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Chiral Hydride and Dihydrogen Pincer-Type Complexes of Osmium

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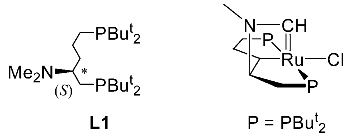
Reaction of $[OsCl_6]^{2-}$ with a pincer-type ligand, (*S*)-$Bu^t_2PCH_2CH(NMe_2)C_3H_6PBu^t_2$, afforded a chiral square-pyramidal 16-electron carbene complex, OsCl(PGP) (**1**), PGP = $[\kappa^4\text{-}Bu^t_2PCH_2CH(N(Me)CH{=})CHC_2H_4PBu^t_2]$, in excellent yield. Reactions of **1** with hydrogen under different conditions resulted in the hydride and dihydrogen species $OsH_2Cl(PGP)$, $[Os(H_2)_2(PGP)]^+$, and $OsH_3(PGP)$, which have been characterized by a combination of spectroscopic and DFT computational techniques.

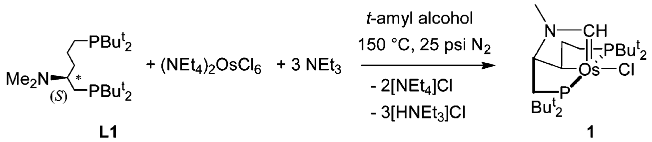
Introduction

Complexes of tridentate pincer-type ligands display a wide range of catalytic activities and have found applications in organic synthesis.[1] In recent years, a growing number of *chiral* pincer ligands have been developed and appeared in the literature.[2] In the course of our recent work with new chiral pincer-type ligands[3] we studied the reaction of (*S*)-1,5-bis(di-*tert*-butylphosphino)-2-(dimethylamino)pentane (**L1**) with ruthenium. This resulted in unexpected dehydrogenation of **L1** and afforded a cyclometalated carbene product, RuCl(PGP), shown in Chart 1.[3a,4] This 16-electron complex was thermally stable and relatively unreactive; therefore we wondered whether an analogous osmium compound could be made and might possess some useful reactivity. This paper reports the preparation of OsCl(PGP) (**1**) and a series of hydride and dihydrogen species derived from **1**.

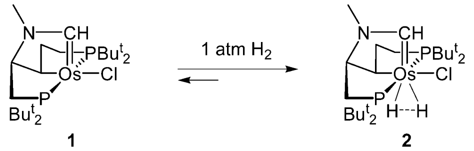
Chart 1



Scheme 1



Scheme 2



Results and Discussion

Heating $[NEt_4]_2OsCl_6$ with **L1** afforded the cyclometalated carbene complex OsCl(PGP) (**1**) isolated in 85% yield as a single diastereomer according to Scheme 1. This reaction was carried out in a glass autoclave at 150 °C in order to solubilize sparingly soluble $[NEt_4]_2OsCl_6$ and promote C−H activation. *tert*-Amyl alcohol was used as the solvent to avoid possible dehydrogenation and decarbonylation reactions known for primary or secondary alcohols that might compete with dehydrogenation of **L1**. Solutions of **1** rotate plane-polarized light ($[\alpha]_D^{20}$ +1137, *c* 0.029, toluene), providing evidence that formation of the complex occurred without racemization.

NMR spectra of **1** show the characteristic carbene Os=CH resonances at δ 13.84 (^{1}H) and 202.3 (^{13}C). The Os−CH group

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[1] For reviews see: (a) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527. (b) Beletskaya, I. P.; Cheprakov, A. V. *J. Organomet. Chem.* **2004**, *689*, 4055. (c) Bedford, R. B. *Chem. Commun.* **2003**, 1787. (d) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837. (e) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (f) Milstein, D. *Pure Appl. Chem.* **2003**, *75*, 2003. (g) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (h) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917. (i) Vigalok, A.; Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798. (j) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3006. (k) Jensen, C. M. *Chem. Commun.* **1999**, 2443.

[2] (a) Aydin, J.; Kumar, K. S.; Sayah, M. J.; Wallner, O. A.; Szabó, K. J. *J. Org. Chem.* **2007**, *72*, 4689. (b) Rubio, M.; Suárez, A.; del Rio, D.; Galindo, A.; Álvarez, E.; Pizzano, A. *Dalton Trans.* **2007**, *4*, 407. (c) Yoon, M. S.; Ramesh, R.; Kim, J.; Ryu, D.; Ahn, K. H. *J. Organomet. Chem.* **2006**, *691*, 5927. (d) Baber, R. A.; Bedford, R. B.; Betham, M.; Blake, M. E.; Coles, S. J.; Haddow, M. F.; Hursthouse, M. B.; Orpen, A. G.; Pilarski, L. T.; Pringle, P. G.; Wingad, R. L. *Chem. Commun.* **2006**, 3880. (e) Gosiewska, S.; Huis in't Veld, M.; De Pater, J. J. M.; Bruijnincx, P. C. A.; Lutz, M.; Spek, A. L.; Van Koten, G.; Klein Gebbink, R. J. M. *Tetrahedron: Asymmetry* **2006**, *17*, 674. (f) Benito-Garagorri, D.; Bocokiæ, V.; Mereiter, K.; Kirchner, K. *Organometallics* **2006**, *25*, 3817. (g) Wallner, O. A.; Olsson, V. J.; Eriksson, L.; Szabó, K. J. *Inorg. Chim. Acta* **2006**, *359*, 1767. (h) Hao, X.-Q.; Gong, J.-F.; Du, C.-X.; Wu, L.-Y.; Wu, Y.-J.; Song, M.-P *Tetrahedron Lett.* **2006**, *47*, 5033. (i) Soro, B.; Stoccoro, S.; Minghetti, G.; Zucca, A.; Cinellu, M. A.; Manassero, M.; Gladiali, S. *Inorg. Chim. Acta.* **2006**, *359*, 1879. (j) Motoyama, Y.; Shimozono, K.; Nishiyama, H. *Inorg. Chim. Acta* **2006**, *359*, 1725. (k) Benito-Garagorri, D.; Becker, E.; Wiedermann, J.; Lackner, W.; Pollak, M.; Mereiter, K.; Kisala, J.; Kirchner, K. *Organometallics* **2006**, *25*, 1900. (l) Medici, S.; Gagliardo, M.; Williams, S. B.; Chase, P. A.; Gladiali, S.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *Helv. Chim. Acta* **2005**, *88*, 694. (m) Morales-Morales, D.; Cramer, R. E.; Jensen, C. M. *J. Organomet. Chem.* **2002**, *654*, 44. (n) Williams, B. S.; Dani, P.; Lutz, M.; Spek, A. L.; van Koten, G. *Helv. Chim. Acta* **2001**, *84*, 3519. (o) Dani, P.; Albrecht, M.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2000**, *19*, 4468. (p) Longmire, J. M.; Zhang, X.; Shang, M. *Organometallics* **1998**, *17*, 4374. (q) Karlen, T.; Dani, P.; Grove, D. M.; Steenwinkel, P.; van Koten, G. *Organometallics* **1996**, *15*, 5687. (r) Gorla, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607.

[3] (a) Kuznetsov, V. F.; Lough, A. J.; Gusev, D. G. *Chem. Commun.* **2002**, 2432. (b) Kuznetsov, V. F.; Lough, A. J.; Gusev, D. G. *Inorg. Chim. Acta* **2006**, *359*, 2806.

[4] The backbone of **L1** was derived from glutamic acid, and for convenience, the coordinated ligand $[\kappa^4\text{-}Bu^t_2PCH_2CH(N(Me)CH{=})CHC_2H_4\text{-}PBu^t_2]$ is abbreviated as PGP.

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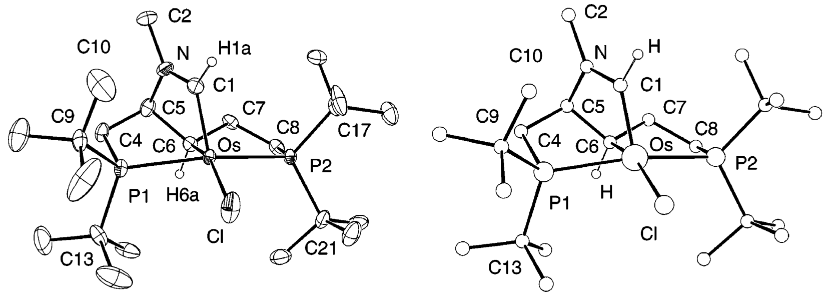

Figure 1. (left) ORTEP and atom-labeling scheme for **1a** with the ellipsoids at 30%; (right) DFT-calculated structure **1′**. Most of the hydrogen atoms are omitted for clarity.

Table 1. Experimental and Calculated Structural Data (deg and Å) for 1

	crystal structure **1a**	crystal structure **1b**	calculated structure **1′**	crystal structure **1c**	calculated structure **1″**
C6−Os−Cl	159.2(2)	167.0(2)	164.3	154.9(1)	155.2
C6−Os−C1	75.1(3)	75.0(4)	75.1	74.0(2)	74.7
Os−C1	1.897(8)	1.880(8)	1.894	1.920(4)	1.902
Os−C6	2.156(7)	2.128(8)	2.151	2.145(3)	2.140
Os−Cl	2.410(2)	2.448(2)	2.469	2.437(1)	2.463
C1−N	1.337(10)	1.333(11)	1.345	1.337(5)	1.346
Os−P1	2.329(2)	2.339(2)	2.353	2.336(1)	2.358
Os−P2	2.346(2)	2.356(2)	2.381	2.373(1)	2.395

resonates at δ 3.4 (^1H) and 38.5 (^{13}C). The $^{31}P\{^1H\}$ NMR spectrum of **1** exhibits an AB pattern with a large $^2J_{PP} = 261$ Hz coupling consistent with *trans* coordination of the two inequivalent PBu^t_2 groups. The structure of **1** was confirmed by X-ray diffraction using two samples, crystallized from diglyme and isooctane. The first crystal had two independent molecules, **1a** and **1b**, in the unit cell, whereas the second contained one unique structure, **1c**, without cocrystallized solvent in either case. Structure **1a** is shown in Figure 1, and key crystallographic data for **1a**−**c** are collected in Table 1.

The coordination geometry of **1** can be described as distorted square-pyramidal; this 16-electron complex has a vacant site *trans* to the carbene ligand. The molecule of **1** has three chiral centers: (*R*)-C5, (*R*)-C6, and (Λ)-Os. This implies that formation of **1** did not involve C−H bond activation at C5, which retained the original configuration found around this carbon in **L1**. The Os═C1 bond length is 1.90 Å, while the single Os−C6 bond is ca. 2.14 Å; both are within the normal range for Fischer carbene and alkyl−osmium species, respectively. The short C1−N distance of 1.34 Å and the planarity of the four-atom C5−N−C2−C1 fragment indicate expected partial double-bond character of the C1−N bond. The structural features of **1** are similar to those of the previously reported ruthenium analogue, RuCl(PGP).[3a]

A closer examination of **1a**, **1b**, and **1c** reveals differences involving the C6−Os−Cl angle, which ranges from 154.9° to 167.0° in the three structures (Table 1). To better understand the structural properties of **1**, we carried out a series of DFT calculations. A relaxed potential energy scan (PES), conducted by varying the C6−Os−Cl angle between 155° and 170°, found very small (<0.5 kcal/mol) energy changes produced by the angular deformation. Furthermore, the scan located two minima separated by 0.2 kcal/mol and corresponding to two slightly different structures, **1′** and **1″**, one with C6−Os−Cl = 164.3° (structure **1′** in Figure 1) and another with C6−Os−Cl = 155.5° (**1″**). Key structural data for **1′** and **1″** are listed in Table 1. The calculated structures of **1′** and **1″** also differ by rotation of the Bu^t groups around the P1−C9 and P1−C13 bonds, with C4−P1−C9−C10 = 79.1° and 52.6° in **1′** and **1″**, respectively. It appears that structure **1a** (C4−P1−C9−C10 = 72.5° and C6−Os−Cl = 159.2°) is related to **1′**, whereas **1c** (C4−P1−C9−C10 = 55.0° and C6−Os−Cl = 154.9°) is close to **1″**.[5] We conclude that the observed structural differences between **1a**, **1b**, and **1c** are due to the very “soft” nature of the C6−Os−Cl bend and are caused by packing in the crystal lattice.

Complex **1** is unsaturated, and it reversibly binds H_2 in solution to give a labile product, $OsH_2Cl(PGP)$ (**2**). At room temperature, the conversion was 67% in toluene-d_8 under 1 atm H_2. NMR data confirmed that this reaction did not involve hydrogenation of the PGP ligand. The Os═CH group of **2** was observed at δ 11.5 (^1H) and 248.9 (^{13}C), and the Os−CH group gave resonances at δ 2.1 (^1H) and 31.4 (^{13}C). The OsH_2 resonance appeared as a triplet of triplets at δ −5.8, exhibiting couplings to two phosphorus and two proton spins; the latter were identified via decoupling as the protons of the Os═CH and Os−CH groups. There was a strong NOE between the OsH_2 resonance and that of Os−CH at δ 2.1, in agreement with their *cis* arrangement in **2** (Scheme 2). The large $^2J_{PP} = 250$ Hz coupling is consistent with a *trans* arrangement of the PBu^t_2 groups in **2**.

T_1 relaxation times were measured for the OsH_2 resonance of **2** in two solvents. The minima were found: $T_{1min} = 42$ ms in CD_2Cl_2 (at −75 °C) and $T_{1min} = 50$ ms (at −55 °C) in toluene-d_8. The relaxation time was longer, as expected, in OsHDCl(PGP) (**2**-d_1) at $T_{1min} = 205$ ms. The methodology of Halpern and co-workers allows calculating H···H distances from the T_{1min} times.[6] This approach afforded r(H···H) = 1.36 Å in CD_2Cl_2 and 1.41 Å in toluene-d_8. The $^1H\{^{31}P\}$ NMR spectra of **2**-d_1 exhibited well-resolved H−D couplings: $J_{HD} = 9.6$ Hz in CD_2Cl_2 and 8.9 Hz in toluene-d_8 at 10 °C, corresponding to r(H···H) = 1.40 and 1.43 Å, respectively.[7] The coupling slightly decreased on lowering the temperature in CD_2Cl_2: $J_{HD} = 9.57$

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(5) The calculated bonds involving heavy atoms Os−P and Os−Cl in **1′** and **1″** are 0.025−0.035 Å longer than the experimental ones, which is common in DFT calculations with 5d metals. It is worth pointing out that the experimental distances are also different between **1a**, **1b**, and **1c** by as much as 0.038 Å (Os−Cl), 0.010 Å (Os−P1), and 0.027 Å (Os−P2) despite the fact that the standard deviations are all within 0.002 Å.

(6) (a) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173. (b) Relevant formulas: $r(H\cdots H) = 2.248/R_{HH}^{1/6}$ (at 300 MHz) and $R_{HH} = [1/T_{1min}(\mathbf{2}) - 1/T_{1min}(\mathbf{2}\text{-}d_1)]/0.937$.

(7) (a) Gusev, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 14249. (b) Calculated using eq 3 from ref 7a.

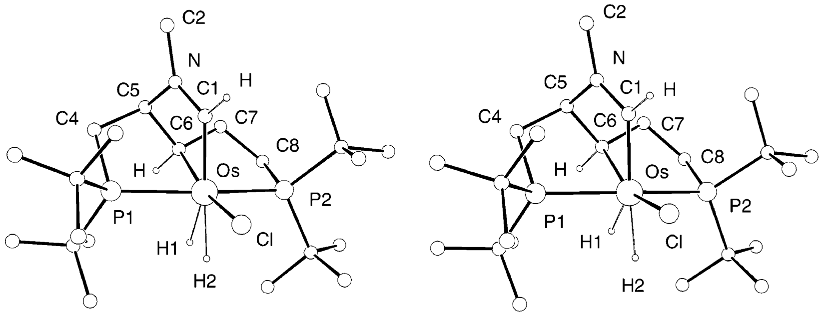

Figure 2. Calculated structures of **2a** (left) and **2b** (right). For clarity, nonessential hydrogens are not shown. Selected bond distances [Å] and angles [deg]: **2a**, Os−H1 1.68, Os−H2 1.69, Os−C1 1.999, C1−N 1.325, Os−C6 2.163, Os−Cl 2.537, Os−P1 2.374, Os−P2 2.383, P1−Os−P2 163.1, C1−Os−C6 76.5, C1−Os−Cl 88.5, C6−Os−Cl 165.0, H1−Os−C6 83.9, H2−Os−Cl 76.7; **2b**, Os−H1 1.61, Os−H2 1.64, Os−C1 2.044, C1−N 1.319, Os−C6 2.180, Os−Cl 2.523, Os−P1 2.374, Os−P2 2.379, P1−Os−P2 161.5, C1−Os−C6 74.3, C1−Os−Cl 82.9, C6−Os−Cl 157.2, H1−Os−C6 72.7, H2−Os−Cl 73.8.

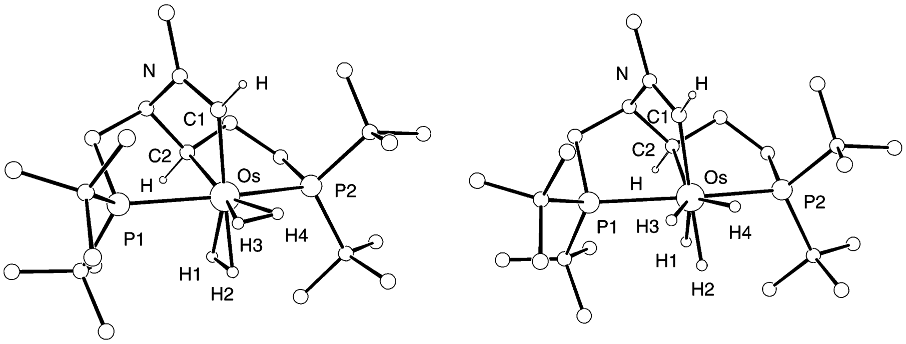

Figure 3. Calculated structures of **3a** (left) and **3b** (right). Most of the hydrogen atoms are not shown for clarity. Selected bond distances [Å] and angles [deg]: **3a**, Os−H1 1.71, Os−H2 1.73, Os−H3 1.73, Os−H4 1.72, H1−H2 0.93, H3−H4 0.94, Os−C1 2.010, C1−N 1.316, Os−C2 2.185, Os−P1 2.417, Os−P2 2.415, P1−Os−P2 161.0, C1−Os−C2 75.9; **3b**, Os−H1 1.63, Os−H2 1.64, Os−H3 1.64, Os−H4 1.63, H1−H2 1.50, H3−H4 1.50, Os−C1 2.066, C1−N 1.311, Os−C2 2.228, Os−P1 2.429, Os−P2 2.412, P1−Os−P2 156.2, C1−Os−C2 73.9.

(10 °C), 9.26 (0 °C), 9.16 (−10 °C), 8.86 Hz (−20 °C), corresponding to $r(\mathrm{H}\cdots\mathrm{H})$ increasing from 1.40 to 1.43 Å in this range.

Unstable complex **2** could not be isolated or crystallographically characterized. Therefore, the structure of **2** was studied by DFT calculations. Two energy minima were found for this compound, corresponding to two tautomers (Figure 2), one with $r(\mathrm{H}\cdots\mathrm{H}) = 1.01$ Å (**2a**) and another with $r(\mathrm{H}\cdots\mathrm{H}) = 1.53$ Å (**2b**). The calculated dihydride **2b** is only marginally more stable than the dihydrogen tautomer **2a** ($\Delta H = 0.53$ and $\Delta G = 0.14$ kcal/mol). The H···H distance, 1.40 ± 0.03 Å, derived from the NMR data is consistent with the idea that the main form of **2** in solution is a dihydride, like **2b**. Furthermore, the temperature dependence of the J_{HD} coupling is in agreement with the expected increase of the amount of **2b** at low temperature.

Complex **2** has a labile chloride ligand, which is rapidly and quantitatively displaced by H_2 in methanol or, in the presence of $NaBPh_4$, in THF to give $[OsH_4(PGP)]^+$ (**3**). Isolation and characterization of **3**·BPh_4 was complicated by facile H_2 loss. When a sample of the isolated material was dissolved in CD_2Cl_2 in a nitrogen glovebox, the NMR spectra revealed formation of a mixture of **3** with two new species, most likely produced by N_2/H_2 displacement. Only when the sample was refilled with hydrogen was complex **3** obtained quantitatively. The presence of the PGP ligand in **3** was confirmed by NMR spectroscopy. The carbene Os=CH group was observed at δ 10.7 (^{1}H) and 224.4 (^{13}C). The Os−CH group gave resonances at δ 3.1 (^{1}H) and 46.9 (^{13}C). The OsH_4 resonance appeared as a broad signal at δ −7.5 at 20 °C. No decoalescence was observed at low temperature, down to −110 °C in THF-d_8. The ^{31}P NMR spectrum of **3** exhibited an AB pattern with $^2J_{\mathrm{PP}} = 161$ Hz.

Complex **3** is a polyhydride that would be difficult to characterize experimentally. We therefore conducted a thorough DFT search of all relevant tautomers of **3** by varying the H−Os−H angles. No minimum corresponding to a dihydrido-dihydrogen Os$^{\mathrm{IV}}$ complex was found for **3**. Two minima were located by the DFT calculations corresponding to the bis-dihydrogen structure $[Os(H_2)_2(PGP)]^+$ (**3a**) and the tetrahydride $[OsH_4(PGP)]^+$ (**3b**), shown in Figure 3. The octahedral Os$^{\mathrm{II}}$ complex **3a** has two H_2 ligands with similar H−H distances (0.93−0.94 Å) and is more stable ($\Delta H = 1.43$, $\Delta G = 0.54$ kcal/mol) than the dodecahedral Os$^{\mathrm{VI}}$ species **3b**. Experimental exchange-averaged $T_{1\mathrm{min}} = 19.8$ ms and $^{\mathrm{av}}J_{\mathrm{HD}} = 6.8$ Hz values measured in THF-d_8 for $[OsH_4(PGP)]BPh_4$ and $[OsHD_3(PGP)]BPh_4$, respectively, are consistent with the bis-dihydrogen formulation. Assuming two equal H−H bonds and $^2J_{\mathrm{HD}} = 0$ Hz, we calculated $r(\mathrm{H{-}H}) = 1.11$ Å in **3** from the $^1J_{\mathrm{HD}} = 3 \times {}^{\mathrm{av}}J_{\mathrm{HD}} = 20.4$ Hz coupling in $[Os(HD)(D_2)(PGP)]^+$. A few other bis-dihydrogen compounds are known,[8] including unstable osmium species $[Os(H_2)_2H_3(PPr^i_3)_2]^+$ and *trans*-$Os(H_2)_2Cl[2,6\text{-}(CH_2PBu^t_2)_2C_6H_3]$.[8a,b]

The cationic dihydrogen complex **3** can be deprotonated by triethylamine to give a trihydride, $OsH_3(PGP)$ (**4**), according to Scheme 4. With NEt_3:**3**·BPh_4 = 2.1:1 in THF-d_8 and under H_2, we observed formation of a mixture of **4**:**3** = 0.9:1, indicating an equilibrium constant $K = 0.28$; therefore $[HNEt_3]^+$ is apparently slightly more acidic (ΔpK_a = ca. 0.6) than **3**. The

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[8] (a) Smith, K.-T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473. (b) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Yu. *Organometallics* **2001**, *20*, 1001. (c) Grellier, M.; Vendier, L; Chaudret, B.; Albinati, A.; Rizzato, S. Mason, S.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2005**, *127*, 17592, and references therein.

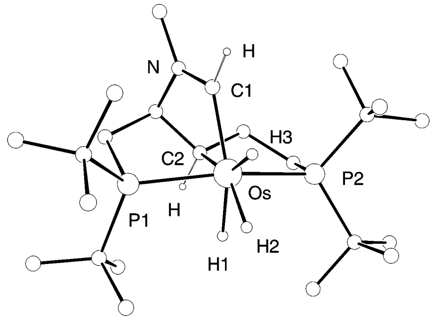
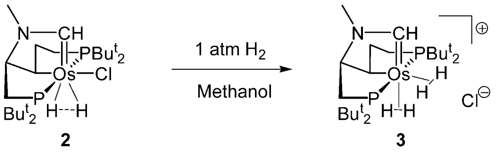
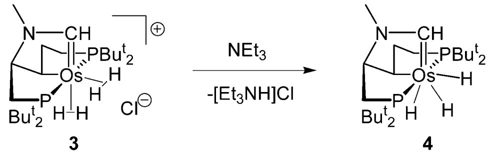


Figure 4. Calculated structure of **4**. Most of the hydrogen atoms are not shown for clarity. Selected bond distances [Å] and angles [deg]: Os−H1 1.65, Os−H2 1.65, Os−H3 1.65, H1···H2 1.82, H2···H3 1.70, Os−C1 2.040, C1−N 1.326, Os−C2 2.217, Os−P1 2.351, Os−P2 2.346, P1−Os−P2 161.4, C1−Os−C2 74.4, C2−Os−H1 78.9, C1−Os−H3 78.0.

Scheme 3



Scheme 4



reactivity of **3** was also explored toward transfer hydrogenation of acetophenone in 2-propanol. This resulted in no reaction, and **3** was the only observable osmium species in the reaction solution.

Trihydride **4** was isolated and spectroscopically characterized by a combination of conventional techniques. Among salient NMR features of **4** are the Os═CH resonances observed at δ 11.49 (^{1}H) and 231.9 (^{13}C) and those of the Os−CH group at δ 2.65 (^{1}H) and 42.1 (^{13}C). The ^{31}P{^{1}H} NMR spectrum showed a characteristic AB pattern ($^2J_{PP}$ = 242 Hz) of the two inequivalent phosphorus groups. The hydride region of the ^{1}H NMR spectrum of **4** displayed two 2:1 resonances at δ −9.30 and −9.51 assigned to the three osmium hydrides. Apparent equivalency of two hydrides at δ −9.30 was somewhat surprising in a chiral molecule and could be explained by either rapid site exchange or incidental degeneracy of the chemical shifts. This problem was tackled with the help of DFT calculations, which established the coordination geometry of **4** shown in Figure 4.

The pentagonal-bipyramidal Os^{IV} structure of **4** contains three inequivalent hydrides in the equatorial plane. The overall shape of the molecule is mostly similar to that of the parent compound **3**. We further studied two pairwise exchange processes of the hydrides, H2/H3 and H1/H2, and found the corresponding transition state structures, **4**ts1 and **4**ts2, presented in Figure 5. These are associated with $\Delta G^\ddagger$ values of 7.0 and 20.3 kcal/mol, respectively. The low 7.0 kcal/mol barrier for the H2/H3 exchange is consistent with a very facile process on the NMR time scale, resulting in the observation of a single chemical shift for the two hydrides at δ −9.30 at and above −100 °C. The relatively high 20.3 kcal/mol barrier for the H1/H2 exchange explains the observation of a unique resonance for H1 at δ −9.51.

In conclusion, the chiral pincer-type ligand **L1** studied in this paper and in our previous work has shown a strong tendency to undergo triple C−H activation on Os and Ru. These reactions afforded a thermally and chemically robust four-coordinate structural motif, [M(PGP)], possessing 15 valence electrons and capable, in the case of M = Os, of incorporating up to three additional small ligands. In future work, we are planning to explore the chemistry of less bulky versions of **L1** and [M(PGP)], e.g., with Pr^i groups on phosphorus, which should be more reactive and thus, potentially, more interesting for catalysis.

Experimental and Computational Details

All manipulations were performed under argon or hydrogen atmospheres using standard Schlenk techniques or in a nitrogen drybox, where the anhydrous solvents were stored and used. FT IR spectra were recorded on a Perkin-Elmer Spectrum BXII spectrometer. All NMR measurements were done on a Varian UNITY Inova 300 spectrometer. Osmium tetroxide was purchased from Pressure Chemicals; all other chemicals were obtained from Aldrich. [NEt$_4$]$_2$OsCl$_6$[9] and **L1**[3a] were prepared according to published methods.

OsCl(PGP) (1). [NEt$_4$]$_2$OsCl$_6$ (1.06 g, 1.595 mmol), **L1** (0.72 g, 1.784 mmol), triethylamine (0.8 g, 7.92 mmol), and *tert*-amyl alcohol (8 mL) were loaded in a glass autoclave, and the system was charged with nitrogen to 25 psi and stirred at 150 °C for 40 h. The resulting red-brown solution was evaporated and dried under vacuum at 100 °C. The residue was treated with ether (12 mL) to give a red-brown solution and a white precipitate, which was filtered off and washed with ether (4 × 3 mL). The combined filtrate was reduced in volume to ca. 6 mL and chromatographed on a column with basic alumina (25 × 150 mm, ether/hexane, 1:4−1:1). The red-brown eluate was collected and evaporated to dryness to give a dark brown, crystalline solid (852 mg, 1.360 mmol, 85%). Anal. Calcd for $C_{23}H_{48}ClNOsP_2$: C, 44.11; H, 7.73; N, 2.24. Found: C, 44.01; H, 7.80; N, 2.23. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 63.8, 71.2 (J_{PP} = 261 Hz). ^{1}H NMR (C$_6$D$_6$): δ 0.41 (m, 1H), 0.96−1.10 (m, 2H), 1.12 (d, J_{HP} = 12, 9H), 1.29 (d, J_{HP} = 12, 9H), 1.36 (d, J_{HP} = 11.7, 9H), 1.44 (d, J_{HP} = 11.7, 9H), 1.48−1.75 (m, 2H), 1.79−1.88 (m, 1H), 2.21 (s, 3H), 2.98 (d, J_{HP} = 27.6, 1H), 3.40 (dd, J_{HH} = 5.5, 11.4, 1H), 13.84 (d, J_{HP} = 4.2, 1H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 21.3 (dd, J_{CP} = 1.4, 24.5, *C*H$_2$), 29.0 (d, J_{CP} = 25.3, *C*H$_2$), 29.4 (dd, J_{CP} = 1.0, 5.0, *C*H$_3$), 29.5 (dd, J_{CP} = 1.5, 4.2, *C*H$_3$), 30.3 (dd, J_{CP} = 1.1, 4.1, *C*H$_3$), 31.1 (dd, J_{CP} = 0.9, 3.8, *C*H$_3$), 34.6 (dd, J_{CP} = 3.2, 10.4, *C*Me$_3$), 35.7 (dd, J_{CP} = 1.3, 10.4, *C*Me$_3$), 36.3 (dd, J_{CP} = 2.3, 8.4, *C*H$_2$), 36.3 (s, *C*H$_3$), 36.5 (dd, J_{CP} = 1.6, 18.2, *C*Me$_3$), 37.4 (dd, J_{CP} = 5.0, 9.7, *C*Me$_3$), 38.5 (d, J_{CP} = 1.1, *C*H), 79.4 (dd, J_{CP} = 3.4, 8.5, *C*H), 202.3 (dd, J_{CP} = 4.7, 6.8, *C*H). $[\alpha]_D^{20}$ +1137 (*c* 0.029, toluene).

OsH$_2$Cl(PGP) (2). Complex **1** (15 mg) was dissolved in toluene-*d*$_6$ (0.6 mL) in an NMR tube with a J. Young valve. The dark red solution was degassed, and the tube was filled with hydrogen, shaken for 5 min, and then sealed. At room temperature, the resulting pink solution contained a mixture of **1** (33%) and **2** (67%), according to ^{31}P{^{1}H} and ^{1}H NMR. Another sample, prepared in CD$_2$Cl$_2$, was found to contain **1** (11%), **2** (84%), and **3** (5%). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 54.4 (d, J_{PP} = 250.1 Hz), 62.4 (d, J_{PP} = 250.1 Hz). ^{1}H NMR (CD$_2$Cl$_2$): δ −5.83 (tt, $^2J_{HP}$ = 11.4, $^3J_{HH}$ = 4.5, 3.2, 2H), 0.82−0.98 (m, 1H), 1.05 (d, J_{HP} = 12.9, 9H), 1.26 (d, J_{HP} = 11.7, 9H), 1.31 (d, J_{HP} = 11.7, 9H), 1.35 (d, J_{HP} = 12.0, 9H), 1.37−1.68 (m, 4H), 1.91 (m, 1H), 2.09 (m, 1H), 3.14 (d, J_{HP} = 2.4, 3H), 3.67 (d, J_{HP} = 26.7, 1H), 11.53 (m, 1H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 21.1 (dd, J_{CP} = 1.4, 26.5, *C*H$_2$), 29.4 (dd, J_{CP} = 0.9,

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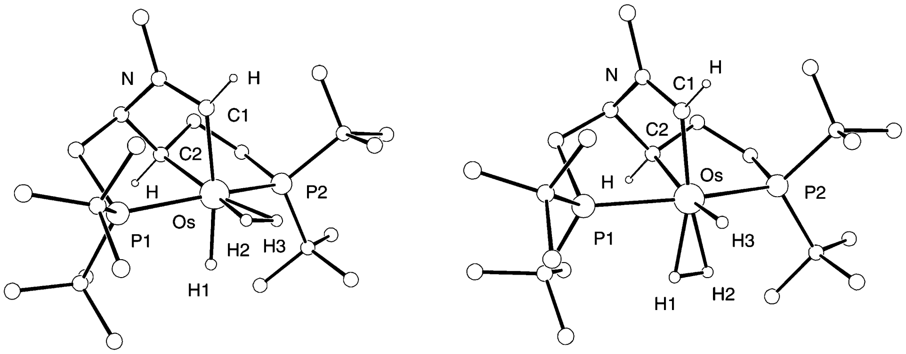

Figure 5. Calculated structures of **4**ts1 (left) and **4**ts2 (right). Most of the hydrogen atoms are not shown for clarity. Selected bond distances [Å]: **4**ts1, H2−H3 0.91; **4**ts2, H1−H2 0.83.

3.5, CH_3), 30.2 (m, CH_3), 30.5 (d, J_{CP} = 24.6, CH_2), 31.1 (dd, J_{CP} = 0.7, 4.4, CH_3), 31.4 (d, J_{CP} = 2.6, CH), 34.5 (dd, J_{CP} = 4.0, 18.7, CMe_3), 34.9 (dd, J_{CP} = 2.9, 8.9, CH_2), 35.5 (dd, J_{CP} = 2.4, 22.7, CMe_3), 35.7 (dd, J_{CP} = 4.2, 10.9, CMe_3), 36.8 (dd, J_{CP} = 2.9, 9.2, CMe_3), 43.6 (d, J_{CP} = 1.5, CH_3), 80.3 (dd, J_{CP} = 1.5, 6.9, CH), 248.9 (dd, J_{CP} = 5.6, 9.2, CH).

Preparation of 2-d_1. Solutions of **2** were prepared as above in CD_2Cl_2 or toluene-d_8. These solutions were subjected to three freeze−pump−thaw cycles, then back-filled with gaseous D_2 and shaken for 15 min. Integration of the ^1H NMR spectra established about 90% D incorporation in the hydride positions in each sample.

[Os(H$_2$)$_2$(PGP)]BPh$_4$ (3·BPh$_4$). OsCl(PGP) (30 mg, 0.048 mmol), $NaBPh_4$ (16.5 mg, 0.048 mmol), and THF-d_8 (0.6 mL) were placed in an NMR tube with a J. Young valve. The dark red solution was degassed, and the tube was filled with hydrogen and shaken for 5 min to give a colorless solution of [OsH$_4$(PGP)]BPh$_4$. $^{31}P\{^1H\}$ NMR (THF-d_8): 70.1 (d, J_{CP} = 161.1 Hz), 84.5 (d, J_{CP} = 161.1 Hz). ^1H NMR (THF-d_8): δ −7.49 (br, $\Delta_{1/2}$ = 21 Hz, 4H), 0.98 (d, J_{PH} = 13.8, 9H), 1.18 (d, J_{PH} = 13.2, 9H), 1.20 (d, J_{PH} = 12.9, 9H), 1.29 (d, J_{PH} = 13.5, 9H), 1.44−1.53 (m, 1H), 1.55−1.71 (m, 2H), 1.79−1.99 (m, 1H), 2.02−2.27 (m, 2H), 2.83 (d, J_{HP} = 1.8, 3H), 3.12 (m, 1H), 4.07 (d, J_{HP} = 32.8, 1H), 6.73 (d, J_{HH} = 6.9, 4H), 6.88 (d, J_{HH} = 7.2, 8H), 7.30 (m, 8H), 10.70 (s, 1H). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 21.2 (d, J_{CP} = 26.5, CH_2), 29.4 (d, J_{CP} = 3.5, CH_3), 29.9 (d, J_{CP} = 2.9, CH_3), 30.2 (br, $\Delta_{1/2}$ = 6.9 Hz, CH_3), 30.4 (d, J_{CP} = 3.5, CH_3), 31.0 (d, J_{CP} = 24.7, CH_2), 34.3 (dd, J_{CP} = 4.4, 9.3, CH_2), 34.5 (dd, J_{CP} = 0.6, 23.7, CMe_3), 35.7 (dd, J_{CP} = 1.6, 24.3, CMe_3), 37.0 (dd, J_{CP} = 1.1, 21.4, CMe_3), 36.8 (dd, J_{CP} = 1.6, 21.9, CMe_3), 44.5 (d, J_{CP} = 1.4, CH_3), 46.9 (m, CH), 80.6 (dd, J_{CP} = 3.1, 6.2, CH), 122.1 (s, CH), 125.9 (q, J_{CB} = 2.8, CH), 137.4 (q, J_{CB} = 1.4, CH), 165.4 (q, J_{CB} = 48.9, *ipso*-C), 224.4 (dd, J_{CP} = 5.4, 8.5, CH).

Preparation of 3-d_3·BPh$_4$. A solution of **3**·BPh$_4$ was prepared as above. This solution was subjected to three freeze−pump−thaw cycles, then back-filled with gaseous D_2 and shaken for 15 min. Integration of the ^1H NMR spectrum established about 90% D incorporation in the hydride positions.

Synthesis of OsH$_3$(PGP) (4). A mixture of OsCl(PGP) (200 mg, 0.319 mmol), $NaBPh_4$ (110 mg, 0.321 mmol), KH (16 mg, 0.4 mmol), and THF (10 mL) was stirred under hydrogen for 1 h. The resulting pale yellow solution was filtered, the colorless precipitate was washed with THF (2 × 2 mL), and the combined filtrate was evaporated to dryness under vacuum. The obtained solid was stirred with benzene (3 mL), and the resulting gray suspension was filtered through a pad of basic alumina (5 × 5 mm). The pale yellow filtrate was evaporated and dried under vacuum to give OsH$_3$(PGP) as a white solid with a yellow tint (184 mg, 0.310 mmol, 97%). $[\alpha]_D^{20}$ +35.2 (*c* 0.389, toluene). Anal. Calcd for $C_{23}H_{51}NOsP_2$: C, 46.52; H, 8.66; N, 2.36. Found: C, 46.33; H, 8.61; N, 2.28. IR (hexane, cm^{-1}): ν_{Os-H} = 2093, 2014, 1976, ν_{C-N} = 1502. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 83.6 (J_{PP} = 242.1 Hz), 73.4 (J_{PP} = 242.1 Hz). ^1H NMR (C_6D_6): δ −9.51 (m, 1H), −9.30 (t, J_{HH} = 8.2, 2H), 0.68−0.86 (m, 1H), 0.95 (d, J_{HP} = 12.0, 9H), 1.02−1.11 (m, 1H), 1.26 (d, J_{HP} = 11.4, 9H), 1.39 (d, J_{HP} = 12.0, 18H), 1.44−1.55 (m, 2H), 1.90−2.12 (m, 2H), 2.34 (d, J_{HP} = 2.1, 3H), 2.66 (m, 1H), 3.62 (d, J_{HP} = 25.8, 1H), 11.49 (d, J_{HH} = 8.1, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 22.8 (dd, J_{CP} = 1.3, 22.8, CH_2), 29.8 (dd, J_{CP} = 1.1, 5.9, CH_3), 30.8 (br d, J_{CP} = 3.5, CH_3), 30.4 (dd, J_{CP} = 0.9, 5.6, CH_3), 30.8 (br d, J_{CP} = 3.9, CH_3), 31.7 (dd, J_{CP} = 3.0, 11.6, CMe_3), 30.3 (dd, J_{CP} = 3.4, 9.5, CH_2), 33.3 (dd, J_{CP} = 4.4, 20.0, CMe_3), 34.1 (dd, J_{CP} = 2.3, 10.6, CMe_3), 34.5 (dd, J_{CP} = 22.5, CH_2), 35.5 (dd, J_{CP} = 3.0, 20.1, CMe_3), 42.1 (t, J_{CP} = 0.9, CH), 42.2 (d, J_{CP} = 1.3, CH_3), 78.3 (dd, J_{CP} = 3.0, 7.9, CH), 231.9 (dd, J_{CP} = 5.3, 9.5, CH).

Computational Details. Complexes **1**−**4** were fully optimized using the MPW1PW91 functional implemented in Gaussian 03,[10] which included modified Perdew−Wang exchange and Perdew−Wang 91 correlation.[11] The barriers for hydride exchange in **4** were obtained from the calculations of **4**, **4**ts1, and **4**ts2 using the MPW1K functional.[12] The nature of all stationary points was verified by frequency calculations. The basis sets employed in this work included SDD (associated with ECP) for Os, 6-31G for the CH_3 groups of PBu^t_2, 6-31G(d) for the rest of the heavy atoms, and 6-31G(p) for the hydrides and hydrogen atoms of the Os═CH and Os−CH groups.[13] All other hydrogen atoms were modeled using the 6-31G basis set.

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(13) For more information about basis sets implemented in Gaussian 03 and references see: Frish, A.; Frish, M. J.; Trucks, G. W. *Gaussian 03 User's Reference*; Gaussian, Inc.: Pittsburgh, PA, 2003. The basis sets are also available from the Extensible Computational Chemistry Environment Basis Set Database, which is developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352 (www.emsl.pnl.gov/forms/basisform.html).

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Supporting Information Available: CIF files for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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