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Cyclometalated Osmium Complexes Containing a Tridentate PCP Ligand

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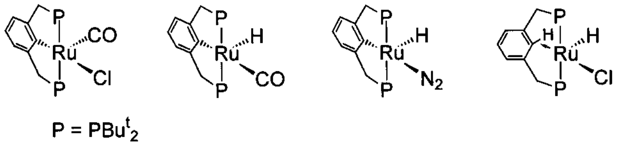
Reactions between $[Et_4N]_2OsCl_6$ and 1,3-$(CH_2PBu^t{}_2)_2C_6H_4$ afforded the 16-e chloride complexes OsCl(CO)(PCP) (**1**) and $OsH_2Cl(PCP)$ (**2**) (PCP = $[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]^-$) in methanol/isoamyl alcohol and 2-propanol, respectively. The iodide $OsH_2I(PCP)$ (**3**) was obtained from **2** in methyl iodide. Treatment of **1** and **2** with $[BH_4]^-$ gave the hydride and dihydrogen compounds OsH(CO)(PCP) (**4**), $OsH(H_2)(CO)(PCP)$ (**5**), and $OsH_3(H_2)(PCP)$ (**6**), while formation of the dihydrogen complexes $Os(H_2)_2Cl(PCP)$ (**7a**) and $OsH_2(H_2)Cl(PCP)$ (**7b**) was observed by NMR in solution of **2** under H_2. The structures of **1**, **2**, and **3** were determined by X-ray crystallography.

Introduction

Diphosphines are common ligands in transition metal chemistry. Their use is motivated by the property of lending the products increased thermal stability (chelate effect) and by the possibility of incorporating a variety of "spacers" between the phosphorus groups for synthetic, structural, and catalytic research. Chelating phosphines normally bind to metal via the phosphorus atoms, in a cis fashion. Less common, in this regard, diphosphines are *m*-xylenyldiphosphine (pincer) ligands, such as PCP = $[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]^-$, where the meta-substituted C_6H_3 group imposes constraints that result in trans addition of the phosphorus atoms to metal.[1] Pincer complexes structurally resemble compounds of monodentate bulky phosphines (normally trans arranged) more than those of regular chelating diphosphines. The bulky PCP system is a good ligand choice for the preparation of thermally stable unsaturated products.[2] We have recently isolated a series of pincer complexes of ruthenium (examples shown in Scheme 1) featuring a number of interesting structural, spectroscopic, and reactivity properties.[3]

To date, only one group of osmium compounds containing a *m*-xylenyldiphosphine PCP-type ligand has been synthesized from the reactions of $OsCl(PPh_3)[2,6\text{-}(CH_2PPh_2)_2C_6H_3]$ with terminal acetylenes.[4] We report here the preparation of new 16-electron complexes of osmium with the bulky PCP = $[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]^-$ ligand and the products of their reactions with $[BH_4]^-$ and H_2.

Scheme 1



Results

Synthetic results are graphically summarized in Scheme 2. Prolonged heating of $[Et_4N]_2OsCl_6$ with the diphosphine 1,3-$(CH_2PBu^t{}_2)_2C_6H_4$ in the presence of triethylamine resulted in the isolation of the cyclometalated carbonyl chloride OsCl(CO)(PCP) (**1**) and hydrido-chloride $OsH_2Cl(PCP)$ (**2**) in primary and secondary alcohols, respectively. The chloro complex **2** slowly undergoes metathesis to the corresponding iodide $OsH_2I(PCP)$ (**3**) in methyl iodide. The structural characterization of **1**−**3** was accomplished by X-ray crystallography, and the ORTEP plots are shown in Figure 1.

Chloride **1** gave a mixture of the hydrides **4** and **5** upon treatment with $[Bu_4N]BH_4$ in ethanol. The loss of H_2 from **5** was incomplete in the reaction solution even at high temperature, and we could not obtain the monohydride **4** in pure form. Borohydride reaction of **2** afforded a polyhydride **6**. The ^1H NMR data (T_{1min} and J_{HD}) imply the presence of a dihydrogen ligand in this molecule, formulated as $OsH_3(H_2)(PCP)$. Unfortunately, this polyhydride is fluxional and does not show decoalescence in the hydride region above −150 °C. Thus, the structure of **6** could not be ascertained; one possible isomer is depicted in Scheme 2. Formation of the dihydrogen species **7a** and **7b** in solution was observed

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[1] Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

[2] Recent reports on pincer complexes: (a) Sundermann, A.; Uzan, O.; Milstein, D.; Martin, J. M. L. *J. Am. Chem. Soc.* **2000**, *122*, 7095. (b) Cao, Z.; Hall, M. B. *Organometallics* **2000**, *17*, 3338. (c) Vigalok, A.; Milstein, D. *Organometallics* **2000**, *19*, 2061. (d) Morales-Morales, D.; Grause, C.; Kasaoka, K.; Redon, R.; Cramer, R. E.; Jensen, C. M. *Inorg. Chim. Acta* **2000**, *300*, 958. (e) Yao, J. Z.; Wong, W. T.; Jia, G. C. *J. Organomet. Chem.* **2000**, *598*, 228. (f) Dani, P.; Van Klink, G. P. M.; Van Koten, G. *Eur. J. Inorg. Chem.* **2000**, *7*, 1465, and references therein.

[3] (a) Gusev, D. G.; Madott, M.; Dolgushin, F. M.; Lyssenko, K. A.; Antipin, M. Yu. *Organometallics* **2000**, *19*, 1734. (b) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Yu. *Organometallics* **2000**, *19*, 3429.

[4] Wen, T. B.; Cheung, Y. K.; Yao, J.; Wong, W.-T.; Zhou, Z. Y.; Jia, G. *Organometallics* **2000**, *19*, 3803.

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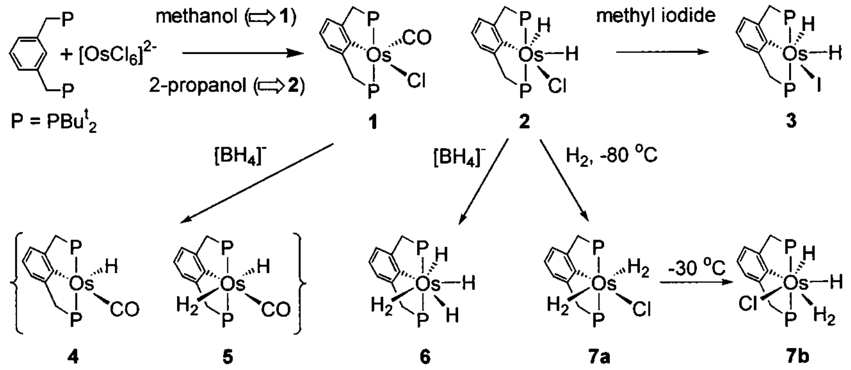
Scheme 2



by NMR upon addition of H_2 to the unsaturated precursor **2**. The assigned structures of new compounds **1**−**5** and **7** are supported by single-crystal diffractometry and spectroscopic data and will be discussed in some detail in the following section.

Discussion

OsCl(CO)(PCP) (1). Formation of **1** from $OsCl_6^{2-}$ requires two-electron reduction of osmium. Presumably, this reaction involves methanol, and it can be balanced as follows:

$$[Et_4N]_2OsCl_6 + 1,3\text{-}(CH_2PBu^t_2)_2C_6H_4 + 3Et_3N + CH_3OH \rightarrow OsCl(CO)[2,6\text{-}(CH_2PBu^t_2)_2C_6H_3]\ (\mathbf{1}) + 2[Et_4N]Cl + 3[Et_3NH]Cl + H_2$$

The square pyramidal molecular geometry of **1** is shown in Figure 1. This compound is isostructural with the ruthenium analogue, RuCl(CO)(PCP),[3a] and most of the bond distances (listed in Table 1) are very similar in both: M−C(2) = 2.080(7) (Os) vs 2.076(4) Å (Ru), M−Cl = 2.413(2) (Os) vs 2.420(1) Å (Ru), M−P (average) = 2.370 (Os) vs 2.376 Å (Ru). Only the metal−carbonyl bond is slightly longer for osmium: 1.786(7) vs 1.757(5) Å. This correlates with a shorter C−O bond in **1**: 1.174(9) vs 1.183(6) Å; however the C−O stretching frequency is actually lower for osmium: 1890 vs 1908 cm^{-1}. The 16-electron coordinatively unsaturated compound **1** is air-stable in the solid state. Some signs of decomposition become apparent only when it is exposed to air for more than 4 weeks at room temperature.

$OsH_2Cl(PCP)$ (2) and $OsH_2I(PCP)$ (3). When $[Et_4N]_2OsCl_6$ is heated with the diphosphine in 2-propanol under argon, the solvent is not decarbonylated and the dihydride **2** is formed in a low yield (46%). The yield increases to 76% when the reaction is carried out under an H_2 atmosphere. Our attempts to further improve the preparation included the use of the better soluble $[Bu_4N]_2OsCl_6$, a higher boiling secondary alcohol 2-pentanol (at 120 °C), and a greater excess of the diphosphine. Counterintuitively, these attempts resulted in lower yields of **2**. NMR monitoring of the filtrates obtained in the isolation of **2** showed $OsH_2Cl(PCP)$ as the sole detectable product. Since the yields varied, there might be some undetected (e.g., paramagnetic) byproduct unobservable by NMR.

Molecular structures of the chloride **2** and the iodide **3** are shown in Figure 1. The C(2)−Os distance, C(2)−Os−X (X = halide) and C(5)−C(2)−Os angles are particularly important for the understanding of ligand bonding in **2** and **3**. Schematic drawings of the equatorial molecular cross-sections in Chart 1 illustrate likely differences between a six-coordinate d^4 Os(IV) dihydride (**A**) and an *idealized* five-coordinate d^6 Os(II) agostic monohydride (**B**).

Crystallographic data listed in Table 1 suggest that **2** and **3** are better regarded as distorted six-coordinate dihydrides (**A** type), different from the related agostic compounds $RuHCl[1,3\text{-}(CH_2PBu^t_2)_2C_6H_4]$ (Scheme 1) and $RuHI[1,3\text{-}(CH_2PBu^t_2)_2C_6H_4]$ that adopt the **B** type structure.[3a] This conclusion is based on the following three pieces of structural evidence that we discuss in connection with Chart 1. (i) The C(2)−Os bonds are normal and show no elongation: 2.070(4) (**2**) and 2.067(3) (**3**) vs 2.080(7) Å in **1**. (ii) The C(5)−C(2)−Os fragment is almost linear in **2** (172.6°) and slightly bent in **3** (165.9°). (iii) The C(2)−Os−X angles of 152.4° (**2**) and 156.3° (**3**) are reduced in comparison with the corresponding angles in $RuHCl[1,3\text{-}(CH_2PBu^t_2)_2C_6H_4]$ (165.2°) and $RuHI[1,3\text{-}(CH_2PBu^t_2)_2C_6H_4]$ (165.1°). We explain this difference by increased C(2)···H(1) separation in **2** and **3**.

Complexes **2** and **3** are fluxional in ^1H NMR and show decoalescence at −60 and −90 °C, respectively, in methylcyclohexane-d_{14}. In the slow exchange regime, the inequivalent hydrides are observed at δ −16.6/−20.3 (**2**) and −19.0/−21.8 (**3**), in agreement with the dihydride formulation. Since these low-temperature spectra were broad and did not reveal any couplings in the hydride region, we studied **2** in other solvents: CD_2Cl_2, THF-d_8, toluene-d_8, and $CDFCl_2/CDF_2Cl$. Unfortunately, the decoalescence temperature was solvent-dependent and decreased in the chlorinated solvents, e.g., to −95 °C in $CDFCl_2/CDF_2Cl$. The least broadened spectrum of **2** was recorded in THF-d_8 at −100 °C. The two resonances at −16.6 and −20.5 ppm were observed as poorly resolved doublets of triplets with the corresponding constants of similar magnitude, ca. 11 Hz.

The coordination geometry of **2** and **3** cannot be described in terms of a regular polyhedron. At best, this can be thought of as derived from a pentagonal bipyramid by removal of an equatorial ligand, with the resulting vacant site formed between the halide and carbon ligands. Structural distortions are common for six-coordinate d^4 osmium compounds. A series of the hydrides $OsHCl_3(PPr^i_3)_2$, $OsH_2Cl_2(PPr^i_3)_2$, and $OsH_3Cl(PPr^i_3)_2$ can be mentioned as related to **2**.[5] These three

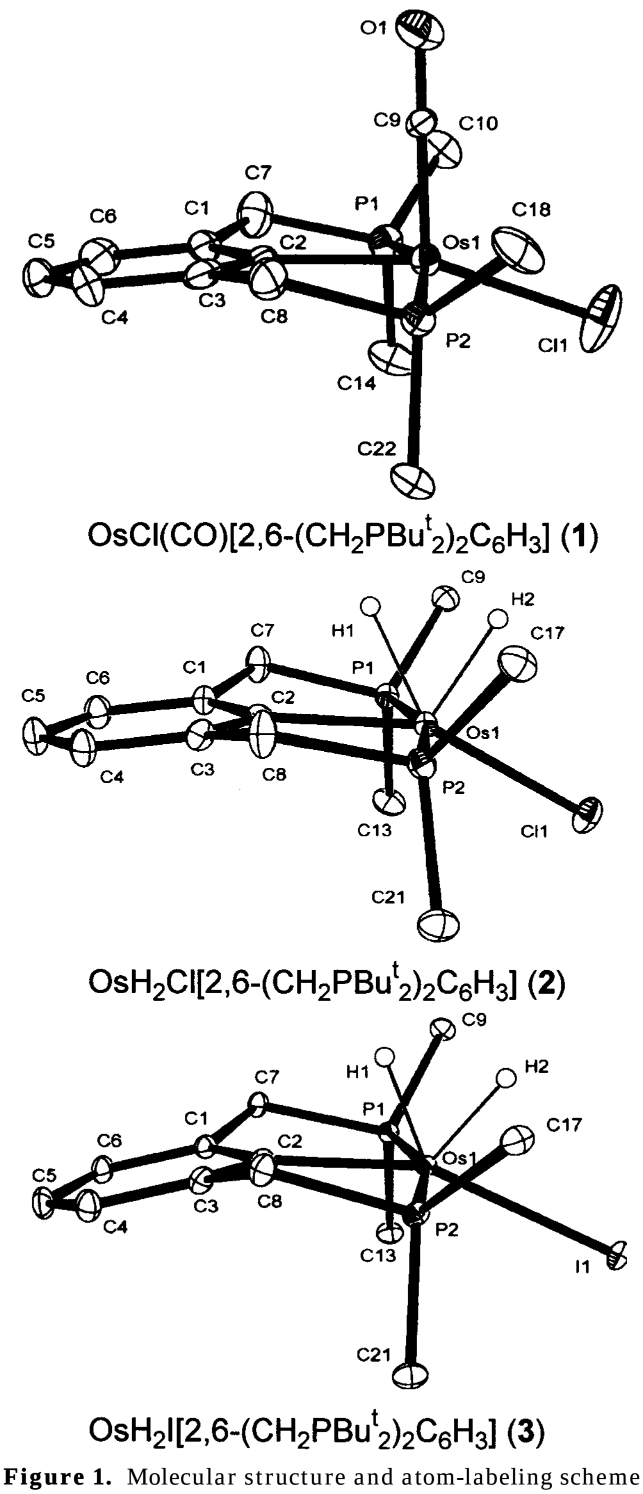


Figure 1. Molecular structure and atom-labeling scheme for complexes **1**−**3**. Thermal ellipsoids are at the 50% probability level. Nonmetal hydrogens and methyl groups are omitted for clarity.

molecules are distorted by bending of the ligands with the strongest trans influence that serves to maximize π-bonding of the chlorides. The structures are amenable to theoretical computational analysis; however they are not intuitively obvious or predictable without calculations.

OsH(CO)(PCP) (4) and OsH(H_2)(CO)(PCP) (5). We recently reported a simple, high-yield preparation of the ruthenium monohydride RuH(CO)(PCP).[3b] The osmium analogue OsH(CO)(PCP) (**4**) can be similarly obtained from **1** and $[BH_4]^-$; however, it could not be isolated in a pure form. The preparation, carried out using a slight excess of $[BH_4]^-$ in boiling ethanol under argon, resulted in a 1:1 mixture of **4** and the thermally stable dihydrogen complex OsH(H_2)(CO)(PCP) (**5**).

OsH(CO)(PCP) is apparently isostructural with RuH(CO)(PCP), which adopts a square pyramidal geometry with the hydride located at the apical site. Both compounds show very negative ^{1}H NMR shifts (δ −37.8 OsH, −27.9 RuH) consistent with the hydride trans to the vacant site. The dihydrogen complex **5** possesses ^{1}H NMR characteristics similar to those of the related osmium complex[6] $OsH(H_2)(CO)Cl(PPr^i_3)_2$: $T_{1\text{min}} = 7.9$ and 6.0 ms (at 300 MHz), and $^1J_{HD} = 29.8$ and 30.9 Hz, respectively.[6b]

At room temperature, the hydride resonances of **5** (δ −8.8) and **4** (δ −37.8) are ca. 56 Hz broad because of the reversible H_2 loss from **5**. There is, however, no saturation transfer (i.e., no exchange) between the dihydrogen (δ −4.75) and the hydride in **5**, consistent with a trans arrangement of these ligands. We also noticed the absence of H/D scrambling between the hydride and dihydrogen sites when the **4**/**5** mixture was dissolved in CD_2Cl_2 under an atmosphere of deuterium. In ca. 15 min, the ^{1}H and ^{31}P NMR spectra revealed formation of a statistical mixture of OsH(H_2)(CO)(PCP), OsH(HD)(CO)(PCP), and OsH(D_2)(CO)(PCP) isotopomers. The appearance of HD in this system is surprising. Another such example has been known for a long time: hydrogen atoms of the H_2 ligand in $W(H_2)(CO)_3(PPr^i_3)_2$ undergo exchange with D_2 to give HD, even in the solid state.[7a] One of us has recently prepared $Re(HD)Br_2(NO)(PPr^i_3)_2$ from the dihydrogen precursor and deuterium gas.[7b] Mechanistically, it is unclear how an 18-electron dihydrogen compound can effect formation of HD from H_2 and D_2.

$OsH_3(H_2)$(PCP) (6). The borohydride reaction of OsH_2Cl(PCP) afforded a polyhydride **6**. The presence of five osmium-bonded hydrogen atoms and a PCP ligand in **6** was established with certainty from the ^{1}H and hydride-coupled ^{31}P NMR spectra. Unfortunately, the OsH_5 resonance at δ −8.5 did not show decoalescence even at −150 °C in $CDFCl_2/CDF_2Cl$, and the fluxionality precluded a definitive structural assignment.

When **6** is dissolved in C_6D_6, deuterated **6**-d is formed by H/D exchange with the solvent (18 mol % in 2 h). The $^2H\{^1H\}$ NMR spectrum of this solution showed a triplet of OsD at δ −8.47 ($^2J_{DP} = 1.1$ Hz) and an equal amount of deuterium at δ 1.14 incorporated in the Bu^t groups of the PCP ligand. After 2 weeks at room temperature, both sites were 60% D-enriched, without decomposition of the compound. Complex **6** is probably losing H_2 in solution, and the transient OsH_3(PCP) species is stabilized as either a solvent complex or an

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[5] (a) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288. (b) Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685. (c) Kuhlman, R.; Gusev, D. G.; Eremenko, I. L.; Berke, H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1997**, *536*, 139.

[6] (a) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (b) Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775.

[7] (a) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (b) Gusev, D. G.; Llamazares, A.; Artus, G.; Jacobsen, H.; Berke, H. *Organometallics* **1999**, *18*, 75.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 1−3

complex **1**		complex **2**		complex **3**	
Os(1)−C(2)	2.080(7)	Os(1)−C(2)	2.070(4)	Os(1)−C(2)	2.067(3)
Os(1)−C(9)	1.786(7)	Os(1)−H(1)	1.57(5)	Os(1)−H(1)	1.54(5)
Os(1)−Cl(1)	2.413(2)	Os(1)−Cl(1)	2.404(1)	Os(1)−I(1)	2.7321(4)
Os(1)−P(1)	2.365(2)	Os(1)−P(1)	2.348(1)	Os(1)−P(1)	2.3587(7)
Os(1)−P(2)	2.376(2)	Os(1)−P(2)	2.336(1)	Os(1)−P(2)	2.3460(7)
C(9)−O(1)	1.174(9)	Os(1)−H(2)	1.62(5)	Os(1)−H(2)	1.51(4)
C(2)−Os(1)−Cl(1)	161.6(2)	C(2)−Os(1)−Cl(1)	152.4(1)	C(2)−Os(1)−I(1)	156.29(7)
C(2)−Os(1)−P(1)	82.6(2)	C(2)−Os(1)−P(1)	83.1(1)	C(2)−Os(1)−P(1)	82.53(7)
C(2)−Os(1)−P(2)	82.2(2)	C(2)−Os(1)−P(2)	82.5(1)	C(2)−Os(1)−P(2)	81.83(8)
P(1)−Os(1)−P(2)	161.30(7)	P(1)−Os(1)−P(2)	165.60 (4)	P(1)−Os(1)−P(2)	164.11(2)
Cl(1)−Os(1)−P(1)	96.26(8)	Cl(1)−Os(1)−P(1)	96.53(4)	I(1)−Os(1)−P(1)	97.20(2)
Cl(1)−Os(1)−P(2)	94.73(8)	Cl(1)−Os(1)−P(2)	95.48(4)	I(1)−Os(1)−P(2)	96.00(2)
C(9)−Os(1)−P(1)	94.0(2)	H(1)−Os(1)−H(2)	60(2)	H(1)−Os(1)−H(2)	61(2)
C(9)−Os(1)−P(2)	95.8(2)	H(1)−Os(1)−C(2)	64(2)	H(1)−Os(1)−C(2)	67(2)
C(9)−Os(1)−Cl(1)	112.0(2)	H(2)−Os(1)−Cl(1)	85(2)	H(2)−Os(1)−I(1)	77(2)
C(9)−Os(1)−C(2)	86.3(3)	C(2)···H(1)	2.00(5)	C(2)···H(1)	2.03(5)
C(5)−C(2)−Os(1)	174.7(1)	C(5)−C(2)−Os(1)	172.58(9)	C(5)−C(2)−Os(1)	165.93(9)

Table 2. Crystallographic Data for Complexes 1−3

	1	2	3
formula	$C_{25}H_{43}ClOP_2Os$	$C_{24}H_{45}ClP_2Os$	$C_{24}H_{45}IP_2Os$
fw	647.21	621.22	712.67
T, K	153	110	110
cryst syst	orthorhombic	triclinic	monoclinic
space group	*Pbca*	$P\bar{1}$	$P2_1/n$
a, Å	11.425(3)	11.874(3)	15.846(3)
b, Å	15.731(3)	15.122(4)	10.781(2)
c, Å	29.500(5)	16.066(4)	16.360(4)
α, deg	90	66.082(5)	90
β, deg	90	85.615(5)	108.572(4)
γ, deg	90	87.943(5)	90
V, Å^3	5302(2)	2629(1)	2649(1)
Z	8	4	4
D(calcd), g/cm^3	1.622	1.569	1.787
abs coeff, mm^{-1}	5.047	5.082	6.108
no. of total reflns	6032	30 698	30 253
no. of unique reflns	6031	15 049	7655
R,[a] %	5.61	3.56	2.56
R_w,[a] %	13.51	7.93	6.31

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

Chart 1

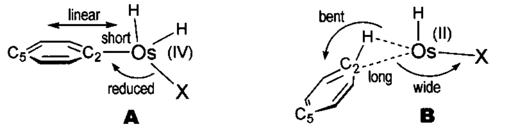
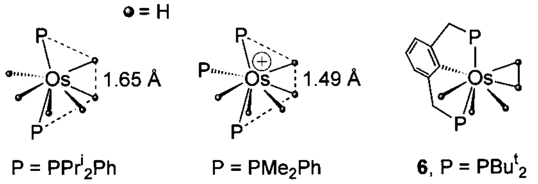


Chart 2



agostic compound capable of activating the C−D and C−H bonds. Thus **6** shows reactivity similar to that of IrH_4(PCP), which loses H_2 to give IrH_2(PCP), a known catalyst for dehydrogenation of cyclic alkanes.[8]

The $OsDH_4$ resonance of **6**-d is a triplet in the $^1H\{^{31}P\}$ NMR spectrum with the exchange-averaged constant $^{av}J_{HD} = 2.7$ Hz. The T_{1min} time is 54 ms (300 MHz) for **6**, a value indicative of a short H/H separation in this molecule when compared with the longer $T_{1min} = 120$ ms (300 MHz) for the *hexahydride* $OsH_6(PPr^i_3)_2$.[9] We tentatively assign a nonclassical formulation $OsH_3(H_2)$(PCP) to **6**. In this case, $^1J_{HD} = 10 \times {}^{av}J_{HD} = 27$ Hz,[6b] which corresponds to an H−H distance of 0.97 Å.[10] The infrared spectrum (Nujol) of **6** shows medium-intensity Os−H bands at 2154 and 2089 cm^{-1}, and a broad band at 1889 cm^{-1} that can be due to the Os−H_2 mode.

It is instructive to relate **6** to two osmium polyhydrides structurally characterized by neutron diffraction: $OsH_6(PPr^i_2Ph)_2$ and $[OsH_5(PMe_2Ph)_3]^+$.[11] The first example is a hexahydride with the shortest H···H separation of 1.65 Å in the P···H···H···P trapezoid. The other shows an interesting structure intermediate between that of a dodecahedral pentahydride (eight-coodinate) and that of a pentagonal bipyramidal dihydrogen (seven-coordinate) compound. The H···H separation in the P···H···H···P trapezoid of $[OsH_5(PMe_2Ph)_3]^+$ is reduced to 1.49 Å. While the extent of H···H bonding in **6** cannot be reliably established, we prefer the nonclassical description $OsH_3(H_2)$(PCP) to the pentahydride OsH_5(PCP). A related dihydrogen compound $OsH_3(H_2)Cl(PPr^i_3)_2$ has been characterized in solution.[9]

$Os(H_2)_2Cl(PCP)$ (7a) and $OsH_2(H_2)Cl(PCP)$ (7b). When the 16-electron dihydride **2** is dissolved at low temperature under hydrogen, the initial dark brown color quickly changes to pale yellow. Two unstable products of this reaction were characterized by NMR spectroscopy in methylcyclohexane-d_{14} under H_2 and in $CDFCl_2/CDF_2Cl$ under D_2.

H_2 addition to **2** is expected to the vacant site, between the chloride and metal-bonded carbon atom. The *kinetic* product **7a** is formed when solution of **2** is saturated with hydrogen below −70 °C (Scheme 2). On warming to −30 °C, **7a** quantitatively isomerizes to the *thermodynamic* product **7b**, possessing an H_2 ligand cis to two hydrides. On further warming, **7b** loses H_2 and reversibly regenerates **2** (equilibrium concentrations: 14 mol % at 0 °C and 29% at 20 °C).

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(8) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840.

(9) Gusev, D. G.; Kuznetsov, V. F.; Eremenko, I. L.; Berke, H. *J. Am. Chem. Soc.* **1993**, *115*, 5831.

(10) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396.

(11) Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *Inorg. Chem.* **1987**, *26*, 2930. (b) Johnson, T. J.; Albinati, A.; Koetzle, T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 4966.

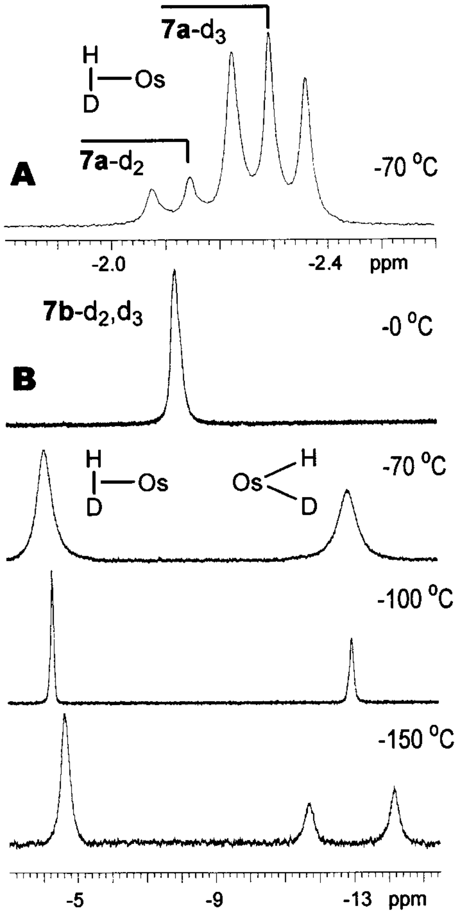
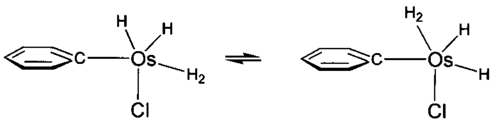


Figure 2. ^1H NMR spectra of partially deuterated **7a** (A) and **7b** (B) in $CDFCl_2/CDF_2Cl$. The sample was prepared as described in the Experimental Part. Spectrum A was recorded at −70 °C. Then, the **7a**/**7b** isomerization was achieved by warming the sample to −30 °C, and spectra B were collected upon recooling the sample in increments.

NMR spectra of **7a** exhibit single ^{31}P and ^1H chemical shifts for the PBu^t_2 groups and all four metal-bonded hydrogens, in agreement with a C_{2v} structure. A deuterated sample (ca. 87% D, according to integration) containing **7a**-d_2 and **7a**-d_3 (ca. 7.5 and 34%, assuming a statistical H/D distribution) shows the H−D coupling of 20.1 Hz (Figure 2A). It is clear that **7a** is not an Os(VI) tetrahydride; furthermore, an exchange-averaged H−D coupling of this magnitude is inconsistent with the dihydride−dihydrogen Os(IV) formulation, $OsH_2(H_2)Cl(PCP)$. In this case, a rapid degenerate (H)(D)-Os(HD) $\rightleftarrows$ (HD)Os(H)(D) equilibrium could result in an exchange-averaged coupling $^{av}J_{HD}$ as large as half of the one-bond constant $^1J_{HD}$. Since $^1J_{HD}$ does not exceed 35 Hz in dihydrogen compounds, the exchange-averaged coupling $^{av}J_{HD}$ cannot exceed 17.5 Hz. We therefore assign a bis-dihydrogen structure to **7a**, *trans*-$Os(H_2)_2Cl(PCP)$ (Scheme 2). The H−D coupling of 20.1 Hz corresponds to an H−H bond distance of 1.08 Å.[10] A few other unstable bis-dihydrogen compounds are known[12] (including an osmium species $[Os(H_2)_2H_3(PPr^i_3)_2]^+$);[12b] however no neutron diffraction crystal structure has been reported to date.[12a,c]

Chart 3



Isomer **7b** was studied under hydrogen and under deuterium by VT NMR. The spectra of the D-enriched system are shown in Figure 2 (part B). After decoalescence at −40 and −130 °C, the presence of two inequivalent hydrides (δ −11.74/−14.17) was established at −150 °C. We suggest a cis arrangement for these ligands on the basis of the fast exchange between the two sites. The single resonance between −4 and −5 ppm we assign to the HD ligand of **7b**-d_2 and **7b**-d_3. Unfortunately, no H−D coupling was observed, which might be due to a combination of (i) rapid deuterium relaxation below −100 °C and (ii) chemical exchange between the hydride and dihydrogen sites, which was detectable by the saturation transfer technique at and above −100 °C.

Exchange-averaged $OsH_2(H_2)$ T_1 times in **7b** are 31 ms at −20 °C, 31 ms at −60 °C, and 69 ms at −80 °C. The T_{1min} value is probably shorter than 30 ms but could not be experimentally accessed because of the decoalescence and significant broadening at −40 °C. The NMR data for **7b** are consistent with a mono-dihydrogen formulation *cis*-$OsH_2(H_2)Cl(PCP)$. Two different pentagonal bipyramidal structures can be considered for this formula. Chart 3 shows the equatorial plane of **7b** where the H_2 ligand is either cis to the chloride or cis to the carbon atom. We prefer the former arrangement, expecting that the H_2 is more likely to form trans (or pseudo-trans) to the ligands possessing the strongest trans effects in **7b**, while the dihydride fragment is more likely to be trans to the ligand of weak trans influence and good π-donor chloride.

One interesting feature of the spectra of **7b**-d_3 in Figure 2B is the H/D isotope fractionation, with a substantial preference for *hydrogen* to occupy the Os(HD) site. The value of the equilibrium constant determined from the integration of the HD and hydride resonances lies between 1.3 and 1.4 in the temperature range −70 to −100 °C. An isotope effect of the same magnitude has been previously observed for the deuterated $[ReH_2(H_2)(PMe_2Ph)_3]^+$ and $[ReH_2(H_2)(PMe_3)_3]^+$ compounds.[13] However, the HD site was preferentially occupied by *deuterium* in the rhenium case. Ten years after the original observations, we repeat after Luo and Crabtree[13a] that "a theoretical prediction of the magnitude and direction of the equilibrium isotope effect is not yet possible, because a substantial number of vibrational modes are expected for the system and limited experimental data are available".

Conclusions

This is a third paper in the series[3] reporting the synthesis and reactivity of group 8 metal complexes with

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[12] (a) Abdur-Rashid, K.; Gusev, D. G.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 1652, and references therein. (b) Smith, K. T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473. (c) Borowski, A. F.; Donnadieu, B.; Daran, J. C.; Sabo-Etienne, S.; Chaudret, B. *Chem. Commun.* **2000**, 543. (d) Borowski, A. F.; Donnadieu, B.; Daran, J. C.; Sabo-Etienne, S.; Chaudret, B. *Chem. Commun.* **2000**, 1697.

[13] (a) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912. (b) Gusev, D. G.; Nietlispach, D.; Eremenko, I. L.; Berke, H. *Inorg. Chem.* **1993**, *32*, 3628.

the bulky PCP pincer, $[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]^-$. Osmium(II) carbonyl compounds OsCl(CO)(PCP) and OsH(CO)(PCP) are isostructural with the corresponding ruthenium complexes. In the non-carbonyl species $OsH_2Cl(PCP)$ and $OsH_2I(PCP)$ osmium attains a higher +4 oxidation state. The d^4 electronic configuration results in significant distortions in the structure of the dihydrides.

A distinct feature of the osmium complexes with the PCP ligand is the formation of isolable polyhydrides $OsH(H_2)(CO)(PCP)$ and $OsH_3(H_2)(PCP)$, which have no stable analogues in the ruthenium chemistry.[14] The more labile system of $Os(H_2)_2Cl(PCP)$ and $OsH_2(H_2)Cl(PCP)$ is a structurally unusual case of isomeric dihydrogen complexes that show interesting fluxional behavior in solution. All new species **1**−**7** seem of interest for general synthetic and theoretical chemical research and may have some potential for catalytic applications involving C−H bond activation.

Experimental Part

General Comments. All manipulations carried out under nitrogen and at room temperature were performed in a drybox. When heating was required, the reaction mixtures were prepared in the box, then transferred out, attached to a manifold, and opened under Ar or H_2. The reaction vessels were returned in the box for isolation of the products. Anhydrous deuterated and regular solvents were stored and used in the drybox. FT IR spectra were recorded on a Perkin-Elmer Spectrum BXII spectrometer. NMR measurements were done on a Varian UNITY Inova 300 spectrometer. Throughout this paper, the NMR data are reported with the apparent coupling of observed virtual triplets (vt) denoted as ^{v}J. Osmium tetroxide was purchased from Pressure Chemicals, whereas other chemicals were received from Aldrich. The phosphine $1,3\text{-}(CH_2PBu^t{}_2)_2C_6H_4$ was prepared according to a published procedure.[3a] The solvent mixture $CDFCl_2/CDF_2Cl$ (1:2) was obtained by fractional distillation of the crude product according to a literature method.[15]

Preparation of $[Et_4N]_2OsCl_6$. All manipulations were performed in air. Osmium tetroxide (2 g, 7.87 mmol) was added to a solution of tetraethylammonium chloride hydrate (4 g, ca. 24 mmol) in hydrochloric acid (33%, 30 mL). The flask was placed in an oil bath. Then the hot plate stirrer was turned on and the oil bath was allowed to warm to 120 °C. The mixture was stirred overnight for 19 h and cooled to room temperature. After addition of 30 mL of ethanol and 15 mL of diethyl ether the flask was kept for 3 h at −15 °C. An orange solid precipitated and was isolated by filtration, washed with 4 × 10 mL of ethanol, and dried for 1 h at 100 °C. Yield: 4.95 g (95%). Anal. Calcd for $C_{32}H_{72}C_{16}N_2Os$ (663.46): C, 43.29; H, 8.17; N, 3.16. Found: C, 43.09; H, 8.03; N, 3.11.

Preparation of $OsCl(CO)[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$ (1). A mixture of $[Et_4N]_2OsCl_6$ (2.05 g, 3.09 mmol), $1,3\text{-}(CH_2PBu^t{}_2)_2C_6H_4$ (1.46 g, 3.70 mmol), CH_3OH (1.25 g, 39 mmol), and NEt_3 (0.94 g, 9.29 mmol) in isoamyl alcohol (30 mL) was stirred for 72 h at 130 °C. A yellow-green solid precipitated overnight at room temperature. It was isolated by filtration, washed with 4 × 6 mL of methanol, and dried under vacuum for 1 h. Yield: 1.8 g (90%). Anal. Calcd for $C_{25}H_{43}ClOP_2Os$ (647.25): C, 46.39; H, 6.70. Found: C, 46.58; H, 6.84. IR (Nujol): ν_{CO} 1890 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.20, 1.49 (vt, ^{v}J = 6.3, 36H, CH_3), 3.41 (dvt, $^2J_{HH}$ = 17.1, ^{v}J = 4.1, 2H, CH_2), 3.57 (dvt, ^{v}J = 4.5, 2H, CH_2), 6.86 (t, $^3J_{HH}$ = 7.5, 1H, C_6H_3), 7.14 (d, 2H, C_6H_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 63.9. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 30.0, 30.3 (vt, ^{v}J = 2.1, CH_3), 37.2 (vt, ^{v}J = 13.9, CH_2), 38.1 (vt, ^{v}J = 9.7, P*C*), 38.8 (vt, ^{v}J = 9.7, P*C*), 121.8 (vt, ^{v}J = 7.2, *C*H, Ar), 124.4 (t, $^4J_{CP}$ = 1.1, *C*H, Ar), 153.8 (vt, ^{v}J = 6.4, *C*, Ar), 155.4 (t, $^2J_{CP}$ = 1.1, Os*C*), 178.3 (t, $^2J_{CP}$ = 7.7, *C*O).

Preparation of $OsH_2Cl[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$ (2). A mixture of $[Et_4N]_2OsCl_6$ (2.4 g, 3.62 mmol), $1,3\text{-}(CH_2PBu^t{}_2)_2C_6H_4$ (1.7 g, 4.31 mmol), and NEt_3 (0.95 g, 9.39 mmol) in 30 mL of 2-propanol was stirred under hydrogen for 72 h at 100 °C in a Schlenk flask fitted with a vacuum adapter (with a glass stopcock) in place of a stopper. Then the reaction vessel was purged through the vacuum adapter with a stream of argon (four times for 30 s, 5 min between successive purges). The hot plate was turned off, and a dark solid crystallized overnight. The product was isolated by filtration, washed with 3 × 5 mL of methanol, and dried in vacuo for 3 h. Yield: 1.7 g (76%). Anal. Calcd for $C_{24}H_{45}ClP_2Os$ (621.25): C, 46.40; H, 7.30. Found: C, 46.18; H, 7.31. IR (Nujol): ν_{OsH} 2212, 2191 cm^{-1}. ^{1}H NMR (C_6D_6): δ −18.40 (t, $^2J_{HP}$ = 10.7, 2H, OsH_2), 1.18, 1.30 (vt, ^{v}J = 6.4, 36H, CH_3), 3.11 (m, 4H, CH_2), 7.12 (s, 3H, C_6H_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 57.4. ^{13}C{^{1}H} NMR (C_6D_6): δ 29.5, 30.7 (vt, ^{v}J = 2.5, CH_3), 34.0 (vt, ^{v}J = 9.9, P*C*), 38.0 (vt, ^{v}J = 12.7, CH_2), 40.5 (vt, ^{v}J = 8.3, P*C*), 121.7 (vt, ^{v}J = 7.2, *C*H, Ar), 125.8 (t, $^4J_{CP}$ = 0.9, *C*H, Ar), 154.1 (vt, ^{v}J = 7.9, *C*, Ar), 164.0 (s, Os*C*).

Preparation of $OsH_2I[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$ (3). A 300 mg (0.48 mmol) portion of **2** was dissolved in 6 mL of CH_3I and left at room temperature for 72 h. Then the solution was filtered and evaporated to dryness; the residue was crystallized from 6 mL of hot ethanol. Yield: 0.3 g (87%). Anal. Calcd for $C_{24}H_{45}IP_2Os$ (712.70): C, 40.45; H, 6.36. Found: C, 40.61; H, 7.27. IR (Nujol): ν_{OsH} 2214, 2192 cm^{-1}. ^{1}H NMR (C_6D_6): δ −20.28 (t, $^2J_{HP}$ = 10.7, 2H, OsH_2), 1.25 (vt, ^{v}J = 6.4, 36H, CH_3), 3.14 (m, 4H, CH_2), 7.12, 7.19 (m, 3H, C_6H_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 57.0.

Preparation of a Mixture of $OsH(CO)[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$ (4) and $OsH(H_2)(CO)[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$ (5). A 1.8 g (2.78 mmol) sample of **1** was reacted with 0.8 g (3.11 mmol) of $[Bu_4N]BH_4$ in 15 mL of ethanol at 90 °C in a Schlenk flask fitted with a vacuum adapter (with a glass stopcock) in place of a stopper. In 20 min, the reaction vessel was purged through the vacuum adapter with a stream of argon (four times for 30 s, 5 min between successive purges). The hot plate was turned off, and a dark solid crystallized overnight. It was isolated by filtration, washed with 3 × 3 mL of ethanol, and dried under vacuum for 5 h. Yield: 1.45 g (85%). The ^{1}H and ^{31}P NMR spectra of this solid showed similar amounts of **4** and **5**.

$OsH(CO)[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$ (**4**). Anal. Calcd for $C_{25}H_{44}OP_2Os$ (612.80): C, 49.00; H, 7.24. Found: C, 48.70; H, 7.27. IR (KBr): ν_{OsH} 2200 cm^{-1}, ν_{CO} 1885 cm^{-1}. ^{1}H NMR (CD_2Cl_2, −40 °C, under vacuum): δ −37.81 (t, $^2J_{HP}$ = 13.2, 1H, Os*H*), 1.15, 1.24 (vt, ^{v}J = 6.4, 36H, CH_3), 3.58 (m, 4H, CH_2), 6.92 (t, $^3J_{HH}$ = 7.5, 1H, C_6H_3), 7.16 (d, 2H, C_6H_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, −40 °C, under vacuum): δ 81.6. T_1{OsH}: 393 ms (−80 °C). **$OsH(H_2)(CO)[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$** (**5**): Anal. Calcd. for $C_{25}H_{46}OP_2Os$ (614.81): C, 48.84; H, 7.54. Found: C, 48.70; H, 7.27. ^{1}H NMR (CD_2Cl_2, −40 °C, under vacuum): δ −8.83 (t, $^2J_{HP}$ = 17.8, 1H, Os*H*), −4.75 (br s, line width = 32 Hz, 2H, Os(H_2)), 1.24, 1.32 (vt, ^{v}J = 6.5, 36H, CH_3), 3.16 (dvt, $^2J_{HH}$ = 16.5, ^{v}J = 3.3, 2H, CH_2), 3.49 (dvt, ^{v}J = 4.3, 2H, CH_2), 6.66 (t, $^3J_{HH}$ = 7.5, 1H, C_6H_3), 6.84 (d, 2H, C_6H_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, −40 °C, under vacuum): δ 73.5. T_1{Os(H_2)}: 11.5 ms (−40 °C), 8.2 ms (−60 °C), 7.9 ms (−80 °C), 14.4 ms (−100 °C). T_1{OsH}: 210 ms (−80 °C). **$OsH(HD)(CO)[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$ (5-d)**: 25 mg of the mixture of **4** and **5** (obtained as described above) was loaded in a 5-mm NMR tube fitted with a PTFE valve. 0.6 mL of CD_2Cl_2 was condensed under vacuum and the tube was filled with deuterium gas to ca. 1 atm and sealed. ^{1}H NMR (CD_2Cl_2, −20 °C): δ −8.81 (td, $^2J_{HP}$ = 18.1,

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[14] (a) We have spectroscopic evidence for the formation of unstable $RuH(H_2)(CO)(PCP)$, $RuH(H_2)_2(PCP)$, and $Ru(H_2)_2Cl(PCP)$ complexes in solution under hydrogen.[14b] (b) Gusev, D. G. Manuscript in preparation.

[15] Siegel, J. S.; Anet, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629.

${}^{2}J_{HH}$ = 2.6, 1H, Os*H*), −4.76 (td, ${}^{1}J_{HD}$ = 29.8, ${}^{2}J_{HH}$ = 2.6, 1H, Os(*H*D)). ${}^{13}C\{{}^{1}H\}$ NMR (CD_2Cl_2, −20 °C): δ 29.0, 30.0 (br s, *C*H_3), 33.7 (vt, ${}^{v}J$ = 10.4, *C*H_2), 35.9 (vt, ${}^{v}J$ = 12.6, P*C*), 41.5 (vt, ${}^{v}J$ = 14.5, P*C*), 119.5 (vt, ${}^{v}J$ = 7.5, *C*H, Ar), 122.9 (s, *C*H, Ar), 151.6 (vt, ${}^{v}J$ = 8.9, *C*, Ar), 162.1 (t, ${}^{2}J_{CP}$ = 3.0, Os*C*), 188.6 (t, ${}^{2}J_{CP}$ = 6.0, *C*O). T_1\{Os(HD)\}: 87 ms (−70 °C), 81 ms (−80 °C), 88 ms (−90 °C).

Preparation of $OsH_3(H_2)[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$ (6). One gram (1.61 mmol) of **2** was reacted with 1.24 g (4.82 mmol) of $[Bu_4N]BH_4$ in 5 mL of ethanol for 30 min at 100 °C, under H_2. Then the reaction mixture was cooled and left overnight at room temperature. A white solid was isolated by filtration, washed with 3 × 3 mL of ethanol, and dried under vacuum for 3 h. Yield: 0.81 g (85%). Anal. Calcd for $C_{24}H_{48}P_2Os$ (588.82): C, 48.96; H, 8.22. Found: C, 49.09; H, 8.13. IR (Nujol): ν_{OsH} 2154, 2089, 1889 cm^{-1}. ${}^{1}H$ NMR (C_6D_6): δ −8.50 (t, ${}^{2}J_{HP}$ = 7.6, 5H, OsH_5), 1.17 (vt, ${}^{v}J$ = 6.3, 36H, CH_3), 3.35 (vt, ${}^{v}J$ = 3.9, 4H, CH_2), 7.12 (m, 3H, C_6H_3). ${}^{31}P\{{}^{1}H\}$ NMR (C_6D_6): δ 84.5. ${}^{13}C\{{}^{1}H\}$ NMR (C_6D_6): δ 29.6 (vt, ${}^{v}J$ = 2.2, *C*H_3), 34.0 (vt, ${}^{v}J$ = 11.8, *C*H_2), 41.8 (vt, ${}^{v}J$ = 13.7, P*C*), 120.4 (vt, ${}^{v}J$ = 7.9, *C*H, Ar), 122.8 (t, ${}^{4}J_{CP}$ = 1.2, *C*H, Ar), 149.4 (vt, ${}^{v}J$ = 9.9, *C*, Ar), 158.7 (t, ${}^{2}J$ = 4.9, Os*C*). T_1\{OsH_5\} ($CDFCl_2$/CDF_2Cl): 74 ms (−100 °C), 65 ms (−110 °C), 61 ms (−120 °C), 58 ms (−130 °C), 54 ms (−140 °C), 57 ms (−145 °C).

Preparation of Partially Deuterated $Os(H_2)_2Cl[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$ (7a) and $OsH_2(H_2)Cl[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$ (7b). A 25 mg portion of **2** was loaded in a 5 mm NMR tube fitted with a PTFE valve. A 0.7 mL sample of $CDFCl_2$/CDF_2Cl (1:2) was condensed into the tube under vacuum, and then it was filled with deuterium gas to ca. 1 atm and sealed. The solution was saturated with gas by shaking, keeping the sample portion of the tube in cold (−80 to −90 °C) ethanol. The color changed from dark brown to pale yellow upon shaking. This sample was inserted into a precooled probe, and NMR measurements were started at −60 °C. *NMR data for partially deuterated* **7a**. ${}^{1}H$ NMR (−60 °C): δ −2.31 (t, ${}^{1}J_{HD}$ = 20.1, Os(*H*D)), 1.40 (vt, ${}^{v}J$ = 3, 36H, CH_3), 3.26 (vt, ${}^{v}J$ = 3.8, 4H, CH_2), 6.85 (t, ${}^{3}J_{HH}$ = 7.4, 1H, C_6H_3), 7.00 (d, 2H, C_6H_3). ${}^{31}P\{{}^{1}H\}$ NMR (−60 °C): δ 54.8. *NMR data for partially deuterated* **7b**. ${}^{1}H$ NMR (−60 °C): δ −12.90 (br s, Os*H*), −4.13 (br s, Os(*H*D)), 1.16, 1.44 (br s, 36H, CH_3), 3.49 (dvt, ${}^{2}J_{HH}$ = 16.2, ${}^{v}J$ = 4.2, 2H, CH_2), 3.82 (dvt, ${}^{v}J$ = 3.6, 2H, CH_2), 6.97 (t, ${}^{3}J_{HH}$ = 6.6, 1H, C_6H_3), 7.16 (d, 2H, C_6H_3). ${}^{31}P\{{}^{1}H\}$ NMR (−60 °C): δ 70.5. T_1\{OsH_4\} averaged data for **$OsH_2(H_2)Cl[2,6\text{-}(CH_2PBu^t{}_2)_2C_6H_3]$ (7b)** in methylcyclohexane-d_{14} under H_2: 44 ms (0 °C), 31 ms (−20 °C), 31 ms (−60 °C), 69 ms (−80 °C).

Crystal Structure Determination. Crystallographic Data for 1. Intensities of 6031 independent reflections were collected on a Syntex $P2_1$ diffractometer at 153 K using Mo Kα radiation (λ = 0.71073 Å). The absorption correction was applied using the ψ-scan technique (T_{max} = 0.983, T_{min} = 0.462). The structure was solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the calculation in the riding model approximation. The refinement converged to wR_2 = 0.1500 and GOF = 1.003 for all reflections (R_1 = 0.0561 was calculated against *F* for 3646 observed reflections with $I > 2\sigma(I)$).

Crystallographic Data for 2. Intensities of 30 698 independent reflections were collected on a Smart 1000 CCD diffractometer at 110 K (λ(Mo Kα) = 0.71073 Å, ω-scan with 0.3° step and 20 s per frame exposure, $2\theta \le 60°$); 15 049 independent reflections (R_{int} = 0.0261) were used in refinement. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 in the anisotropic approximation for all non-hydrogen atoms. The hydrides were located and refined isotropically. The refinement converged to wR_2 = 0.0861 and GOF = 0.971 for all independent reflections (R_1 = 0.0356 was calculated against *F* for 11 114 observed reflections with $I > 2\sigma(I)$). Complex **2** shows two independent molecules in the unit cell. Being crystallographically distinct, the two structures and their corresponding bond lengths and bond angles are chemically indistinguishable. One of the two molecules is shown in Figure 1. Selected averaged bond distances and angles are reported in Table 1.

Crystallographic Data for 3. Intensities of 30 253 reflections were measured on a Smart 1000 CCD diffractometer at 110 K (λ(Mo Kα) = 0.71073 Å, ω-scan with 0.3° step and 10 s per frame exposure, $2\theta \le 60°$); 7655 independent reflections (R_{int} = 0.0273) were used in further refinement. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 in the anisotropic approximation for all non-hydrogen atoms. The hydrides were located and refined isotropically. The refinement converged to wR_2 = 0.0646 and GOF = 1.071 for all independent reflections (R_1 = 0.0256 was calculated against *F* for 6902 observed reflections with $I > 2\sigma(I)$). Data reduction and further calculations were performed using SAINT and SHELXTL-97 programs.

Acknowledgment. This work was supported by Wilfrid Laurier University, Natural Sciences and Engineering Research Council (NSERC) of Canada, Petro-Canada, and Research Corporation.

Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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