Abnormal and Normal N-Heterocyclic Carbene Osmium Polyhydride Complexes Obtained by Direct Metalation of Imidazolium Salts

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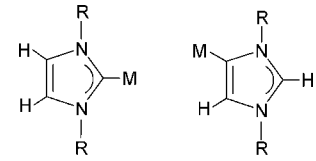
The complex $OsH_6(P^iPr_3)_2$ (**1**) is a basic precursor which promotes the direct metalation of imidazolium salts. Thus, it reacts with 1-mesityl-3-methylimidazolium tetraphenylborate and 1-mesityl-3-ethylimidazolium tetraphenylborate to give the abnormal NHC derivatives $[OsH_5(1\text{-mesityl-3-methylimidazol-4-ylidene})(P^iPr_3)_2]BPh_4$ (**2**) and $[OsH_5(1\text{-mesityl-3-ethylimidazol-4-ylidene})(P^iPr_3)_2]BPh_4$ (**3**), respectively. Treatment of **2** and **3** with NaH produces the deprotonation of the metal center and the formation of the tetrahydride derivatives $OsH_4(1\text{-mesityl-3-methylimidazol-4-ylidene})(P^iPr_3)_2$ (**4**) and $OsH_4(1\text{-mesityl-3-ethylimidazol-4-ylidene})(P^iPr_3)_2$ (**5**). In contrast to the case for the mesityl-substituted imidazolium salts, the reaction with 1-benzyl-3-methylimidazolium tetraphenylborate leads to the normal NHC complex $[OsH_5(1\text{-benzyl-3-methylimidazol-2-ylidene})(P^iPr_3)_2]BPh_4$ (**6**). The deprotonation of **6** with NaH affords $OsH_4(1\text{-benzyl-3-methylimidazol-2-ylidene})(P^iPr_3)_2$ (**7**). Complexes **2** and **4** have been characterized by X-ray diffraction analysis.

Introduction

Transition-metal complexes containing N-heterocyclic carbene ligands (NHC) are an emergent class of compounds, which are receiving increased attention since some of them show high activity in catalytic reactions.[1] Although several methods have been employed for their preparation, undoubtedly the cleanest synthetic strategy is direct metalation. This method requires the presence at the starting complex of strong Brønsted bases, which afford labile Brønsted acid ligands as a result of the deprotonation of the imidazolium salt. Unfortunately, the basic precursors are limited to $[Ir(\mu\text{-OR})(COD)]_2$[2] and $M(OAc)_2$ (M = Ni,[3] Pd,[4] Pt[5]).

Chart 1



The common coordination of the NHC ligands takes place through the C-2 atom of the heterocycle. When the coordination of this atom is unfavored as a consequence of the steric requirement of the N substituents, the NHC metal complexes show groups bound through a backbone C-4 (or C-5) carbon atom (Chart 1). About 2% of the structurally characterized derivatives contain this tautomer.[6] Reported examples include Fe,[7] Ru,[8] Rh,[9] Ir,[10] Pd,[11] Pt,[12] Cu,[13] Ag,[1f] and Y.[14] Both normal

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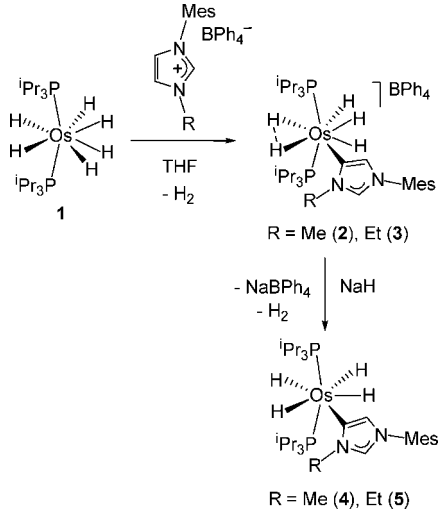
Scheme 1



and abnormal ligands are considered σ-donors and poor π-acceptor groups.[1,6] However, NHC complexes of late transition elements with the metal in a high oxidation state have not been reported.

The d^2 hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) has been shown to activate C−H bonds of organic molecules containing a heteroatom leading group.[15] In this work we prove that, in agreement with the trend of the hydrogen compounds of electropositive metals to liberate H_2 in contact with fairly acidic species, this complex is also a basic precursor which promotes the direct metalation of imidazolium salts, to afford both abnormal and normal NHC osmium derivatives with the metal center in a high oxidation state.[16]

Results and Discussion

Treatment of a tetrahydrofuran solution of **1** with 1.0 equiv of 1-mesityl-3-methylimidazolium tetraphenylborate at 90 °C for 5 h leads to the OsH_5 derivative $[OsH_5$(1-mesityl-3-methylimidazol-4-ylidene)$(P^iPr_3)_2]BPh_4$ (**2**) (Scheme 1), which is isolated as a white solid in 71% yield. Under the same conditions, the reaction of **1** with 1-mesityl-3-ethylimidazolium tetraphenylborate affords $[OsH_5$(1-mesityl-3-ethylimidazol-4-ylidene)$(P^iPr_3)_2]BPh_4$ (**3**) in 67% yield.

The structure of complex **2** (Figure 1) proves the abnormal coordination of the heterocycle, which is bonded to the metal center through the less sterically encumbered carbon atom C(19). The Os−C(19) bond length (2.120(4) Å) agrees well with those found in the first structurally characterized abnormal Os NHC complex $[OsH(\eta^2\text{-}H_2)\{\kappa C^5,N$-[1-(2-pyridylmethyl)-3-methylimidazol-5-ylidene]$\}(P^iPr_3)_2]BPh_4$ (2.123(6) Å),[17] the scarce normal

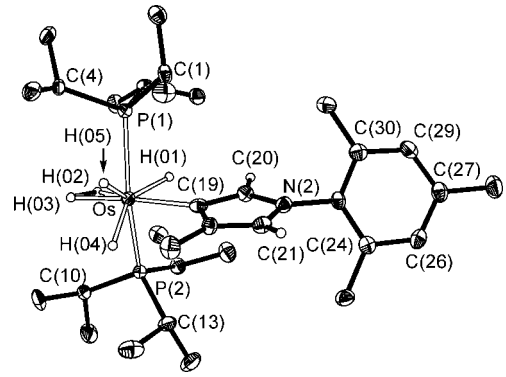


Figure 1. Molecular diagram of the cation of **2**. Selected bond lengths (Å) and angles (deg): Os−P(1) = 2.3716(10), Os−P(2) = 2.3709(11), Os−C(19) = 2.120(4), H(02)···H(03) = 1.25(5); P(1)−Os−P(2) = 151.72(4), P(1)−Os−C(19) = 95.92(11), P(2)−Os−C(19) = 92.83(12).

NHC osmium complexes reported (2.108(2)–1.993(9) Å),[17,18] the NH tautomer of 8-methylquinoline $OsCl_2(\eta^2\text{-}H_2)\{\kappa C$-$(HNC_8H_6Me)\}(P^iPr_3)_2$ (2.005(6) Å),[19] and the NH tautomer of benzo[*h*]quinoline $OsCl_2(\eta^2\text{-}H_2)\{\kappa C$-[HNbq]$\}(P^iPr_3)_2$ (2.055(11) Å).[20] In agreement with the abnormal nature[6] of the metalated carbons of **2** and **3**, their resonances in the $^{13}C\{^1H\}$ NMR spectra appear at 136.3 and 137.1 ppm, respectively.

At 100 K, the hydrogen atoms H(01), H(02), H(03), H(04), and H(05) of **2** were located in the difference Fourier maps and refined as isotropic atoms together with the remaining non-hydrogen atoms of the structure. Thus, the coordination geometry around the osmium atom can be rationalized as being derived from a distorted dodecahedron, which is defined by two intersecting orthogonal (89.9(8)°) trapezoidal planes. One of them contains the atoms P(1), H(05), H(04), and P(2) with a P(1)−Os−P(2) angle of 151.72(4)°, while the second one contains the atoms H(01), H(02), H(03), and C(19). The separation between the hydrogen atoms H(02) and H(03) of 1.25(5) Å is consistent with the presence of an elongated dihydrogen ligand[21] in these OsH_5 species. In agreement with the structure shown in Figure 1 and with the presence of a dihydrogen in the plane containing the heterocycle, in the high-field region, the ^1H NMR spectra of **2** and **3** at 193 K show three resonances in a 1:2:2 intensity ratio at about −6.8, −7.6, and −11.2 ppm (Figure 2).

Treatment of **2** and **3** with NaH in tetrahydrofuran produces the abstraction of one of the hydrogen atoms bonded to the metal center instead of the rupture of the normal C−H bond of the heterocycle. These reactions lead to the species OsH_4(1-mesityl-3-methylimidazol-4-ylidene)$(P^iPr_3)_2$ (**4**) and OsH_4(1-mesityl-3-ethylimidazol-4-ylidene)$(P^iPr_3)_2$ (**5**), which are isolated as white solids in 60% and 40% yields, respectively. The X-ray structure of the methyl derivative **4** (Figure 3) strongly supports the notion that the abnormal NHC ligands of the starting compounds do not undergo any change during the deprotonation.

The geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with axial phosphines

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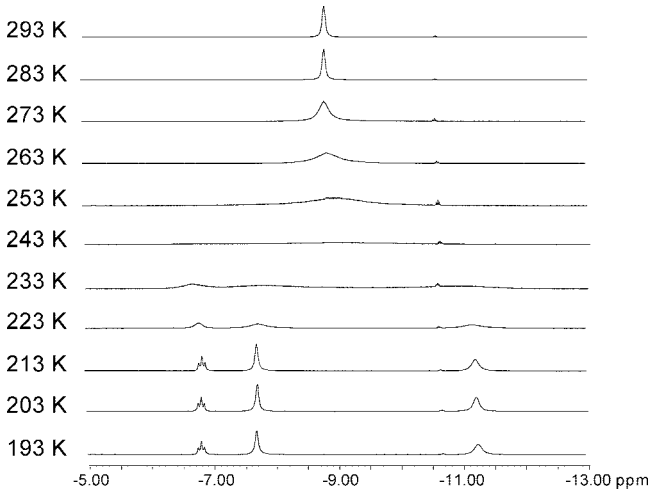


Figure 2. Variable-temperature ^{1}H NMR spectra (400 MHz, CD_2Cl_2) in the high-field region of $[OsH_5$(1-mesityl-3-methylimidazol-4-ylidene)$(P^iPr_3)_2]BPh_4$ (**2**).

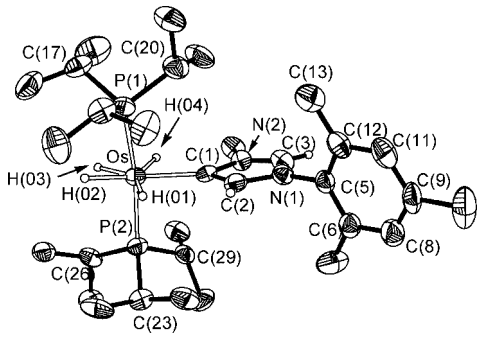


Figure 3. Molecular diagram of complex **4**. Selected bond lengths (Å) and angles (deg): Os−P(1) = 2.319(2), Os−P(2) = 2.321(3), Os−C(1) = 2.087(9); P(1)−Os−P(2) = 170.98(10), P(1)−Os−C(1) = 91.7(2), P(2)−Os−C(1) = 94.0(2).

(P(1)−Os−P(2) = 170.98(10)°). The metal coordination sphere is completed by the hydride ligands (H−H > 1.70 Å) and the carbon atom C(1) of the NHC ligand, which lies between H(01) and H(04). The Os−C(1) distance of 2.087(9) Å is about 0.03 Å shorter than the Os−NHC separation in **2**, suggesting that the abstraction of the hydrogen atom from the metal center increases the π-back-bonding ability of the metal. This is also supported by the $^{13}C\{^1H\}$ NMR spectra of **4** and **5**, which show the OsC resonance at about 154 ppm: i.e., shifted about 18 ppm to lower field with regard to those of **2** and **3**.

The abnormal coordination certainly minimizes the steric hindrance between the isopropyl groups of the phosphines and the NHC ligands, as can be seen in the structures of **2** and **4**. In agreement with this, in solution, the NHC ligand rotates around the Os−C bond. Thus, at room temperature, the ^{1}H NMR spectra contain two hydride resonances at about −10.2 and −10.5 ppm, which are converted into three signals in a 1:1:2 intensity ratio (the last one is broad) at about −8.3, −8.5, and −12.2 ppm, when the rotation is stopped at 203 K (Figure 4).

The replacement of the mesityl substituent by a benzyl group in the 1-mesityl-3-methylimidazolium cation disminishes the steric hindrance near the normal carbon atom, increasing the accessibility of this atom. Thus, in contrast to the case for the mesitylimidazolium salt, the treatment of a tetrahydrofuran solution of **1** with 1.0 equiv of 1-benzyl-3-methylimidazolium tetraphenylborate at 90 °C for 5 h leads to the normal complex $[OsH_5$(1-benzyl-3-methylimidazol-2-ylidene)$(P^iPr_3)_2]BPh_4$ (**6**)

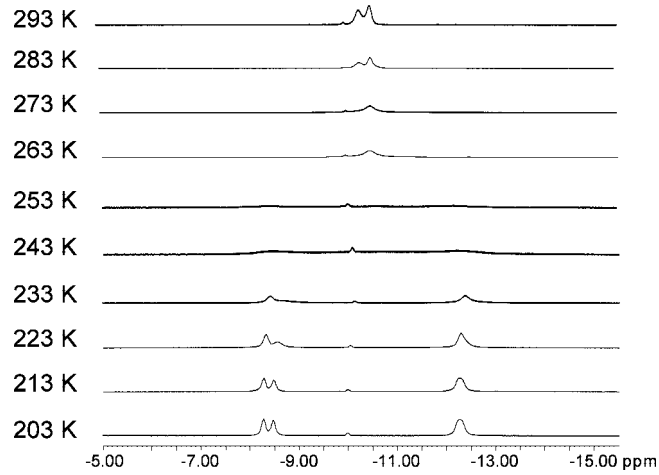
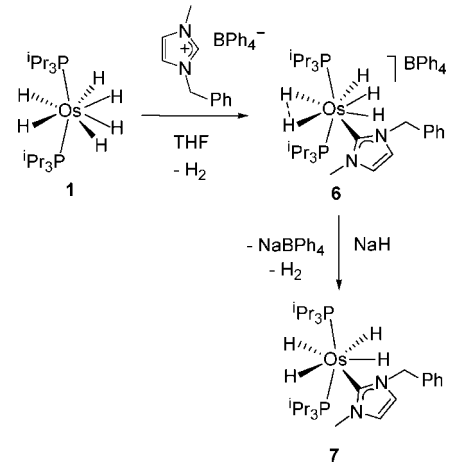


Figure 4. Variable-temperature ^{1}H NMR spectra (400 MHz, C_7D_8) in the high-field region of OsH_4(1-mesityl-3-ethylimidazol-4-ylidene)$(P^iPr_3)_2$ (**5**).

Scheme 2



(Scheme 2), which is isolated as a white solid in 69% yield. The normal coordination of the NHC ligand is supported by the $^{13}C\{^1H\}$ NMR spectrum, which shows the OsC resonance at 163.9 ppm, shifted 27.6 ppm to lower field in comparison to that of **2**. In agreement with the X-ray structure of the latter compound, at 200 K, the high-field region of the ^{1}H NMR spectrum of **6** shows three resonances in a 1:2:2 intensity ratio at −6.22, −7.55, and −11.09 ppm. In addition, the spectrum contains resonances of very low intensity, which may be due to a small amount of the abnormal isomer (about 7%).

The OsH_5 unit shows the same behavior as those of **2** and **3**. In the presence of NaH, complex **6** undergoes the abstraction of one of the hydrogen atoms bonded to the metal center to afford the tetrahydride OsH_4(1-benzyl-3-methylimidazol-2-ylidene)$(P^iPr_3)_2$ (**7**), related to **4** and **5** but with a normal NHC ligand. The loss of the proton also appears to increase the π-back-bonding power of the osmium center. Thus, the OsC resonance (δ 183.1) in the $^{13}C\{^1H\}$ NMR spectrum of **7** is observed shifted 19.2 ppm to lower field with regard to that of **6**. In solution the normal NHC ligand of **7** rotates as the abnormal NHC ligands of **4** and **5**. In agreement with this, the behavior of the ^{1}H NMR spectrum of **7** with the temperature is similar to those of **4** and **5**. At room temperature, one signal is observed for the four inequivalent hydride ligands (δ, −10.65), which splits into four resonances at −8.60, −8.80, −12.80 and −13.25 ppm at 178 K.

Concluding Remarks

In conclusion, neutral transition-metal polyhydride complexes are basic enough to produce the deprotonation of imidazolium salts. Thus, families of transition-metal polyhydride derivatives containing both abnormal and normal NHC ligands should be easily prepared by the direct metalation of imidazolium cations. This fact has allowed us to synthesize and characterize osmium derivatives containing either abnormal or normal NHC ligands.

Experimental Section

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Gemini 2000, Bruker ARX 300 MHz, Bruker Avance 300 MHz, or Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or to external 85% H_3PO_4 (^{31}P{^{1}H}). Coupling constants *J* and *N* are given in hertz. Infrared spectra were recorded on a Perkin-Elmer Spectrum One or Spectrum 100 spectrometer as Nujol mulls. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. $OsH_6(P^iPr_3)_2$ (**1**),[22] 1-mesitylimidazole,[23] and 1-mesityl-3-methylimidazolium iodide[24] were prepared according to published methods. 1-Methylimidazole was purchased from commercial sources.

Synthesis of 1-Mesityl-3-methylimidazolium Tetraphenylborate. 1-Mesityl-3-methylimidazolium iodide (436 mg, 1.33 mmol) and $NaBPh_4$ (455.1 mg, 1.33 mmol) were dissolved in acetone (15 mL) and MeOH (5 mL), and this mixture was stirred for 2 h. The resulting solution was taken to dryness. Dichloromethane (15 mL) was added, giving a suspension of NaI. After filtering, the resulting solution was evaporated to dryness and the addition of diethyl ether caused the precipitation of a white solid that was washed with diethyl ether (3 × 15 mL) and dried in vacuo. Yield: 553 mg (80%). Anal. Calcd for $C_{37}H_{37}BN_2$: C, 85.38; H, 7.16; N, 5.38. Found: C, 85.32; H, 7.37; N, 5.56. ^{1}H NMR (CD_2Cl_2, 300 MHz, 293 K): δ 7.31 (s, 8H, *o*-BPh_4), 7.06 (s, 2H, mesityl), 6.92 (t, J_{H-H} = 7.2, 8H, *m*-BPh_4), 6.81 (t, J_{H-H} = 7.2, 4H, *p*-BPh_4), 6.70 (t, J_{H-H} = 1.5, 1H, C*H* imidazole), 6.63 (t, J_{H-H} = 1.5, 1H, C*H* imidazole), 5.79 (s, 1H, NC*H*N), 2.92 (s, 3H, N−CH_3), 2.40 (s, 3H, CH_3 mesityl), 1.85 (s, 6H, CH_3 mesityl). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.56 MHz, 293 K, plus apt): δ 164.1 (q, J_{C-B} = 49.2, C_{ipso} BPh_4), 142.0 (C_{ipso} mesityl), 136.5 (s, NC*H*N), 136.2 (s, *o*-BPh_4), 134.5 (s, mesityl), 130.7 (s, mesityl), 130.0 (s, *C*H mesityl), 126.1 (q, J_{C-B} = 2.4, *m*-BPh_4), 123.8 (s, *C*H imidazole), 123.7 (s, *C*H imidazole), 122.4 (s, *p*-BPh_4), 36.6 (s, N−*C*H_3), 21.3 (s, *C*H_3 mesityl), 17.5 (s, *C*H_3 mesityl).

Synthesis of 1-Mesityl-3-ethylimidazolium Iodide. Over a solution of 1-mesitylimidazole (250 mg, 1.34 mmol) in tetrahydrofuran (2 mL), EtI (539 μL, 6.7 mmol) was added dropwise. The mixture was refluxed while the white product precipitated. After 24 h, the solvent was removed. Addition of diethyl ether caused the precipitation of a white solid that was washed with diethyl ether. Yield: 386 mg (84%). Anal. Calcd for $C_{14}H_{19}IN_2$: C, 49.13; H, 5.59; N, 8.18. Found: C, 49.32; H, 5.39; N, 8.36. ^{1}H NMR (CD_2Cl_2, 300 MHz, 293 K): δ 10.01 (br s, 1H, NC*H*N), 7.73 (t, J_{H-H} = 1.8, 1H, C*H* imidazole), 7.25 (t, J_{H-H} = 1.8, 1H, C*H* imidazole), 7.06 (s, 2H, mesityl), 4.66 (q, J_{H-H} = 7.5, 2H, −CH_2−), 2.36 (s, 3H, CH_3 mesityl), 2.10 (s, 6H, CH_3 mesityl), 1.66 (t, J_{H-H} = 7.5, 3H, −CH_3).

Synthesis of 1-Mesityl-3-ethylimidazolium Tetraphenylborate. 1-Mesityl-3-ethylimidazolium iodide (386 mg, 1.13 mmol) and $NaBPh_4$ (387 mg, 1.13 mmol) were dissolved in acetone (15 mL) and MeOH (5 mL), and the mixture was stirred for 2 h. The resulting solution was taken to dryness. Dichloromethane (15 mL) was added, giving a suspension of NaI. After filtering, the resulting solution was evaporated to dryness and the addition of diethyl ether caused the precipitation of a white solid that was washed with diethyl ether (3 × 15 mL) and dried in vacuo. Yield: 525 mg (87%). Anal. Calcd for $C_{38}H_{39}BN_2$: C, 85.38; H, 7.36; N, 5.24. Found: C, 85.47; H, 7.57; N, 5.36. ^{1}H NMR (CD_2Cl_2, 300 MHz, 293 K): δ 7.31 (s, 8H, *o*-BPh_4), 7.07 (s, 2H, mesityl), 6.93 (t, J_{H-H} = 7.2, 8H, *m*-BPh_4), 6.81 (t, J_{H-H} = 7.2, 4H, *p*-BPh_4), 6.74 (d, J_{H-H} = 1.8, 1H, C*H* imidazole), 6.69 (d, J_{H-H} = 1.8, 1H, C*H* imidazole), 6.00 (s, 1H, NC*H*N), 3.31 (q, J_{H-H} = 7.4, 2H, −CH_2−), 2.41 (s, 3H, CH_3 mesityl), 1.86 (s, 6H, CH_3 mesityl), 1.18 (t, J_{H-H} = 7.4, 3H, −*C*H_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.56 MHz, 293 K, plus apt): δ 164.1 (q, J_{C-B} = 49.2, C_{ipso} BPh_4), 142.0 (C_{ipso} mesityl), 136.2 (*o*-BPh_4), 135.4 (s, NC*H*N), 134.5 (s, mesityl), 130.7 (s, mesityl), 130.0 (s, *C*H mesityl), 126.1 (q, J_{C-B} = 2.4, *m*-BPh_4), 124.0 (s, *C*H imidazole), 122.4 (br, *p*-BPh_4), 122.0 (s, *C*H imidazole), 45.5 (s, N−*C*H_2−), 21.3 (s, −*C*H_3), 17.4 (s, *C*H_3 mesityl), 15.3 (s, *C*H_3 mesityl).

Synthesis of 1-Benzyl-3-methylimidazolium Chloride. To a Schlenk flask was added 1-methylimidazole (0.5 g, 0.48 mmol), benzyl chloride (0.70 mL, 0.48 mmol), and tetrahydrofuran (15 mL). The reaction mixture was stirred at room temperature for 14 h. After this time the solvent was removed, giving a colorless oil. After the oil was washed with pentane, a white solid precipitated in diethyl ether. Yield: 0.76 g (60%). Anal. Calcd for $C_{11}H_{13}ClN_2$: C, 63.31; H, 6.28; N, 13.42. Found: C, 62.98; H, 6.45; N, 13.58. ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 10.67 (s, 1H, NC*H*N), 7.44–7.42 (m, 2H, Ph), 7.40 (s, 1H, C*H* imidazole), 7.38 (s, 1H, C*H* imidazole), 7.28–7.27 (m, 3H, Ph), 5.58 (s, 2H, N−CH_2Ph), 3.98 (N−CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, 293 K): δ 138.3 (N*C*HN), 134.2 (C_{ipso} Ph), 129.4, 129.3, 129.1 (all s, Ph), 123.7 (*C*H imidazole), 122.1 (*C*H imidazole), 53.1 (N−*C*H_2Ph), 36.7 (N−CH_3).

Synthesis of 1-Benzyl-3-methylimidazolium Tetraphenylborate. 1-Benzyl-3-methylimidazolium chloride (400 mg, 1.595 mmol) and $NaBPh_4$ (0.55 g, 1.61 mmol) were dissolved in CH_2Cl_2 (15 mL), giving a white suspension after 3 h. The suspension was filtered through Celite, and a colorless solution was obtained, which was evaporated to dryness. Addition of diethyl ether caused the precipitation of a white solid that was washed with diethyl ether (3 × 15 mL) and dried in vacuo. Yield: 0.67 g (71%). Anal. Calcd for $C_{35}H_{33}BN_2$: C, 85.36; H, 6.75; N, 5.69. Found: C, 85.43; H, 6.37; N, 5.56. ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 7.45 (s, 8H, *o*-BPh_4), 7.36–7.34 (m, 3H, Ph), 6.95 (m, 10H, *m*-BPh_4 and Ph), 6.76 (t, J_{H-H} = 7.2, 4H, *p*-BPh_4), 6.36 (s, 1H, C*H* imidazole), 6.34 (s, 1H, C*H* imidazole), 4.92 (s, 1H, NC*H*N), 4.44 (s, 2H, N−CH_2−Ph), 2.98 (s, 3H, N−CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, 293 K): δ 164.6 (q, J_{C-B} = 49.2, C_{ipso} BPh_4), 136.0 (*o*-BPh_4), 132.5 (C_{ipso} Ph), 129.8, 129.7, 128.5 (all s, Ph), 126.4 (q, J_{C-B} = 2.6, *m*-BPh_4), 123.1 (N*C*HN), 122.5 (*p*-BPh_4), 121.2 (*C*H imidazole), 53.4 (N−*C*H_2Ph), 36.4 (N−*C*H_3).

Reaction of 1 with 1-Mesityl-3-methylimidazolium Tetraphenylborate. Preparation of [OsH_5(1-mesityl-3-methylimidazol-4-ylidene)(P^iPr_3)$_2$]BPh_4 (2). A solution of **1** (155 mg, 0.3 mmol) in THF (15 mL) was treated with the stoichiometric amount of 1-mesityl-3-methylimidazolium tetraphenylborate (156.1 mg, 0.3 mmol). The resulting colorless solution was stirred at 90 °C for 5 h. After this time, it was cooled to room temperature and filtered through Celite and the solvent removed. Addition of diethyl ether caused the precipitation of a white solid that was washed with further portions of diethyl ether (4 × 5 mL) and dried in vacuo. Yield: 220 mg (71%). Anal. Calcd for $C_{55}H_{82}BN_2OsP_2$: C, 63.87;

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H, 7.99; N, 2.71. Found: C, 63.80; H, 7.59; N, 3.21. IR (cm^{-1}): ν(Os−H) 2094 (w), 2001 (w); ν(C═N) 1580 (m), 1554 (m). ^1H NMR (CD_2Cl_2, 300 MHz, 293 K): δ 7.31 (m, 8H, *o*-BPh_4), 7.17 (d, J_{H-H} = 1.7, 1H, C*H* imidazole), 7.01 (s, 2H, mesityl), 6.97 (t, J_{H-H} = 8.4, 8H, *m*-BPh_4), 6.83 (t, J_{H-H} = 8.4, 4H, *p*-BPh_4), 6.33 (d, J_{H-H} = 1.7, 1H, C*H* imidazole), 3.61 (s, 3H, N−CH_3), 2.35 (s 3H, CH_3 mesityl), 2.01 (m, 6H, PC*H*CH_3), 1.87 (s, 6H, CH_3 mesityl), 1.17 (dvt, N = 13.8, J_{H-H} = 6.9, 18H, PCHCH_3), 1.08 (dvt, N = 14.1, J_{H-H} = 7.2, 18H, PCHCH_3), −8.64 (br, 5H, OsH_5). ^1H NMR (CD_2Cl_2, 400 MHz, 183 K, high-field region): δ −6.81 (t, J_{H-P} = 20.0, 1H, Os−H), −7.66 (br, 2H, Os−H), −11.22 (br, 2H, Os−H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.56 MHz, 293 K, plus apt): δ 164.2 (q, J_{C-B} = 49.2, C_{ipso} BPh_4), 140.9 (s, C_{ipso} mesityl), 136.3 (t, J_{C-P} = 5.4, *C*−Os), 136.2 (br, *o*-BPh_4), 134.4 (s, mesityl), 131.7 (s, *C*H imidazole), 131.6 (s, mesityl), 130.0 (s, *C*H imidazole), 129.8 (s, mesityl), 126.0 (q, J_{C-B} = 2.8, *m*-BPh_4), 122.2 (s, *p*-BPh_4), 41.3 (N−*C*H_3), 27.8 (vt, N = 30.8, P*C*HCH_3), 21.2 (s, *C*H_3 mesityl), 19.9, 19.4 (both s, PCH*C*H_3), 17.2 (s, *C*H_3 mesityl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz, 293 K): δ 41.0 (s). T_1(min) (ms, OsH, 400 MHz, CD_2Cl_2, 253 K): 78 ± 2.

Reaction of 1 with 1-Mesityl-3-ethylimidazolium Tetraphenylborate. Preparation of [OsH_5(1-mesityl-3-ethylimidazol-4-ylidene)(P^iPr_3)$_2$]BPh_4 (3). This complex was prepared in a manner analogous to that for complex **2**, starting from 1-mesityl-3-ethylimidazolium tetraphenylborate (124.1 mg, 0.23 mmol) and **1** (120 mg, 0.23 mmol), giving a white solid. Yield: 161 mg (67%). Anal. Calcd for $C_{56}H_{85}BN_2OsP_2$: C, 64.10; H, 8.17; N, 2.67. Found: C, 64.32; H, 8.37; N, 2.41. IR (cm^{-1}): ν(Os−H) 2094 (w), 2001 (w); ν(C═N) 1580 (m), 1554 (m). ^1H NMR (CD_2Cl_2, 300 MHz, 293 K): δ 7.69 (s, 1H, C*H* imidazole), 7.29 (m, 8H, *o*-BPh_4), 7.02 (s, 2H, mesityl), 6.96 (t, J_{H-H} = 7.7, 8H, *m*-BPh_4), 6.83 (t, J_{H-H} = 7.7, 4H, *p*-BPh_4), 6.43 (s, 1H, C*H* imidazole), 4.30 (q, J_{H-H} = 7.3, 2H, N−CH_2), 2.34 (s, 3H, CH_3 mesityl), 2.03 (m, 6H, PC*H*CH_3), 1.90 (s, 6H, CH_3 mesityl), 1.45 (t, J_{H-H} = 7.3, 3H, −CH_3), 1.16 (dvt, N = 13.4, J_{H-H} = 7.2, 18H, PCHCH_3), 1.09 (dvt, N = 14.4, J_{H-H} = 7.2, 18H, PCHCH_3), −8.62 (br, 5H, OsH_5). ^1H NMR (CD_2Cl_2, 300 MHz, 193 K, high-field region): δ −6.80 (t, J_{H-P} = 20.1, 1H, Os−H), −7.54 (br, 2H, Os−H), −11.15 (br, 2H, Os−H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.42 MHz, 293 K, plus apt): δ 164.3 (q, J_{C-B} = 49.2, C_{ipso} BPh_4), 141.2 (s, C_{ipso} mesityl), 137.1 (t, J_{C-P} = 5.1, *C*−Os), 136.3 (br, *o*-BPh_4), 134.6 (s, mesityl), 131.9 (s, *C*H imidazole), 131.8 (s, mesityl), 131.6 (s, *C*H imidazole), 130.1 (s, mesityl), 126.1 (q, J_{C-B} = 2.6, *m*-BPh_4), 122.2 (s, *p*-BPh_4), 48.9 (s, N−*C*H_2−), 27.9 (vt, N = 30.8, P*C*HCH_3), 21.2 (s, −*C*H_3), 19.9, 19.5 (both s, PCH*C*H_3), 17.2 (s, *C*H_3 mesityl), 15.2 (s, *C*H_3 mesityl). $^{31}P\{^1H\}$ NMR (C_2Cl_2, 121.4 MHz, 293 K): δ 40.6 (s). T_1(min) (ms, OsH, 400 MHz, CD_2Cl_2, 248 K): 75 ± 3.

Reaction of 2 with NaH: Preparation of OsH_4(1-mesityl-3-methylimidazol-4-ylidene)(P^iPr_3)$_2$ (4). Inside the drybox, **2** (200 mg, 0.19 mmol), NaH (9.3 mg, 0.39 mmol), and THF (10 mL) were combined in a Schlenk tube provided with a stir bar. The resulting mixture was stirred for 30 min at room temperature, and the solvent was removed. Addition of toluene leads to a white suspension of sodium tetraphenylborate that was filtered through Celite. The obtained solution was evaporated to dryness and washed with pentane, giving a white solid. Yield: 80 mg (58%). Anal. Calcd for $C_{31}H_{62}BN_2OsP_2$: C, 52.07; H, 8.74; N, 3.92. Found: C, 51.67; H, 8.73; N, 3.79. IR (cm^{-1}): ν(Os−H) 2041 (w), 2005 (w); ν(C═N) 1552 (m). ^1H NMR (C_6D_6, 400 MHz, 293 K): δ 6.56 (s, 1H, C*H* imidazole), 6.56 (s, 2H, mesityl), 6.30 (s, 1H, C*H* imidazole), 3.63 (s, 3H, N−CH_3), 2.03 (s, 3H, CH_3 mesityl), 1.97 (m, 6H, PC*H*CH_3), 1.75 (s, 6H, CH_3 mesityl), 1.33 (dvt, N = 12.6, J_{H-H} = 6.6, 36H, PCHCH_3), −10.21 (br, 2H, Os−H_4), −10.46 (t, J_{H-P} = 13.5, 2H, Os−H_4). ^1H NMR (C_7D_8, 300 MHz, 203 K, high-field region): δ −8.30 (t, J_{H-P} = 11.7, 1H, Os−H), −8.54 (br, 1H, Os−H), −12.20 (br, 2H, Os−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz, 293 K, plus apt): δ 154.7 (t, J_{C-P} = 7.7, *C*−Os), 139.0 (s, mesityl), 134.6 (s, mesityl), 133.0 (s, mesityl), 132.9 (s, *C*H imidazole), 129.2 (s, *C*H mesityl), 126.4 (s, *C*H imidazole), 40.5 (s, −*C*H_3), 29.0 (vt, N = 22.2, P*C*HCH_3), 21.1 (s, PCH*C*H_3), 20.8 (s, *C*H_3 mesityl), 20.7 (s, PCH*C*H_3), 17.0 (s, *C*H_3 mesityl). $^{31}P\{^1H\}$ NMR (C_7D_8, 161.9 MHz, 293 K): δ 41.7 (s). $^{31}P\{^1H\}$ NMR (C_7D_8, 161.9 MHz, 183 K): δ 40.7 (br). T_1(min) (ms, OsH, 400 MHz, C_7D_8, 253 K): 146 ± 3.

Reaction of 3 with NaH: Preparation of OsH_4(1-mesityl-3-ethylimidazol-4-ylidene)(P^iPr_3)$_2$ (5). This complex was prepared in a manner analogous to that for complex **4**, starting from **3** (130 mg, 0.124 mmol) and NaH (6.0 mg, 0.248 mmol), but with washing with pentane at 223 K. A white solid was obtained. Yield: 35 mg (39%). Anal. Calcd for $C_{32}H_{64}BN_2OsP_2$: C, 52.72; H, 8.85; N, 3.84. Found: C, 52.62; H, 8.82; N, 3.58. IR (cm^{-1}): ν(Os−H) 2029 (w), 2004 (w); ν(C═N) 1549 (m). ^1H NMR (C_7D_8, 500 MHz, 293 K): δ 6.63 (s, 1H, C*H* imidazole), 6.60 (s, 2H, mesityl), 6.58 (s, 1H, C*H* imidazole), 4.57 (q, J_{H-H} = 7.5, 2H, N−CH_2), 2.07 (s, 3H, CH_3 mesityl), 1.97 (m, 6H, PC*H*CH_3), 1.78 (s, 6H, CH_3 mesityl), 1.34 (dvt, N = 12.5, J_{H-H} = 6.5, 18H, PCHCH_3), 1.31 (dvt, N = 12.0, J_{H-H} = 6.5, 18H, PCHCH_3), 1.03 (t, J_{H-H} = 7.5, 3H, −CH_3), −10.23 (br, 2H, Os−H_4), −10.47 (br, 2H, Os−H_4). ^1H NMR (C_7D_8, 400 MHz, 203 K): δ −8.27 (br, 1H, Os−H), −8.46 (br, 1H, Os−H), −12.30 (br, 2H, Os−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.68 MHz, 293 K, plus apt): δ 154.2 (t, J_{C-P} = 7.5, *C*−Os), 139.0 (s, mesityl), 134.7 (s, mesityl), 133.2 (s, mesityl), 132.4 (s, *C*H imidazole), 129.2 (s, *C*H mesityl), 126.3 (s, *C*H imidazole), 47.1 (s, N−CH_2−), 29.0 (vt, N = 21.9, P*C*HCH_3), 21.2 (s, PCH*C*H_3), 20.9 (s, *C*H_3 mesityl), 20.7 (s, PCH*C*H_3), 17.0 (s, *C*H_3 mesityl), 15.3 (s, −*C*H_3). $^{31}P\{^1H\}$ NMR (C_7D_8, 161.9 MHz, 293 K): δ 41.5 (s). T_1(min) (ms, OsH, 400 MHz, C_7D_8, 253 K): 150 ± 3.

Reaction of 1 with 1-Benzyl-3-methylimidazolium Tetraphenylborate: Preparation of [OsH_5(1-benzyl-3-methylimidazol-2-ylidene)(P^iPr_3)$_2$]BPh_4 (6). This complex was prepared in a manner analogous to that for complex **2**, starting from 1-benzyl-3-methylimidazolium tetraphenylborate (143 mg, 0.194 mmol) and **1** (150 mg, 0.194 mmol), giving a white solid. Yield: 143 mg (69%). Anal. Calcd for $C_{57}H_{89}BN_2OsP_2$: C, 64.26; H, 8.42; N, 2.63. Found: C, 64.18; H, 8.15; N, 2.97. IR (cm^{-1}): ν(Os−H) 2102 (w), 2038 (w); ν(C═N) 1579 (m). ^1H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 7.40 (m, 13H, *o*-BPh_4 and Ph), 7.03 (t, 8H, *m*-BPh_4), 6.98 (d, J_{H-H} = 1.8, 1H, C*H* imidazole), 6.93 (d, J_{H-H} = 1.8, 1H, C*H* imidazole), 6.87 (t, 4H, *p*-BPh_4), 5.45 (s, 2H, N−CH_2−Ph), 3.78 (s, 3H, N−CH_3), 1.91 (m, 6H, PC*H*CH_3), 1.05 (dvt, N = 12.8, J_{H-H} = 6.8, 18H, PCHCH_3), 1.01 (dvt, N = 13.2, J_{H-H} = 7.2, 18H, PCHCH_3), −8.42 (t, J_{H-P} = 8.4, 5H, Os−H_5). ^1H NMR (CD_2Cl_2, 300 MHz, 178 K, high-field region): δ −6.22 (br, 1H, Os−H), −7.52 (br, 2H, Os−H), −11.09 (br, 2H, Os−H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz, 293 K): δ 164.4 (q, J_{C-B} = 49.2, C_{ipso} BPh_4), 163.9 (t, J_{C-P} = 5.4, *C*−Os), 136.1 (s, *o*-BPh_4), 134.9 (C_{ipso} Ph), 129.4, 128.9, 128.4 (all s, Ph), 126.1 (q, J_{C-B} = 2.7, *m*-BPh_4), 123.6 (*C*H imidazole), 123.3 (*C*H imidazole), 122.1 (s, *p*-BPh_4), 58.5 (N−*C*H_2Ph), 43.0 (N−*C*H_3), 28.7 (vt, N = 31.0, P*C*HCH_3), 19.6 (PCH*C*H_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz, 293 K): δ 38.9 (s). T_1(min) (ms, OsH, 400 MHz, CD_2Cl_2, 243 K): 90 ± 2.

Reaction of 6 with NaH: Preparation of OsH_4(1-benzyl-3-methylimidazol-2-ylidene)(P^iPr_3)$_2$ (7). This complex was prepared in a manner analogous to that for complex **4**, starting from **6** (141 mg, 0.14 mmol) and NaH (7.0 mg, 0.28 mmol). It was obtained as a pale yellow oil (that was found to be pure by NMR spectroscopy). The complex could be isolated as a white solid in very low yield after cooling a pentane solution in a 2-propanol/dry ice bath. Anal. Calcd for $C_{33}H_{68}N_2OsP_2$: C, 53.19; H, 9.20; N, 3.75. Found: C, 53.50; H, 9.04; N, 3.64. IR (cm^{-1}): ν(Os−H) 2008 (w), 1922 (m). ^1H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 7.28 (m, 5H, Ph), 6.90 (d, J_{H-H} = 2.2, 1H, C*H* imidazole), 6.71 (d, J_{H-H} = 2.2, 1H, C*H* imidazole), 5.78 (s, 2H, N−CH_2−Ph), 3.93 (s, 3H, N−CH_3), 1.69 (m, 6H, PC*H*CH_3), 1.00 (dvt, N = 12.3, J_{H-H} = 6.9, 18H, PCHCH_3), 0.97 (dvt, N = 12.3, J_{H-H} = 6.9, 18H,

Table 1. Crystal Data and Data Collection and Refinement for 2 and 4

	2	4
	Crystal Data	
formula	$C_{55}H_{83}BN_2OsP_2$	$C_{31}H_{62}N_2OsP_2$
mol wt	1035.18	714.97
color; habit	colorless; irregular block	colorless; prism
size, mm	0.20,0.20,0.16	0.07, 0.07, 0.04
symmetry; space group	monoclinic; $P2_1$	orthorhombic; $P2_12_12_1$
a, Å	13.467(3)	11.396(5)
b, Å	13.713(3)	13.801(6)
c, Å	14.322(3)	21.640(9)
α, deg	90	90
β, deg	101.286(3)	90
γ, deg	90	90
V, Å^3	2593.8(9)	3403(2)
Z	2	4
D(calcd), g cm^{-3}	1.325	1.395
	Data Collection and Refinement	
diffractometer	Bruker Smart APEX	
λ(Mo Kα), Å	0.710 73	
monochromator	graphite oriented	
scan type	ω scans	
μ, mm^{-1}	2.556	3.861
2θ range, deg	3−58	3−58
temp, K	100.0(2)	100.0(2)
no. of data collect	32 985	42 952
no. of unique data	12 561 (R_{int} = 0.0377)	8462 (R_{int} = 0.1519)
no. of params/restraints	593/6	360/5
Flack param	0.000(4)	
R^1 [a] ($F^2 > 2\sigma(F^2)$)	0.0296	0.0640
ωR^2 [b] (all data)	0.0573	0.1037
S[c] (all data)	0.931	0.856

[a] $R^1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $\omega R^2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] GOF = $S = \{\sum[(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

PCHCH_3), −10.65 (t, J_{H-P} = 19.6, 4H, Os−H_4). ^{1}H NMR (C_7D_8, 400 MHz, 178 K): δ −8.60 (br, 1H, Os−H), −8.80 (br, 1H, Os−H), −12.80 (br, 1H, Os−H), −13.25 (br, 1H, Os−H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.4 MHz, 293 K): δ 183.1 (t, J_{C-P} = 7.1, C−Os), 138.7 (C_{ipso} Ph), 128.7, 128.6, 127.4 (all s, Ph), 121.1 (CH imidazole), 120.1 (CH imidazole), 58.2 (N−CH$_2$Ph), 43.1 (N−CH$_3$), 29.2 (t, N = 23.5, PCHCH$_3$), 20.5, 20.2 (both s, PCHCH$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 38.9 (s). T_1(min) (ms, OsH, 400 MHz, CD_2Cl_2, 243 K): 144 ± 2.

Structural Analysis of Complexes 2 and 4. Crystals suitable for the X-ray diffraction study were obtained by slow diffusion (−20 °C, freezer drybox) of diethyl ether into a concentrated solution of **2** in dichloromethane or of pentane into a solution of **4** in toluene. X-ray data were collected for all complexes on a Bruker Smart APEX CCD diffractometer equipped with a normal-focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.710 73 Å) operating at 50 kV and 30 mA (**2**) or 40 mA (**4**). Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[25] The structures of both compounds were solved by the Patterson method. The refinements, by full-matrix least squares on F^2 with SHELXL97,[26] were similar for all complexes, including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms were observed or calculated and refined freely or refined using a restricted riding model. Hydride ligands were observed in the difference Fourier maps but refined with a restrained Os−H bond length (1.59(1) Å, CSD). All the highest electronic residuals were observed in the close proximity of the Os center and make no chemical sense. Crystal data and details of the data collection and refinement are given in Table 1.

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Supporting Information Available: CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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