spite of the high $R(F^2)$ and $R_w(F^2)$ values (*ca.* 0.20) caused by the large number of weak reflections and the restriction to an isotropic model for P and C, the goodness-of-fit ($S$) of 1.25 indicates a satisfactory refinement.

The final difference Fourier map showed no significant features. Neutron scattering lengths were taken from the literature.[12] All calculations were carried out on a $\mu$VAX computer using programs described by Lundgren.[13] Final positional and displacement parameters are given in the supplementary material, and selected distances and angles appear in Table 2; Figure 1 shows two views of the cation. A list of observed and calculated squared structure factors and a drawing of the full $Os(H)_5(PMe_2Ph)_3^+$ unit are provided as supplementary material.

***cis,mer*-$[OsH(CO)_2(PMe_2Ph)_3]BF_4$.** A 100-mL flask containing $[OsH_5(PMe_2Ph)_3]BF_4$ (100 mg, 0.14 mmol) in 25 mL of $CH_2Cl_2$ was freeze−pump−thaw-degassed three times and then pressurized to 1 atm (ca. 3 mmol) with carbon monoxide. After being warmed to 25

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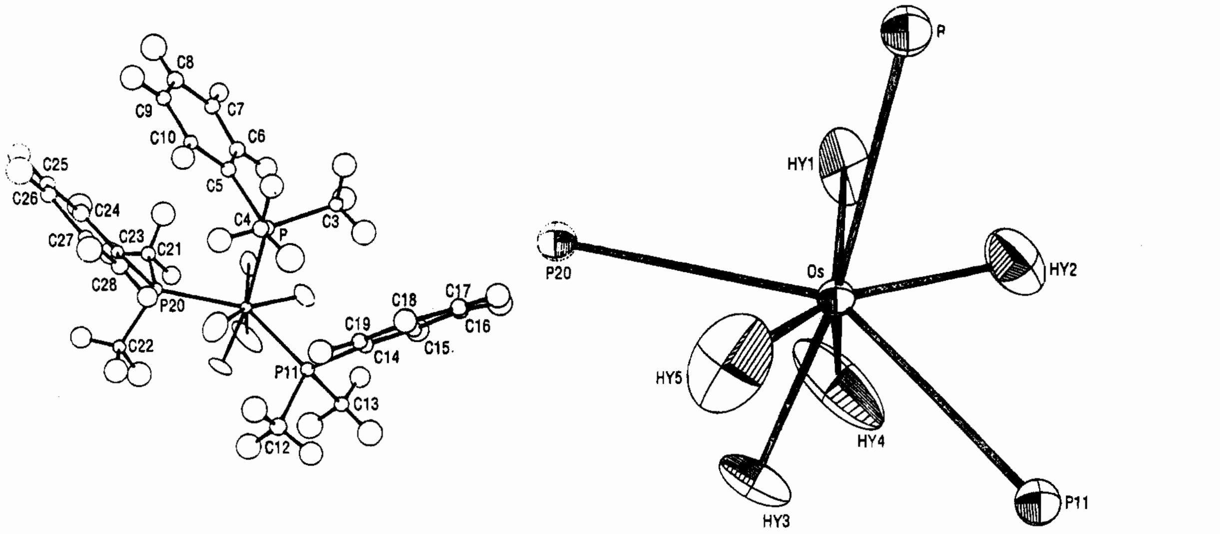

**Figure 1.** ORTEP drawings of the inner coordination sphere and the full ion of $Os(H)_5(PMe_2Ph)_3^+$. The two trapezoidal planes of the dodecahedron are (P, HY5, HY3, HY4) and P11, P20, HY1, HY2).

°C, the solution was stirred for 3 h. The volume was then reduced to 5 mL *in vacuo*. To the concentrated solution, 40 mL of $Et_2O$ was added, causing immediate precipitation of a cream colored solid. The excess solvent was removed via cannula, and the solid was dried *in vacuo*. Yield: 98%. $^1H$ NMR (25 °C): $\delta$ 7.60–7.00 (m, 15H, Ph), 1.97 (overlapping vt, 3 Hz, 12H, PMe), 1.33 (d, $J_{PH}$ = 9 Hz, 6H, PMe), −7.04 (dt, $J_{PH}$ = 19, 19 Hz, 1H, OsH). $^{31}P\{^1H\}$ NMR (25 °C): $\delta$ −41.55 (t, $J_{PP}$ = 27 Hz, 1P), −39.30 (d, $J_{PP}$ = 27 Hz, 2P). IR: $\nu_{CO}$ = 2008, 1985 cm$^{-1}$, $\nu_{OsH}$ = 1933 cm$^{-1}$. Anal. Calcd for $OsC_{26}H_{34}O_2P_3BF_4$: C, 41.67; H, 4.71. Found: C, 41.74; H, 4.51.

**Attempted High-Pressure Reaction of $H_2$ with *cis,mer*-[OsH$(CO)_2(PMe_2Ph)_3$]$BF_4$.** A stainless steel vessel was charged with *cis,mer*-[OsH$(CO)_2(PMe_2Ph)_3$]$BF_4$ (100 mg, 0.13 mmol) and 10 mL of $CH_2Cl_2$. This system was placed under 1000 psi of $H_2$ gas and was stirred for 24 h. The excess solvent was removed *in vacuo*, and $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopy of the resulting powder matched that for authentic *cis,mer*-[OsH$(CO)_2(PMe_2Ph)_3$]$BF_4$.

**[*cis,mer*-OsH$(C_2H_4)_2(PMe_2Ph)_3$]$BF_4$ (2).** A 100 mL flask containing [$OsH_5L_3$]$BF_4$ (100 mg, 0.14 mmol) in 25 mL of $CH_2Cl_2$ was freeze–pump–thaw-degassed three times and then pressurized to 1 atm with ethylene. After being warmed to 25 °C, the solution was stirred for 90 min. The volume was then reduced to 5 mL *in vacuo*. To the concentrated solution, 40 mL of $Et_2O$ was added, causing immediate precipitation of a cream-colored solid. The excess solvent was removed via cannula, and the solid was dried *in vacuo*. Yield: 95%. $^1H$ NMR (24 °C, $CD_2Cl_2$): $\delta$ −6.77 (dt, $J$(PH) = 30, 21 Hz, 1H), 1.32 (d, $J$(PMe) = 8 Hz, 6H), 1.40 (br s, $C_2H_4$ *cis* to H, 4H), 1.47 (vt, 3 Hz, 6H), 1.61 (vt, 3 Hz, 6H), 2.84 (dt, $C_2H_4$ *trans* to H, $J(C_2H_4-P) = J(C_2H_4-P')$ = 3 Hz, 4H), 7.30 (m, PPh). $^{31}P\{^1H\}$ (146 MHz, 24 °C, $CD_2Cl_2$): $\delta$ = −41.5 (t, $J$(P–P) = 14 Hz, 1P), −36.5 (d, $J$(P–P) = 14 Hz, 2P). IR: $\nu$(OsH) = 1967 cm$^{-1}$. Anal. Calcd for $C_{29}H_{44}Cl_2P_3BF_4Os$: C, 41.79; H, 5.32. Found: C, 41.48; H, 5.25.

**[$OsD_5(PMe_2Ph)_3$]$BF_4$.** A stainless steel vessel was charged with [$OsH_5L_3$]$BF_4$ (50 mg, 0.07 mmol) and 10 mL of $CH_2Cl_2$. This reaction vessel was pressurized to 250 psi with deuterium gas, and the solution was stirred for 20 h. An NMR tube was charged with this solution within 10 min after venting the bomb. $^2H$ NMR (25 °C, $CH_2Cl_2$): $\delta$ −7.02 (s, Os–D), 7.25 (br s, PPh).

**[*cis,mer*-OsH$(^{13}C_2H_4)_2(PMe_2Ph)_3$]$BF_4$.** An NMR tube containing 50 mg (0.067 mmol) of *cis,mer*-[OsH$(C_2H_4)_2L_3$]$BF_4$ dissolved in $CD_2Cl_2$ was freeze–pump–thaw-degassed three times, pressurized to 1 atm with $^{13}C_2H_4$, and flame sealed. The following spectral data were recorded within 5 min of thawing the tube and indicate complete exchange; also seen are $^{12}C_2H_4$ and $^{13}C_2H_4$. $^1H$ NMR (25 °C, $CD_2Cl_2$): $\delta$ −6.77 (dt $J$(PH) = 30, 21 Hz, 1H), 1.32 (d, $J$(PMe) = 8 Hz, 6H), 1.40 (dd, $C_2H_4$ *trans* to P, $J$(CH) = 159 Hz, $J(P-C_2H_4)$ = 9.3 Hz, 4H), 1.47 (vt, 3 Hz, 6H), 1.61 (vt, 3 Hz, 6H), 2.84 (ddt, $C_2H_4$ *trans* to H, $J$(CH) = 159 Hz, $J(P-C_2H_4) = J(P'-C_2H_4)$ = 3 Hz, 4H), 7.30 (m, PPh). $^{13}C\{^1H\}$ NMR of the 99% $^{13}C$-enriched ethylene carbons (24 °C, $CD_2Cl_2$): $\delta$ 40.28 (d, $J$(C–P) = 11 Hz), 42.83 (s). No C/C coupling between olefin sites was detected by $^{13}C$ NMR. In the $^{31}P\{^1H\}$ NMR, only the −41.5 ppm resonance showed additional 11 Hz coupling (tt, $J_{PP}$ = 14 Hz).

**Reaction of [*cis,mer*-OsH$(C_2H_4)_2(PMe_2Ph)_3$]$BF_4$ with $^{13}C_2H_4$ at Low Temperature.** An NMR tube was charged with *cis,mer*-[OsH$(C_2H_4)_2L_3$]$BF_4$ (0.082 mmol) dissolved in $CD_2Cl_2$, pressurized to 1 atm with $^{13}C_2H_4$, and flame sealed at −196 °C. The tube was warmed slowly to −78 °C and placed in a spectrometer probe precooled to −70 °C. The sample showed only free $^{13}C_2H_4$ by $^{13}C\{^1H\}$ NMR in the temperature range −70 to −20 °C. A doublet (40.28 ppm, $^{13}C_2H_4$ *trans* to P) was observed at −10 °C; no signal was present for the ethylene *trans* to hydride. At 0 °C, the first spectrum recorded now showed a 42.83 ppm singlet of intensity comparable to that of the peak at 40.28 ppm.

**Reaction of [$OsD_5(PMe_2Ph)_3$]$BF_4$ with $C_2H_4$.** An NMR tube charged with [$OsD_5L_3$]$BF_4$ (0.082 mmol) dissolved in $CH_2Cl_2$ was pressurized to 1 atm with ethylene and flame sealed at −196 °C. The solution was thawed and was monitored over the course of 90 min by $^2H$ NMR at 25 °C. Within the first 5 min, $C_2H_{6-x}D_x$ (0.7 ppm) was observed. Resonances of $C_2H_{4-x}D_x$ (2.85 and 1.40 ppm) coordinated at *both* olefinic sites of [*cis,mer*-OsH$(C_2H_4)_2L_3$]$BF_4$ were seen after 20 min. No free $C_2H_{4-x}D_x$ (5.38 ppm) was detected until [$OsD_5L_3$]$BF_4$ was totally consumed.

**Reaction of [*cis,mer*-OsH$(C_2H_4)_2(PMe_2Ph)_3$]$BF_4$ with $C_2D_4$.** An NMR tube charged with [*cis,mer*-OsH$(C_2H_4)_2L_3$]$BF_4$ (0.082 mmol) dissolved in $CD_2Cl_2$ was pressurized to 1 atm with $C_2D_4$ and flame sealed at −196 °C. The reaction products were observed via $^1H$ NMR after 90 min at 25 °C. $^1H$ NMR showed no hydride signal at −6.77 ppm (Os–H), nor was there any signal at 2.84 ppm (Os–$C_2H_4$ *trans* to hydride). However, free ethylene and a signal at 1.40 ppm (Os–$C_2D_{4-x}H_x$ *cis* to hydride) were detected. All other proton signals for [*cis,mer*-OsH$(C_2H_4)_2L_3$]$BF_4$ remained isotopically normal.

**Hydrogenation of [*cis,mer*-OsH$(C_2H_4)_2(PMe_2Ph)_3$]$BF_4$.** An NMR tube charged with [*cis,mer*-OsH$(C_2H_4)_2L_3$]$BF_4$ (0.082 mmol) dissolved in $CD_2Cl_2$ was pressurized to 1 atm with $H_2$ and flame sealed at −196 °C. The tube was thawed and placed into an NMR spectrometer probe at 25 °C. This reaction was monitored by $^1H$ NMR for 90 min, recording a spectrum every 10 min. Products of the reaction were [$OsH_5L_3$]$BF_4$ and ethane; no intermediates were detected, except for free ethylene, which was observed during the course of the reaction but was eventually reduced to ethane after 90 min.

**X-ray Diffraction Study of [*cis,mer*-OsH$(C_2H_4)_2(PMe_2Ph)_3$]$BF_4$ (2).** A suitable crystal was located and transferred to the goniostat using standard inert atmosphere handling techniques and cooled to −155 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and

**Table 3.** Crystallographic Data for $[OsH(C_2H_4)_2(PMe_2Ph)_3]BF_4{\cdot}CH_2Cl_2$

| | | | |
|---|---|---|---|
| chem formula | $C_{29}H_{44}BF_4P_3Cl_2Os$ | fw | 833.50 |
| $a$, Å | 13.134(7) | space group | $P\bar{1}$ (No. 2) |
| $b$, Å | 13.300(8) | T, °C | −155 °C |
| $c$, Å | 11.011(7) | $\lambda$, Å | 0.710 69 |
| α, deg | 111.25(2) | $\varrho_{calcd}$, g cm$^{-3}$ | 1.699 |
| $\beta$, deg | 113.15(3) | $\mu$(Mo Kα), cm$^{-1}$ | 42.7 |
| $\gamma$, deg | 89.26(3) | $R$ | .0280 |
| $V$, Å$^3$ | 1629.34 | $R_w$ | .0298 |
| $Z$ | 2 | | |

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

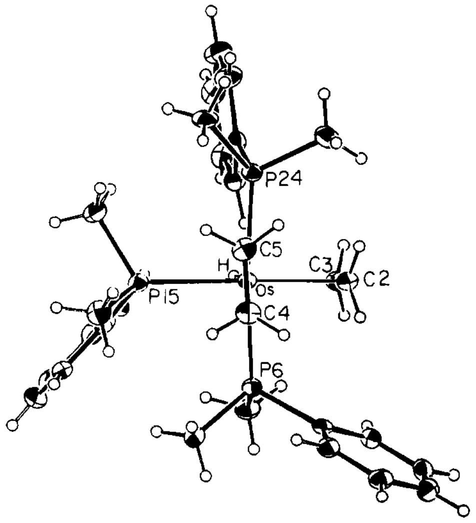

Figure 2. ORTEP drawing of $OsH(C_2H_4)_2(PMe_2Ph)_3^+$ viewed down the Os−H vector.

refinement of the structure confirmed the centrosymmetric data choice, $P\bar{1}$. Data were collected (6 ° ≤ 2$\theta$ ≤ 45°) in the usual manner[14] using a continuous $\theta$−2$\theta$ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated $\sigma$'s in the usual manner. Parameters of the unit cell and data set are shown in Table 3.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters. All hydrogen atoms (including the hydride and those on the $CH_2Cl_2$ solvent molecule) were refined isotropically, and non-hydrogen atoms, anisotropically in the final cycles. The crystal was well formed and nearly equidimensional. An absorption correction was made on the basis of 14 well-defined faces using the analytical technique (AGNOST program). The $R$ factor for averaging of equivalent data improved from 0.035 to 0.029 for the corrected data, with minimum and maximum transmission varying from 0.72 to 0.81.

A final difference Fourier was featureless, with the largest peak being 1.45 e/Å$^3$ at the metal position and the four next largest peaks (0.74−1.1 e/Å$^3$) associated with the $BF_4^-$ anion. The results of the structure determination are shown in Figure 2 and Table 4. Further crystallographic details and anisotropic thermal parameters are available as supplementary material. The C−H distances range from 0.77(6) to 1.12(7) Å. Those on ethylene range from 0.91(7) to 1.01(5) Å. The geometries within the phosphines, the $BF_4^-$, and the $CH_2Cl_2$ molecule contained in the lattice are all unremarkable.

**Table 4.** Selected Bond Distances (Å) and Angles (deg) for $[OsH(C_2H_4)_2(PMe_2Ph)_3]BF_4{\cdot}CH_2Cl_2$

| | | | |
|---|---|---|---|
| Os1−P6 | 2.3740(19) | Os1−C4 | 2.235(6) |
| Os1−P15 | 2.3876(22) | Os1−C5 | 2.247(6) |
| Os1−P24 | 2.3999(19) | C2−C3 | 1.390(9) |
| Os1−C2 | 2.207(6) | C4−C5 | 1.401(9) |
| Os1−C3 | 2.220(6) | Os1−H1 | 1.36(6) |
| | | | |
| P6−Os1−P15 | 90.75(7) | C2−Os1−C4 | 81.86(24) |
| P6−Os1−P24 | 162.09(5) | C2−Os1−C5 | 83.97(24) |
| P6−Os1−C2 | 88.95(18) | C3−Os1−C4 | 116.45(24) |
| P6−Os1−C3 | 83.52(17) | C3−Os1−C5 | 118.64(23) |
| P6−Os1−C4 | 80.80(16) | C4−Os1−C5 | 36.43(22) |
| P6−Os1−C5 | 117.22(17) | Os1−C2−C3 | 72.2(3) |
| P15−Os1−P24 | 94.18(7) | Os1−C3−C2 | 71.2(3) |
| P15−Os1−C2 | 172.27(16) | Os1−C4−C5 | 72.3(3) |
| P15−Os1−C3 | 150.95(16) | Os1−C5−C4 | 71.3(3) |
| P15−Os1−C4 | 90.47(18) | P6−Os1−H1 | 85.7(26) |
| P15−Os1−C5 | 89.30(18) | P15−Os1−H1 | 77.4(25) |
| P24−Os1−C2 | 88.42(18) | P24−Os1−H1 | 78.6(26) |
| P24−Os1−C3 | 83.83(17) | C2−Os1−H1 | 110.3(25) |
| P24−Os1−C4 | 116.30(16) | C3−Os1−H1 | 73.8(26) |
| P24−Os1−C5 | 80.09(17) | C4−Os1−H1 | 161.7(26) |
| C2−Os1−C3 | 36.58(23) | C5−Os1−H1 | 153.9(26) |

**Synthesis of *fac*-[OsH($\eta^4$-1,5-cyclooctadiene)(PMe$_2$Ph)$_3$]BF$_4$.** Via syringe, 2.0 mL (16.0 mmol) of 1,5-cyclooctadiene was added to a 100-mL flask containing a 25-mL $CH_2Cl_2$ solution of $[OsH_5(PMe_2Ph)_3]BF_4$ (50 mg, 0.07 mmol). This solution was allowed to stir at 25 °C for 48 h. The volume of the solution was reduced to 5 mL *in vacuo*. To this concentrated solution, 40 mL of $Et_2O$ was added, which caused immediate precipitation of an off-white solid. The solid material was filtered and dried *in vacuo* on a glass frit. Yield: 95%. $^1$H NMR (25 °C): $\delta$ 7.50-7.00 (m, 15H, Ph), 2.13, 1.87, and 1.59 (each a d, $J_{PH}$ = 7 Hz, 6H, PMe), −8.56 (dt, $J_{PH}$ = 35, 28 Hz, 1H, OsH), 1,5-COD protons 3.86 (br s, 2H, vinyl CH), 2.91 (m, 2H, vinyl CH), 2.27 and 2.00 (each a multiplet, 2H, aliphatic $CH_2$), 1.54 (m, 4H, aliphatic $CH_2$). $^{31}$P{$^1$H} NMR (25 °C): $\delta$ −46.3 (t, $J_{PP}$ = 38 Hz, 1P), −40.4 (d, $J_{PP}$ = 38 Hz, 2P). $^{13}$C{$^1$H} NMR (25 °C) of the 1,5-COD carbons: $\delta$ 30.23 and 33.91 (each a s, aliphatic $CH_2$), 67.74 (dt, $J_{CP}$ = 5, 4 Hz, vinyl CH), 70.41 (br s, vinyl CH). IR: $\nu_{OsH}$ = 1937 cm$^{-1}$.

**Synthesis of *mer*-[OsH(CO)(C$_2$H$_4$)(PMe$_2$Ph)$_3$]BF$_4$ (3).** In a 100-mL flask, a 25-mL $CH_2Cl_2$ solution of *cis,mer*-$[OsH(C_2H_4)_2(PMe_2Ph)_3]BF_4$ (100 mg, 0.13 mmol) was frozen and placed under 1 atm of CO (ca. 3 mmol) at −196 °C. After being warmed to 25 °C, this solution was stirred for 1 h. The solution was then reduced to 5 mL *in vacuo* and 40 mL of $Et_2O$ was added, which caused an immediate precipitation of a yellow solid. This solid was filtered and dried *in vacuo* on a glass frit. Yield: 96%. $^1$H NMR (25 °C): $\delta$ 7.90−7.30 (m, 15H, Ph), 2.85 (dt, $J_{PH} = J_{P'-H}$ = 3 Hz, 4H, $C_2H_4$), 1.98 and 1.92 (each a vt, 3 Hz, 6H, PMe), 0.94 (d, $J_{PH}$ = 9 Hz, 6H, PMe), −6.18 (dt, $J_{PH}$ = 25, 21 Hz, 1H, OsH). $^{31}$P{$^1$H} NMR (25 °C): $\delta$ −46.3 (t, $J_{PP}$ = 26 Hz, 1P), −41.2 (d, $J_{PP}$ = 26 Hz, 2P). IR: $\nu_{CO}$ = 1981 cm$^{-1}$, $\nu_{OsH}$ = 1927 cm$^{-1}$.

**Synthesis of *mer*-[OsH(CO)($^{13}$C$_2$H$_4$)(PMe$_2$Ph)$_3$]BF$_4$.** In a 50-mL flask, a 25-mL $CH_2Cl_2$ solution of $[OsH_5(PMe_2Ph)_3]BF_4$ (50 mg, 0.07 mmol) was frozen and exposed to 0.30 mmol of $^{13}C_2H_4$. This solution was warmed to 25 °C and was stirred for 1 h at this temperature. At this time, 1 atm of CO was placed over the solution, which was then stirred for an additional 10 min. The excess solvent was removed *in vacuo*, leaving a yellow powder. The $^1$H, $^{31}$P{$^1$H}, and $^{13}$C{$^1$H} NMR spectroscopy of this solid in $CD_2Cl_2$ confirmed its identity as *mer*-$[OsH(CO)(^{13}C_2H_4)(PMe_2Ph)_3]BF_4$. $^{13}$C{$^1$H} NMR (25 °C, 99% $^{13}$C enrichment): $\delta$ 39.21 (s, $C_2H_4$), 178.7 (dt, $J_{PC}$ = 87, 10 Hz, CO).

**Synthesis of *mer*-[OsD(CO)(C$_2$D$_4$)(PMe$_2$Ph)$_3$]BF$_4$.** In a 50-mL flask, a 25-mL $CH_2Cl_2$ solution of $[OsD_5(PMe_2Ph)_3]BF_4$ (50 mg, 0.07 mmol) was frozen and exposed to 0.30 mmol of 99% $C_2D_4$. This solution was warmed to 25 °C and was stirred for 1 h at this temperature. At this time, 1 atm of CO was placed over this solution, which was then stirred for an additional 10 min. The excess solvent was removed *in vacuo* to produce a dark yellow solid. The $^{31}$P{$^1$H} NMR spectrum of this material was indistinguishable from that of authentic *mer*-$[OsH(CO)(C_2H_4)(PMe_2Ph)_3]BF_4$ (3). The $^1$H NMR spectrum of this material, however, did not contain any hydride or ethylene resonances and thus confirmed its identity as *mer*-$[OsD(CO)(C_2D_4)(PMe_2Ph)_3]BF_4$.

**Synthesis of *cis,mer*-[Os(C$_2$H$_5$)(CO)$_2$(PMe$_2$Ph)$_3$]BF$_4$ (4).** In a stainless-steel, high-pressure reaction vessel, a 5-mL $CH_2Cl_2$ solution of *mer*-$[OsH(CO)(C_2H_4)(PMe_2Ph)_3]BF_4$ (100 mg, 0.13 mmol) was placed under 1000 psi of CO for 24 h. At this time, the reaction vessel

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(14) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

was vented and taken into the glovebox. Addition of 40 mL of $Et_2O$ to the reaction solution yielded a white solid, which was filtered off and dried *in vacuo* on a glass frit. Yield: 98%. The doubly-enriched $^{13}CO$ species was synthesized by stirring a 25-mL $CH_2Cl_2$ solution of **3** in a 100-mL flask under 1 atm of 99% $^{13}CO$ for 14 d. At this time, the solvent was removed *in vacuo*, leaving **4** as a powder. $^1H$ NMR (25 °C): $\delta$ 7.60−7.30 (m, 15H, Ph), 1.86 and 1.77 (each a vt, 4Hz, 6H, PMe), 1.56 (d, $J_{PH} = 9$ Hz, 6H, PMe), 1.63 (t, $J_{HH} = 8$ Hz, 3H, $CH_3$), 0.92 (q, $J_{HH} = 8$ Hz, 2H, $CH_2$). $^{31}P\{^1H\}$ NMR (25 °C): $\delta$ −47.5 (t, $J_{PP} = 28$ Hz, 1P), −43.7 (d, $J_{PP} = 28$ Hz, 2P). IR: $\nu_{CO} = 2004$, 1986 $cm^{-1}$. $^{13}C\{^1H\}$ NMR (25 °C, 99% $^{13}CO$ enrichment): $\delta$ 179.4 (dt, $J_{PC} = 79$, 11 Hz, CO *trans* to $P_a$), 179.6 (dt, $J_{PC} = 8$, 8 Hz, CO *cis* to all P).

**Synthesis of *cis,mer*-$[Os(^{13}C_2H_5)(CO)_2(PMe_2Ph)_3]BF_4$.** An NMR tube containing *mer*-$[OsH(CO)(^{13}C_2H_4)(PMe_2Ph)_3]BF_4$ (20 mg, 0.03 mmol) dissolved in $CD_2Cl_2$ was exposed to 1 atm of CO (ca. 0.10 mmol) at −196 °C and was sealed at this temperature. The solution was warmed to room temperature, and the tube was periodically shaken over the course of 48 h. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of this solution revealed that *cis,mer*-$[Os(^{13}C_2H_5)(CO)_2(PMe_2Ph)_3]BF_4$ was the major species in solution (ca. 70%). $^{13}C\{^1H\}$ NMR (25 °C, 99% $^{13}C$ enrichment): $\delta$ −6.14 (ddt, $J_{CC} = 33$ Hz, $J_{PC} = 15$, 7.5 Hz, C$\alpha$), 21.78 (dd, $J_{CC} = 33$ Hz, $J_{PC} = 8$ Hz, C$\beta$). $^{31}P\{^1H\}$ NMR (25 °C): $\delta$ −47.5 (tdd, $J_{PP} = 28$ Hz, $J_{PC} = 15$, 8 Hz, 1P), −43.7 (dd, $J_{PP} = 28$ Hz, $J_{PC} = 8$ Hz, 2P).

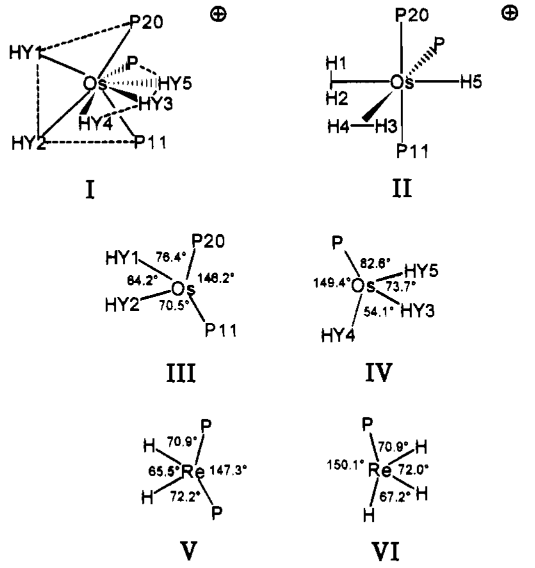
**Synthesis (*in Situ*) of *cis,mer*-$[Os(C(O)Et)(CO)_2(PMe_2Ph)_3]BF_4$ (5).** At −196 °C, an NMR tube containing a frozen solution $CD_2Cl_2$ of *mer*-$[OsH(CO)(C_2H_4)(PMe_2Ph)_3]BF_4$ (20 mg, 0.03 mmol) was exposed to 1 atm of CO (ca. 0.1 mmol) and was sealed. The solution was thawed to room temperature, and after 14 d the reaction was complete. Yield: quantitative. $^1H$ NMR (25 °C): $\delta$ 7.60−7.30 (m, 15H, Ph), 2.67 (q, $J_{HH} = 7$ Hz, 2H, $CH_2$), 1.86 and 1.84 (each a vt, 4 Hz, PMe), 1.71 (d, $J_{PH} = 9$ Hz, 6H, PMe), 1.03 (t, $J_{HH} = 7$ Hz, $CH_3$). $^{31}P\{^1H\}$ NMR (25 °C): $\delta$ −46.4 (t, $J_{PP} = 29$ Hz, 1P), −40.8 (d, $J_{PP} = 29$ Hz, 2P). $^{13}C\{^1H\}$ NMR (25 °C, 99% $^{13}C$ enrichment): $\delta$ 244.9 (dt, $J_{PC} = 10$, 10 Hz, *C*(O)Et *cis* to all P), 179.5 (dt, $J_{PC} = 81$, 10 Hz, CO *trans* to $P_a$), 179.4 (dt, $J_{PC} = 9$, 9 Hz, CO *cis* to all P).

**Synthesis (*in Situ*) of *cis,mer*-$[Os(C(O)^{13}C_2H_5)(CO)_2(PMe_2Ph)_3]BF_4$.** Conditions used to generate **4**-$^{13}C_2H_5$ were employed, and after 14 d, all of **4**-$^{13}C_2H_5$ had been converted into the $^{13}C$-enriched propionyl cation **5**. $^{13}C\{^1H\}$ NMR (25 °C, 99% $^{13}C$ enrichment): $\delta$ 61.84 (d, $J_{CC} = 35$ Hz, $CH_2$), 8.97 (d, $J_{CC} = 35$ Hz, $CH_3$).

**Acidolysis of *cis,mer*-$OsH_2(CO)(PMe_2Ph)_3$ in the Presence of L′ (L′ = CO, $C_2H_4$).** In a 100-mL flask, a 25-mL diethyl ether solution of *cis,mer*-$OsH_2(CO)(PMe_2Ph)_3$[15] (77 mg, 0.16 mmol) was saturated with gas L (L = CO, $C_2H_4$) at 1 atm. To this solution was added 20 $\mu$L of 85% $HBF_4{\cdot}OEt_2$ (0.16 mmol). This addition of acid caused an immediate precipitation of a white solid, which was filtered off and dried *in vacuo* on a glass frit. The $^1H$ and $^{31}P\{^1H\}$ NMR spectra of these powders matched those reported here for *cis,mer*-$[OsH(CO)_2(PMe_2Ph)_3]BF_4$ and *mer*-$[OsH(CO)(C_2H_4)(PMe_2Ph)_3]BF_4$, respectively.

**Reppe Hydroformylation of 1-Hexene.** Typically, 0.02 mmol of *mer*-$[OsH(CO)_2(PMe_2Ph)_3]BF_4$ was dissolved into 15 mL of either THF or $CH_2Cl_2$. These solutions were transferred into a 100-mL flask equipped with a Kontes valve. At 0 °C, 1.50 mL of 1-hexene (11.99 mmol) and 2.5 mL of degassed $H_2O$ were added to this solution. This heterogeneous mixture was frozen, and the system was placed under 2 atm of CO at this temperature (−196 °C). These reactions were stirred for 40−90 h at 25 °C. At the end of the reaction period, the flask was vented and the organic layer was separated from the mixture. In the air, the organic layer was flash-chromatographed on a silica gel column, which was then washed with 2 × 10 mL toluene. The eluents were collected in a flask, which was immediately stoppered to prevent evaporation of products. Capillary gas chromatography was done with a Varian 3700 fitted with a 60-m (0.25 $\mu$m diameter, polar phase) Supelcowax 10 column. This analytical technique was used to identify and quantify the aldehyde products. An integration calibration factor was calculated from the peak area ratio of five known mixtures of 1-hexene and heptanal in toluene.

**Chart 1**



## Results

**Synthesis and NMR Spectra of $[OsH_5(PMe_2Ph)_3]BF_4$.** Addition of excess (10-fold) 85% $HBF_4{\cdot}OEt_2$ to $OsH_4(PMe_2Ph)_3$ in $Et_2O$ affords immediate precipitation of a yellow solid. This reaction proceeds in almost quantitative yield and is a convenient method for isolation of $[OsH_5(PMe_2Ph)_3]BF_4$ (**1**). The metal-bound hydrogens in this compound give a single (exchange-averaged) resonance down to −70 °C at 360 MHz. This metal-bound hydrogen resonance in this compound has a $T_1$ value of 70 ms (360 MHz) at −70 °C in $CD_2Cl_2$, which is consistent with, but does not require, the presence of one or more $H_2$ ligands. For comparison, the $T_1$ value of the hydride resonance of $Os(H)_4(PMe_2Ph)_3$ is 270 ms at 360 MHz and −70 °C in toluene-$d_8$.

**Solid-State Structure of $[OsH_5(PMe_2Ph)_3]BF_4$.** A crystal grown from $CH_2Cl_2$ was subjected to an X-ray diffraction study at −172 °C. However, the hydrogens attached directly to the metal were unobserved ($R(F) = 0.045$), so a larger crystal was subjected to a neutron diffraction structure determination at 11 K. The $Os(PMe_2Ph)_3^+$ substructures from both studies agreed to within $3\sigma$ for all bond distances and angles, and henceforth only the neutron results will be discussed (Figure 1). The shortest (Os) H-to-F separation is 2.69 Å, which rules out any hydrogen bonding. The cation conforms well to a dodecahedral structure of formula $Os(H)_5(PMe_2Ph)_3^+$ in the sense that there are two orthogonal trapezoidal planes, one containing P11, P20, HY1, and HY2 and the other containing P, HY3, HY4, and HY5. The bulkier ligands (phosphines) occupy the more spacious B sites of the dodecahedron. The Os−H distances are identical to within $2\sigma$. The H/H distances, however, contain some interesting inequalities. The HY3/HY5 distance is long (1.98(4) Å), the HY1/HY2 distance is shorter (1.75(3) Å), and the HY3/HY4 distance is shortest (1.49(4) Å). This makes clear the structural relationship of the eight-coordinate polyhedron (**I**) (Chart 1) to the other extreme, a bis(dihydrogen) compound of formula $OsH(H_2)_2(PMe_2Ph)_3^+$ and structure **II**. In particular, the Os/HY1/HY2 plane is orthogonal to the Os/HY3/HY4 plane. While we do *not* feel that the structural data support a dihydrogen formulation, the presence of one uniquely short H/H separation in this cation certainly helps to explain the short $T_1$ value. It also suggests an appropriate way to analyze the dihydrogen/dihydride dichotomy by the fragment molecular orbital procedure (see below). The short HY3/HY4 separation is also significant in comparison to the corresponding distance

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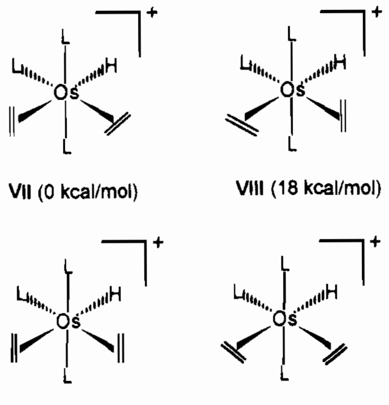
[15] Bell, B.; Chatt, J.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1973**, 997.

**Chart 2**



VII (0 kcal/mol) VIII (18 kcal/mol)

IX (7 kcal/mol) X (61 kcal/mol)

(1.845(7) Å) in isoelectronic $ReH_5(PMePh_2)_3$.[16] The shorter separation in the osmium cation correlates with the higher metal oxidation state moving *toward* collapse of two hydrides to $H_2$ as the metal is less easily oxidized.

The angles within the ligands comprising each trapezoid also show distortions characteristic of H/H attractive interactions. Although the angles between P20/P11 and P/HY4 are very similar, the interhydrogen angles are not (compare **III** and **IV** in Chart 1). In particular, the HY3/HY4 angle is very small and the HY3/HY5 angle is quite large. Taken in comparison to the corresponding values in $ReH_5(PMePh_2)_3$ (average of two independent molecules shown in **V** and **VI** in Chart 1), the evidence that the hydrogens in $Os(H)_5(PMe_2Ph)_3^+$ are distorted away from purely noninteracting hydrides is strong.

**Synthesis of *cis,mer*-$[OsH(C_2H_4)_2(PMe_2Ph)_3]BF_4$.** Reaction of the cation $OsH_5L_3^+$ in $CH_2Cl_2$ with 1 atm of ethylene (25 °C) generates (within 1 h) ethane ($^1H$ NMR evidence) and a high yield of the cream-colored compound *cis,mer*-$[OsH(C_2H_4)_2(PMe_2Ph)_3]BF_4$ (**2**). In the absence of 1 atm ethylene, *cis,mer*-$[OsH(C_2H_4)_2(PMe_2Ph)_3]BF_4$ is stable in $CH_2Cl_2$ for only about 6 h at 25 °C. Solvents such as THF, DME, and acetone also decompose *cis,mer*-$[OsH(C_2H_4)_2(PMe_2Ph)_3]BF_4$ to undetermined products within 1 h at 25 °C without an atmosphere of ethylene present.

Compound **2** is stereochemically rigid at 25 °C in $CD_2Cl_2$. The $^{31}P\{^1H\}$ NMR pattern shows an $AM_2$ spin system, and the P−Me proton signals show two virtual triplets and one doublet, each representing two methyl groups. This indicates the ethylene ligands are *cis* and the phosphines are *mer*. The coordinated ethylene protons show two chemical shifts at 25 °C, indicating rapid rotation of each ethylene about the Os−-(C=C midpoint) line. The $^{13}C\{^1H\}$ NMR spectrum of the ethylene carbons in *cis,mer*-$OsH(^{13}C_2H_4)_2L_3^+$ shows a doublet and a singlet. Assuming $J$(P−C) is larger for *trans* than for *cis* stereochemistry leads to the conclusion that the $^{13}C$ doublet is for the ethylene ligand *trans* to the unique phosphorus. Such a conclusion is supported by the coupling constants (see below) in $OsH(CO)(C_2H_4)L_3^+$. A $^{13}C/^1H$ heteronuclear 2D-NMR spectrum established that the 1.40 ppm proton signal is attached to the ethylene carbon doublet. The 2.84 ppm $^1H$ NMR signal is thus that of the ethylene protons *trans* to hydride.

Ethylene rotation is slowed by −40 °C ($^1H$ NMR at 500 MHz), which gives $\Delta G^{\ddagger} = 12.0(5)$ kcal/mol for the rotational barrier.[17] The number of proton chemical shifts observed below −40 °C (four) fails to uniquely establish the preferred orientation of the ethylene C=C vectors. This was therefore accomplished by an X-ray diffraction study.

**Solid-State Structure.** The unit cell contains noninteracting $BF_4^-$ anions and *cis,mer*-$OsH(C_2H_4)_2L_3^+$ cations and $CH_2Cl_2$. The angles within the cation (Figure 2) are close to 90 and 180°, although the transoid angle P6−Os−P24 is only 162° due to bending of the phosphines toward the small hydride ligand. The Os−P distances span a range of 0.0259 Å; while this represents some 10 esd's, the absolute difference is small, unpredictable (i.e., the "chemically equivalent" transoid phosphines differ most of all), and probably not chemically significant. Of special chemical interest is the fact that the Os−C distances *trans* to hydride and *trans* to phosphine differ by less than 7 esd's. The ethylene *trans* to hydride shows only slightly longer Os−C distances. This lack of difference in Os−C distances is *unexpected* if the *trans* influence of hydride vs phosphine is considered. Similarly, the two ethylenes show C=C distances which are identical to within 1 esd. All of these features are also true of the isoelectronic species $ReH(C_2H_4)_2(PMe_2Ph)_3$.[18]

Having drawn from the data the conclusion that the Os−$C_2H_4$ units *trans* to hydride and to phosphine exhibit no major differences, it must be pointed out that they adopt quite different rotational conformations: the C=C axes are mutually orthogonal (Figure 2), and these eclipse the axes of the octahedron at Os. Such orthogonality avoids competition of the two olefin $\pi^*$ orbitals for back-bonding from the *same* filled $d_\pi$ orbital. The more stable isomer (conformer) among orthogonal alternatives **VII**−**VIII** (Chart 2) originates from a stabilizing overlap of the filled Os−H bonding orbital and the $\pi^*$ orbital of the *cis* olefin which is possible only in conformer **VII**.[1,19] Such a long range interaction should not be construed as an agostic interaction, since the identical Os−C2 and Os−C3 distances preclude C3 being an incipient $sp^3$ (methyl) group. Ethylene/ethylene steric repulsion is worst in **X** (which also has the two olefins competing for the same d orbital). Since **X** is one structure which would accomplish *rotation* of the olefin *trans* to hydride, the observed (12.0 kcal/mol) barrier can be used to rule out **X** as the transition state. It is therefore probable that the vinyl proton site exchange occurs by a *correlated* rotation of both olefins.

**Mechanism of Ethylene Reduction.** The 1:4 stoichiometry of the balanced hydrogenation

$$OsH_5L_3^+ + 4C_2H_4 \rightarrow cis,mer\text{-}OsH(C_2H_4)_2L_3^+ + 2C_2H_6$$

portends a complex reaction pathway. Mechanistic insight has been obtained through reactions of controlled stoichiometry, trapping of transients, and selected isotopic labeling.

Presented in Scheme 1 is a proposed mechanism. The following discussion of individual experimental results will be used to support individual steps. All numbered species have been isolated and characterized, while all upper case lettered species are intermediates implicated by labeling studies.[20]

(a) **Establishing the Intermediates.** Unsaturated polyhydrides are rare and quite reactive. Earlier work involving

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[16] Emge, T. J.; Koetzle, T. F.; Bruno, J. W.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 4012.

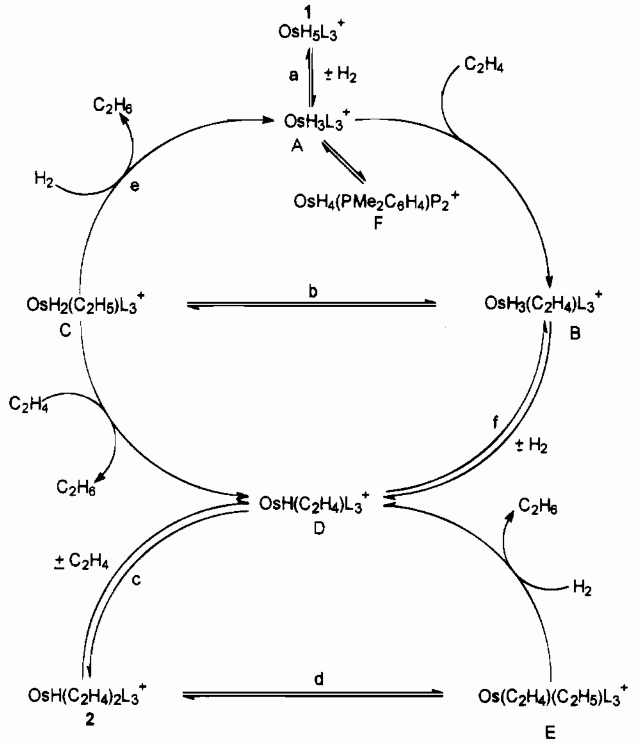
[17] Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 86.

[18] Komiya, S.; Baba, A. *Organometallics* **1991**, *10*, 3105.

[19] (a) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. Os parameters: Tuan, D. F.-T.; Hoffmann, R. *Inorg. Chem.* **1985**, *84*, 871. (b) Van Der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831.

[20] All ethane eliminations in Scheme 1 are written as kinetically irreversible, based on our skepticism that any of the compounds in Scheme 1 can attack ethane at 25 °C in competition with $H_2$ or ethylene.

**Scheme 1**



$OsH_5L_3^+$ had shown evidence for initial loss of $H_2$ (eq a) by trapping with $CH_3CN$.[21] We investigated this in a more subtle way by stirring $OsH_5L_3^+$ in $CH_2Cl_2$ under $D_2$ at 250 psi for 20 h. The $^2H$ NMR spectrum of the resulting solution revealed complete conversion to $OsD_5L_3^+$ along with slight deuterium enrichment at the *ortho* positions of the phosphine phenyl rings. We propose that this exchange occurs by a mechanism dissociative in $H_2$ (eq a), which implicates an unsaturated $OsH_3L_3^+$ species **A**, which *ortho*-metalates the aryl ring to achieve Os−D/C−H exchange (species **F**).[22] Capture of $OsH_3L_3^+$ by $C_2H_4$ then begins a circuit around a hydrogenation loop.

Many attempts were made to either isolate or spectrally observe the intermediate $OsH_3(C_2H_4)L_3^+$ (**B**). A 1:1 reaction of $OsH_5L_3^+$ and $C_2H_4$ yielded only **2**, ethane, and unreacted **1**. Low-temperature $^1H$ NMR investigations of this same reaction did not reveal any intermediates. However, $OsH_3L_3(NCCH_3)^+$ has been characterized from a 1:1 reaction of $OsH_5L_3^+$ and $NCCH_3$.[21]

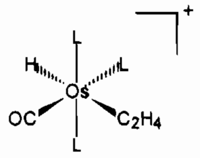
Evidence for the reactivity of **B** comes from the reaction of $OsD_5L_3^+$ with 1 atm of ethylene, monitored by $^2H$ NMR. At 25 °C, the $^2H$ NMR spectrum taken immediately after a frozen $CH_2Cl_2$ solution of $OsD_5L_3^+$ was thawed in the presence of 1 atm of $C_2H_4$ revealed a deuterium NMR singlet at −7.02 ppm ($OsD_5L_3^+$) and another at 0.7 ppm ($C_2H_{6-x}D_x$). Within 20 min, coordinated $C_2H_{4-x}D_x$ was observed at 2.85 and 1.40 ppm, which is consistent with the formation of *cis,mer*-$OsH(C_2H_{4-x}D_x)_2L_3^+$. This observation of coordinated $C_2H_{4-x}D_x$ and very early production of $C_2H_{6-x}D_x$ implies that **B** scrambles Os−D with coordinated ethylene CH by equilibrium b, involving species **C**. The conversion of **B** to **D** by loss of $H_2$ (eq f) is supported by the observation that $OsH_5L_3^+$ reacts with CO to give $OsH(CO)_2L_3^+$ and $H_2$.

The intermediate **C** can then add (eq e) $H_2$ liberated in the initial equilibrium a. Proof of recoordination of the $H_2$ eliminated in equilibrium a (i.e., its subsequent consumption) comes from the reaction of **1** with 2 equiv of 1,5-cyclooctadiene. The products of this reaction are *fac*-$OsHL_3(\eta^4\text{-COD})^+$ and *cyclooctane*; no cyclooctene or $H_2$ is detected.

**(b) Reactivity of *cis,mer*-$[OsH(C_2H_4)_2(PMe_2Ph)_3]BF_4$ (2).** A study of the reactivity of this cation is informative with regard to the way(s) in which the hydrogenation reaction circuit can be re-entered.

Compound **2** readily reacts with $H_2$ (1 atm) at 25 °C in $CH_2Cl_2$ to produce $OsH_5L_3^+$ and ethane but with no *net* production of ethylene. Equilibrium f is included since some route is necessary to convert **2** to **1** under $H_2$. The high reactivity of **2** toward $H_2$ is consistent with the fact that **2** decomposed (e.g., was labile) in $CH_2Cl_2$ in the absence of free ethylene.

An attempt was made to establish the identity of any unsaturated transient arising from thermal ligand dissociation by **2**. Using 1 atm of $^{13}CO$ as a trapping reagent, after 5 min at 25 °C in $CD_2Cl_2$, there is complete and exclusive conversion of **2** to **3** with liberation of 1 mol of ethylene.



**3**

The structure was assigned on the basis of the $^{31}P\{^1H\}$ ($AM_2$ pattern for isotopically normal CO) and P−Me $^1H$ NMR (two virtual triplets and a doublet) and the magnitude of coupling constants within the $^{13}CO$ and $^{13}C_2H_4$ isotopomers. In particular, $OsH(^{13}CO)(C_2H_4)L_3^+$ shows a doublet (87 Hz) of triplets (10 Hz) for the CO ligand; the large *J* value indicates CO is *trans* to the unique phosphine. In contrast, $OsH(CO)(^{13}C_2H_4)L_3^+$ shows an apparent $^{13}C$ singlet, indicating small (therefore *cis*) coupling constants to all three phosphorus nuclei.

Since the structure of **3** would seem to imply that the ethylene *trans* to phosphine is more labile than that *trans* to hydride in **2**, we worked to establish whether **3** is the kinetic product of this reaction or only the thermodynamic product as a consequence of rapid rearrangement of the kinetic isomer. One atmosphere of CO was added to a frozen NMR tube containing a solution of **2** in $CD_2Cl_2$. The tube was warmed to −78 °C, and the $^1H$ NMR spectrum was immediately recorded in a probe precooled to −50 °C. Within 0.5 min, the spectrum showed only equimolar free ethylene and $OsH(CO)(C_2H_4)L_3^+$, isomer **3**. In $CH_2Cl_2$ under 1 atm of $N_2$, **3** does not isomerize or decompose after 14 days. We conclude that **3** is the kinetic product from the trapping of the 16-electron intermediate **D**, via equilibrium c (Scheme 1).

To establish unequivocally which of the chemically inequivalent ethylenes dissociates in equilibrium c, a solution of compound **2** in $CD_2Cl_2$ was exposed to 1 atm of 99% $^{13}C_2H_4$ in a sealed NMR tube at 25 °C for 5 min. Surprisingly, the $^{13}C$ NMR spectrum showed *both* ethylene positions in compound **2** to be equally enriched. This exchange at both (inequivalent) ethylene positions at apparently identical rates is paradoxical. This was clarified by following the exchange at low temperature.

Warming a solution of **2** in $CD_2Cl_2$ from −196 to −10 °C under 1 atm of 99% $^{13}C_2H_4$ reveals exclusive enrichment of the olefinic position *trans* to phosphine. Ethylene exchange in the site *trans* to hydride was first evident upon further warming

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(21) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663.

(22) In the chemistry of $OsH_5(PPh_3)_3^+$, an *o*-metalated aryl ring transient inserts ethylene. See: Desrosiers, P. J.; Cai, L.; Halpern, J. *J. Am. Chem. Soc.* **1989**, *111*, 8513.

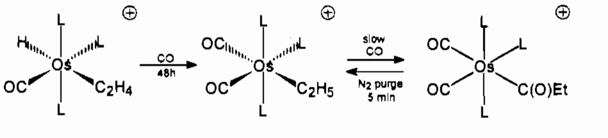
(to 0 °C). The two chemically-inequivalent ethylene ligands thus do exchange at distinct rates, but the associated activation energies are very similar.

In addition to eq c, compound **2** participates in a *second* equilibrium, in which *cis,mer*-$OsH(C_2H_4)_2L_3^+$ (**2**) undergoes a hydrogen shift to form $[Os(C_2H_4)(C_2H_5)L_3]^+$ (**E**). The existence of this equilibrium was established by treating **2** with $C_2D_4$ in $CD_2Cl_2$. The proton NMR spectrum of this solution after 90 min showed no hydride resonance at −6.77 ppm for **2**. Also, free $C_2H_xD_{4-x}$ and coordinated $C_2H_xD_{4-x}$ (1.40 ppm) were observed.

**$OsH_5L_3^+$ as a Catalyst for Hydrogenation of Cyclohexene.** We next tested the reactivity of the osmium polyhydride cation toward an *internal* olefin. An NMR tube charged with cyclohexene and **1** (30:1 mole ratio) under $N_2$ in $CD_2Cl_2$ was monitored by $^1H$ NMR spectroscopy for 1 h at 25 °C. Only cyclohexane and unreacted cyclohexene were detected. The organometallic products were not characterized. Under conditions of excess $H_2$ (1000 psi), **1** catalytically reduced cyclohexene at a rate of 12.5 turnovers/h at 25 °C.

**Coupling of Hydride, $C_2H_4$, and CO.** We next focus attention on the surprising lability of $d^6$ octahedral *cis,mer*-$[OsH(C_2H_4)_2L_3]BF_4$. We established above its rapid reaction with CO and with $^{13}C_2H_4$. A slower CO addition reaction was also detected. Although H and $C_2H_4$ in **2** are mutually *trans*, this cation nevertheless reacts to completion (in 14 days) with CO at 25 °C and 1 atm to give *cis,mer*-$Os[C(O)Et](CO)_2L_3^+$ (**5**). Under 1000 psi of CO, the reaction is complete within 24 h. This compound is stereochemically rigid at 25 °C ,and the NMR data uniquely define the *cis,mer* stereochemistry: $AM_2$ $^{31}P\{^1H\}$ NMR pattern with 2 PMe virtual triplets and one doublet. For the product derived from $^{13}CO$ (i.e., labeled at both the carbonyl and acyl positions), two carbonyl doublets of triplets are observed (179.4 and 179.5 ppm), together with a doublet of triplets for the propionyl carbon (244.9 ppm).[23]

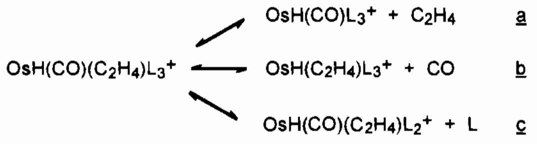
The propionyl cation **5** rapidly (5 min) decarbonylates at 25 °C in $CD_2Cl_2$ solution when CO is replaced by purging with $N_2$. The cation **4** is, however, stable in $CD_2Cl_2$ solution under $N_2$ for at least 2 weeks at 25 °C. In particular, there is no evidence for decarbonylation to **3**. Compound **4** is thus particularly resistant to β-hydrogen migration. The ethyl cation **4** can also be synthesized from **3** under 1 atm of CO in only 48 h, and an NMR study of the reaction under 1 atm CO shows that **4** is an intermediate in the formation of **5** (eq 1).



(1)

**3** **4** **5**

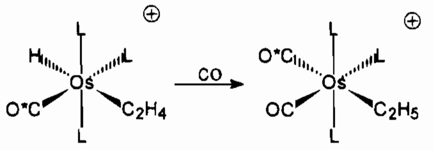
To understand the mechanism of eq 1, we have considered three possible ways (*a*−*c*) to bring H *cis* to $C_2H_4$, prior to



migratory insertion to yield the ethyl group.[24] The resulting five-coordinate species in *b* and *c* would have H *cis* to $C_2H_4$ or could even exist as 18-electron species with an agostic *ethyl* group.

We rule out the occurrence of eq *a* since $OsH(CO)L_3^+$ would be converted to *cis,mer*-$OsH(CO)_2L_3^+$ under 1000 psi of CO. We have made this dicarbonyl independently (see Experimental Section) and find it to be unreactive toward ethylene even at 100 °C for 48 h in $CH_2Cl_2$ (in a stainless steel reactor). In addition, **3** is recovered unenriched ($^{13}C\{^1H\}$ NMR spectrum) after being reacted for 2 weeks at 25 °C under 4 equiv of $^{13}C_2H_4$ (99%).

Equation *b* was evaluated by reaction of **3**-$^{13}CO$ with 3 equiv of natural abundance CO in $CD_2Cl_2$ at 25 °C. Monitoring of this reaction by $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy shows *only* isotopomer **4**-$^{13}CO$ (eq 2) is formed[25] and with complete retention of initial label. The absence of loss of $^{13}C$ label excludes pre-equilibrium loss of CO (eq *b*) as the mechanism for converting H and $C_2H_4$ of **3** into an ethyl group.

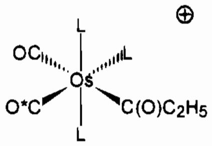


(2)

**3**-$^{13}CO$ **4**-$^{13}CO$

Equation *c* (phosphine dissociation) can also be ruled out by results executed under CO. Under CO, at least *some* of the five-coordinate bis(phosphine) transient should be trapped by CO (1000 psi) to generate bis(phosphine) products. These were absent (by NMR and IR evaluation), as was free phosphine ($^{31}P$ NMR detection). Similarly (under $^{13}CO$), any CO-trapped $Os(C_2H_5)(^{13}CO)(CO)L_2^+$ will have mirror symmetry (or be fluxional), which would lead to incorporation of $^{13}CO$ into *both* carbonyl positions of $Os(C_2H_5)(^{13}CO)(CO)L_3^+$ (**4**-$^{13}CO$). This contradicts observation and thus rules out eq *c* as a participant in the formation of the ethyl group of **4** and **5**. Taken together, the high-pressure CO and the 1-atm $^{13}CO$ results permit rejection of all three dissociative mechanisms (*a*−*c*) for the formation of **4** and **5** from **3**.

Continued monitoring of this reaction shows that the slow conversion of **4**-$^{13}CO$ to **5**-$^{13}CO$ by isotopically normal CO is also stereospecific. The initially coordinated label is entirely *cis* to the propionyl group,



so (with the assumption that the propionyl group is formed from coordinated CO) the incoming CO adds *trans* to the propionyl group. Note that this is opposite to the stereochemistry of CO addition to $OsH(C_2H_4)(CO)L_3^+$, which is *cis* to the formed ethyl group. These data also lead to the interesting conclusion that, while the original Os−CO bond in **3** is never broken during the conversion to **5**, that particular CO never becomes part of the propionyl group.

We have also tested experimentally a bimolecular proton transfer mechanism for formation of the ethyl group (Scheme

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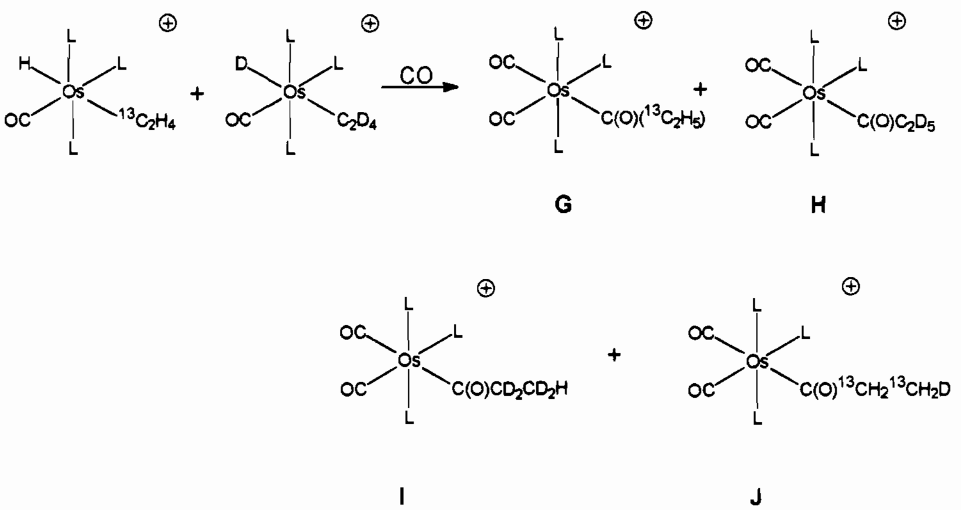
[23] Compare: Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139.

[24] We established that there is no *detectable* isomerization to a cation with H *cis* to $C_2H_4$ by the observation that **3** is unchanged after 2 weeks in $CD_2Cl_2$ at 25 °C under $N_2$.

[25] In the inverse isotope experiment, reaction of $^{13}CO$ with $OsH(CO)(C_2H_4)L_3^+$ gave only the $Os(C_2H_5)(CO)(^{13}CO)L_3^+$ isotopomer with $^{13}CO$ *trans* to the unique phosphine.

**Scheme 2**



2) using a double label experiment. An intramolecular mechanism would produce only **G** and **H**, while a bimolecular mechanism (proton transfer from one HOs species to a second HOs species) would *also* produce **I** and **J**. Our preferred analytical method is $^{13}C\{^1H\}$ NMR, which will detect only **G** and **J**. The $^{13}C$ isotopomers of **H** and **I** will be present at less than 1% of the concentration of **G** and **J**.

Relevant spectral parameters of **G** were determined by following ($^{13}C\{^1H\}$ NMR spectroscopy) the reaction of $[OsH(CO)(^{13}C_2H_4)L_3]BF_4$ with 1 atm of CO. After 14 d at 25 °C,[26] the $^{13}C\{^1H\}$ NMR spectrum of the propionyl complex showed two doublets ($^1J_{CC} = 35$ Hz). Any coupling of these aliphatic carbons to phosphorus is negligible; the full width at half-maximum of the methyl resonance is 3.5 Hz.

Next, an NMR tube containing 0.02 mmol each of $[OsH(CO)(^{13}C_2H_4)L_3]BF_4$ and $[OsD(CO)(C_2D_4)L_3]BF_4$ was exposed to 1 atm of CO (*ca.* 0.1 mmol). After 14 d at 25 °C, propionyl group formation was essentially complete. The $^{13}C\{^1H\}$ NMR spectrum was identical to that of pure **G**. There was no triplet structure (expected $^1J_{CD} = 21$ Hz) due to the presence of some $CH_2D$ group formation at a detection limit of 5 mol %. Product **J** is absent, and *the reaction is thus intramolecular.*

The consequence of the above studies is that an ethyl group is formed from the *trans* H and $C_2H_4$ ligands of $OsH(C_2H_4)(CO)L_3{}^+$ by an intramolecular mechanism in which hydrogen migrates to a position *cis* to ethylene.[27] This reaction is slow perhaps because this intermediate is thermodynamically uphill (none is detected after 2 weeks under $N_2$ at 25 °C).[28] An isotope labeling experiment shows that trapping by dissolved CO is highly stereospecific and occurs *trans* to the formed ethyl group.

**Catalysis.** Addition of 10-fold excess of $HBF_4{\cdot}OEt_2$ to *cis,mer*-$Os(H)_2(CO)(PMe_2Ph)_3$ in $Et_2O$ under 1 atmosphere of $C_2H_4$ or CO results in immediate and quantitative precipitation of $[OsH(CO)(C_2H_4)L_3]BF_4$ or $[OsH(CO)_2L_3]BF_4$, respectively. The high $\nu$(CO) values of the latter cation make it an attractive candidate for catalyzing the water/gas shift reaction.[29] Indeed, a (heterogeneous) 1:1 mixture of $CD_2Cl_2$ and water containing 0.03 mmol of $[OsH(CO)_2L_3]BF_4$ and 0.10 mmol of $^{13}CO$ shows, after 1 h, production of free $H_2$ (4.3 ppm), $OsH(^{13}CO)_2L_3{}^+$, and $^{13}CO_2$ (125 ppm).

This result implies the intermediacy of an unsaturated intermediate which could be trapped by olefin and thus effect Reppe[30-32] hydroformylation eq 3). Indeed, $OsH(CO)(L')L_3{}^+$

$$2CO + H_2O + RHC{=}CH_2 \rightarrow RH_2C{-}CH_2CHO + CO_2 \quad (3)$$

($L' = CO$ or $C_2H_4$) and also $OsEt(CO)_2L_3{}^+$ in either $THF/H_2O$ or $CH_2Cl_2/H_2O$ (each 1:1) under 2 atm of CO convert 1-hexene to heptanal and 2-methylhexanal at 25 °C with turnover numbers of 0.72 ($CH_2Cl_2$) and 2.16 (THF) per day and an *n/iso* ratio of 2.

## Discussion

Our study[33] of the photochemical reactivity of $OsH_4L_3$ originated because of its lack of facile thermal reactivity. All of what we report here supports the idea that protonation is an effective way to markedly increase reactivity. Initially, it appears that the cationic polyhydride reversibly dissociates $H_2$. Although $H_2$ is *not* a ligand in $Os(H)_5L_3{}^+$, $H_2$ serves as a good leaving group and thereby provides access to an unsaturated transient, $OsH_3L_3{}^+$. Also noteworthy is the fact that the several six-coordinate $Os^{II}$ species reported here are unusually labile for $d^6$ octahedral species. In general, $d^6$ octahedra are kinetically inert.

The detailed mechanism by which *cis,mer*-$[OsH(C_2H_4)_2L_3]^+$ exchanges each of its structurally- and chemically-inequivalent

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(26) After only 48 h, the solution contained primarily *cis,mer*-$Os(CO)_2(^{13}C_2H_5)L_3{}^+$, whose NMR parameters are given in the Experimental Section.

(27) A two-step mechanism via an intermediate formyl complex, $Os[C(O)H](C_2H_4)L_3{}^+$, is also attractive, in part since it would be expected to be endergonic. For an intramolecular hydrogen transfer from formyl to nitrene ligands (with the formyl resulting from the bimolecular reaction of $LiBH_4$ and a tungsten carbonyl cation) see: Luan, L.; Brookhart, M.; Templeton, J. L. *Organometallics* **1992**, *11*, 1433.

(28) Isomerizations of six-coordinate species are generally slow, even when one or more hydride ligands are present. See: Muetterties, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5097. $Ru(H)_2(CO)(PPh_3)_3$ exhibits a faster intramolecular isomerization. See: Ball, G. E.; Mann, B. E. *J. Chem. Soc., Chem. Commun.* **1992**, 561.

(29) Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1986**, *108*, 6100.

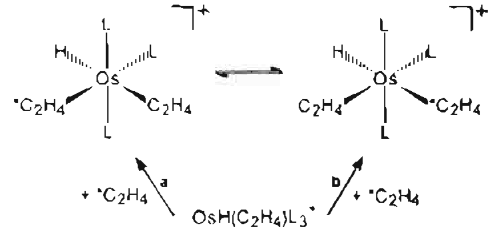
(30) (a) Escaffre, P.; Thorez, A.; Kalk, P. *J. Mol. Catal.* **1985**, *33*, 87. (b) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637. (c) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119. (d) Cheng, C. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1978**, *100*, 5968. (e) Cheng, C. H.; Kuritzkes, L.; Eisenberg, R. *J. Organomet. Chem.* **1980**, *190*, C21. (f) Kaspar, J.; Spogliarich, R.; Cernogoraz, A.; Graziani, M. *J. Organomet. Chem.* **1983**, *255*, 371. (g) Murata, K.; Matsuda, A.; Bando, K.; Sugi, Y. *J. Chem. Soc., Chem. Commun.* **1979**, 785. (h) Okano, T.; Kobayashi, H.; Konishi, H.; Kiji, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3799. (i) Palayi, J.; Marko, L. *J. Organomet. Chem.* **1982**, *236*, 343. (j) Alessio, F.; Vinzi, R.; Mestroni, G. *J. Mol. Catal.* **1984**, *22*, 327.

(31) Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139.

(32) Laine, R. M.; Crawford, E. J. *J. Mol. Catal.* **1988**, *44*, 357.

(33) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Zubkowski, J. D.; Hatfield, W. E.; Caulton, K. G. *Organometallics* **1990**, *9*, 2556.

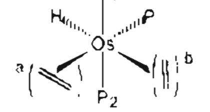
$C_2H_4$ ligands with $^{13}C_2H_4$ warrants comment. The rate of intramolecular site exchange (eq 4) is too slow to account for transfer of label into the less reactive site (*trans* to hydride); no such fluxional process has been detected. We therefore propose that dissociation of the ethylene *trans* to phosphine has a slightly lower activation energy than that of the ethylene *trans* to hydride. Noteworthy, however, is the fact that both processes create the same transient product, $OsH(C_2H_4)L_3^+$. By microscopic reversibility, then, this single species can undergo attack by $^{13}C_2H_4$ from different directions to produce isotopomeric products, with $\Delta G^{\ddagger}(\mathbf{a}) < \Delta G^{\ddagger}(\mathbf{b})$ in eq 4. Moreover, the 18-electron cation, $OsH(C_2H_4)_2L_3^+$, participates in yet another reaction: a hydride shift to an olefin occurs to produce the ethylene/ethyl cation (**E** in Scheme 1) and thus scrambles hydride and vinylic hydrogens. Thus, $OsH(C_2H_4)_2L_3^+$ is an unusually rich source of reactivity types.



(4)

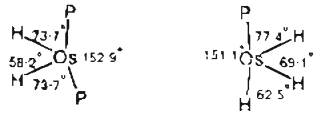
**D**

**Consequences of the Angular Distortion within the $Os(PR_3)_3$ Moiety. (a) Reactivity of $OsH(C_2H_4)_2(PMe_2Ph)_3^+$.** The discovery that ethylene dissociates faster from site a than from site b in **XI** is the sort of classic evidence upon which the *trans* effect is based. In this case, it would lead to the conclusion that $PMe_2Ph$ has a larger *trans* effect than hydride, yet this contradicts the order conventionally cited[34] (i.e., H > $PR_3$). The origin of this paradox is as follows: In $OsH(C_2H_2)_2L_3^+$, the structure has $P_1$ and $P_2$ bent toward the hydride. This has the effect of raising the energy of the $d_\pi$ orbital in the $HOsP_1P_2$ plane, which selectively strengthens the back bonding to $(C_2H_4)^b$. Thus, the different rates of ethylene dissociation are controlled not simply by the *trans* ligand but by distortions of other ligands (which are definitely not simply passive "spectator" ligands) away from octahedral geometry. Such distortions of the coordination sphere of six-coordinate compounds may quite generally frustrate generalized applications of *trans* effect ranking derived from four-coordinate species (e.g., $Pt^{II}$).



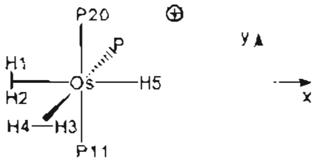
**XI**

**(b) Consequences for the Structure of $OsH_5(PMe_2Ph)_3^+$.** A systematic study at various levels of *ab initio* theory has concluded[35] that $OsH_5(PH_3)_3^+$ is a pentahydride and contains no $H_2$ ligands. This is in agreement with earlier calculations.[36] Apparently then,[37] this is another case where the $T_{1min}$ criterion is not uniquely discriminating for the presence of an $H_2$ ligand since many intermediate H/H separations can accumulate to shorten $T_{1min}$ to nearly that of a single short (i.e., H--H bonded) state. What is important to recognize, however, is that even the very detailed *ab initio* study of $OsH_5(PH_3)_3^+$ (**XII**) fails to reproduce the short distance between at least one pair of hydride ligands found in $OsH_5(PMe_2Ph)_3^+$. Moreover, that study fails to address the question of why the structure does not contain any $H_2$ ligands. We now address this question, as well as that of why (Figure 1) HY1/HY2 is longer than HY3/HY4 and why HY3 is closer to HY4 that it is to HY5.



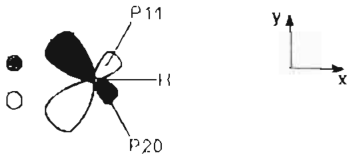
**XII**

An instructional starting point for discussing the structure is that of a $d^6$ octahedron, **6**, with two $H_2$ ligands. The large bulk of the phosphines disfavors either an ideal *mer* or *fac* arrangement with 90° angles between the phosphines. Significant distortions are therefore expected. In $OsH_5L_3^+$ the three phosphines are better viewed as being in a *mer* geometry, with the two *trans* phosphines bent toward the smaller unique ligand HY5 (P11−Os−P20 = 146.2°). This angular distortion results in an increase of the distance from each of the two transoid phosphines to the cisoid one without drastically changing the overall shape of the complex. Very similar angles are found in $ReH_5(PMePh_2)_3$[14] (P−Re−P = 146.5°), $Fe(H)_2(H_2)(PEtPh_2)_3$[17] (P−Fe−P = 149.8°), and even in $OsH(C_2H_4)_2L_3^+$ (P−Os−P = 162.09°).



**6**

This displacement of the two *trans* phosphines has drastic consequences for the coplanar ligands since the *xy* orbital is no longer nonbonding with respect to these two phosphines; it is destabilized and hybridized away from the phosphines, **7**. This orbital becomes a more powerful electron donor into an empty orbital of proper symmetry. In **6**, it thus transforms an $H_2$ ligand into a dihydride (HY1−Os−HY2 = 64.7°, HY1···HY2 = 1.95 Å).



**7**

There are several ways (**8**−**10**) to arrange the remaining H ligands. We first consider interactions of the $d^4$ $OsP_3(H)_2^{2+}$

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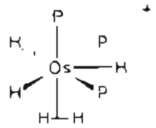
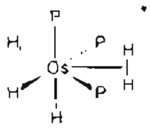
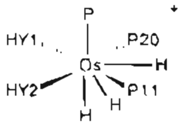


**8**



**9**



**10**

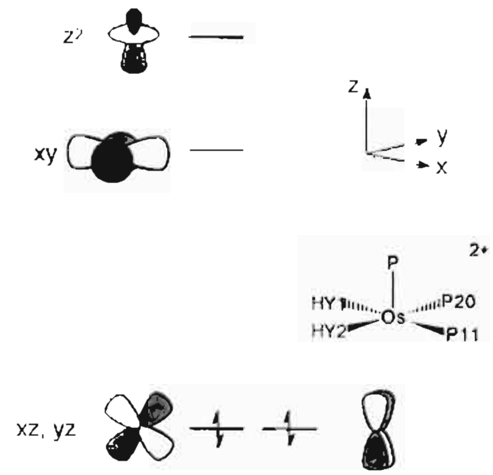
fragment with one H and H$_2$. It can be viewed as square-based with P being the apical site. The d orbitals of this fragment are represented in Scheme 3. Two filled d orbitals, *xz* and *yz*, are essentially nonbonding and nearly degenerate. The *xy* orbital is destabilized by P11 and P20 and by HY1 and HY2. The higher empty orbital is the $\sigma$ hybrid mostly made of $z^2$ extended away from the apical phosphine.

From this energy pattern of the d orbitals, one can understand why structure **8** is a better starting point than the others. It is well-known that hydride has a large *trans* influence; i.e., it is a powerful $\sigma$ donor. It therefore needs to interact with a low-lying empty metal orbital to be efficiently stabilized by the metal, $x^2-y^2$ better than $z^2$. In contrast, H$_2$ is a weakly bonded ligand which can use a higher empty d orbital for making a metal$-$H$_2$ $\sigma$ bond. Therefore, an elongated H$_2$ could use $z^2$ and be *trans* to the apical P. Consequently, in the HY4$-$HY3$-$HY5 group one should expect the HY3$-$HY4 distance to be much shorter (1.49 Å) than HY3$-$HY5 (1.98 Å). However the HY3$-$HY4 bond is in fact broken due to the sufficient back-donation from the *xz* orbital.[38] The HY3$-$HY4 distance remains shorter than the HY1$-$HY2 because the back-donation into $\sigma^*_{\mathrm{HY3-HY4}}$ is done from a nonbonding orbital (*xz*) while that into $\sigma^*_{\mathrm{HY1-HY2}}$ is done from a much higher d orbital ($x^2-y^2$) destabilized by the small angle between the phosphines P11 and P20.

Why are HY3$-$HY4$-$HY5 coplanar? The calculation by Morokuma *et al.* indicates that rotating the HY3$-$HY4 unit would cost more than 10 kcal/mol. No explanation of this fact is given. In this case also, model **6** provides an explanation. We have suggested than an attractive interaction could be at work between a coordinated H$_2$ ligand and a *cis* hydride.[19] This suggests a preference for coplanarity of HY3$-$HY4$-$HY5. The fact that the bond between HY4 and HY3 is cleaved does not apparently affect this preference.[39] This suggests that this interaction does not depend critically on the distance between the hydrides; i.e., the three hydrogen centers would prefer to remain coplanar for any internuclear distance.

Our analysis can be summarized in the following way. The two hydrogens which are in the P11$-$Os$-$P20 plane are forced into a dihydride situation because of the compression of the P11$-$Os$-$P20 angle below 180°. The presence of one phosphine almost perpendicular to the P11$-$Os$-$P20$-$HY1$-$HY2 induces a large *trans* influence so that an elongated H$_2$ unit could be situated *trans* to that phosphine. The remaining hydride would be situated in the P11$-$Os$-$P20$-$HY1$-$HY2 plane. The structural analogy betweeen OsH(C$_2$H$_4$)$_2$(PR$_3$)$_2{}^+$ and OsH$_5$(PR$_3$)$_3{}^+$ (in particular the fact that the more strongly bonded olefin is at the site of the more strongly separated hydrides) also suggests that the d$^2$ polyhydride keeps some memory of its d$^6$ parentage.

**Scheme 3**



## Conclusions

It remains problematic that there are authenticated[40] cases where the H/H separation in a species containing two or more H ligands is in a "gray" region where there may or may not be a direct H/H attractive interaction. The 1.49 Å distance in Os(H)$_5$(PMe$_2$Ph)$_3{}^+$ is one example, and ReH$_7$[P(*p*-tolyl)$_3$]$_2$,[41] with an H/H separation of 1.357 Å, is another. When a distance becomes *twice* that in free H$_2$ itself (0.7 Å), it seems that "dihydrogen" becomes a misleading name,[42,43] yet such distances are less than the sum of van der Waals radii. It must be remembered, however, that the two "gray area" cases cited above are for high coordination numbers (sometimes) involving bulky phosphines, and close H/H contacts may be a consequence of avoidance of H/PR$_3$ contacts. Finally, however, some attractive H/H interactions may exist in the 1.3$-$1.5 Å internuclear distance category and it is probably unwise to imagine that mere names (dihydride and dihydrogen) make a yes/no situation out of what in Nature is surely a continuum.

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**Supplementary Material Available:** Tables of full crystallographic details and atom positional and anisotropic thermal parameters for [OsH(C$_2$H$_4$)$_2$(PMe$_2$Ph)$_3$]BF$_4$·H$_2$Cl$_2$ and full atom positional and thermal parameters for [OsH$_5$(PMe$_2$Ph)$_3$]BF$_4$ (8 pages). For ordering information see any current masthead page.

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(38) The fact that the HY3$-$HY4 bond is broken is beyond the scope of our analysis.

(39) Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1990**, *112*, 7203.

(40) Our experience with hydrogen coordinates derived from X-ray diffraction has shown them to be too unreliable to permit any such example to be *defined* an "unusual" structural type.

(41) Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991**, 241.

(42) The H/H distance in methane is 1.72 Å.

(43) For an opposing opinion, see: Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.