# Influence of the Anion of the Salt Used on the Coordination Mode of an N-Heterocyclic Carbene Ligand to Osmium

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The reactions of the hexahydride $OsH_6(P^iPr_3)_2$ (**1**) with 1.0 equiv of the $BPh_4^-$, $BF_4^-$, and $Br^-$ salts of 1-(2-pyridylmethyl)-3-methylimidazolium, in tetrahydrofuran under reflux, have been studied. In the three cases, mixtures of the abnormal $[OsH(\eta^2\text{-}H_2)\{\kappa C^5,N\text{-}[1\text{-}(2\text{-pyridylmethyl})\text{-}3\text{-methylimidazol-}5\text{-ylidene}]\}(P^iPr_3)_2]A$ (A = $BPh_4$ (**2a**), $BF_4$ (**2b**), Br (**2c**)) and normal $[OsH(\eta^2\text{-}H_2)\{\kappa C^2,N\text{-}[1\text{-}(2\text{-pyridylmethyl})\text{-}3\text{-methylimidazol-}2\text{-ylidene}]\}(P^iPr_3)_2]A$ (A = $BPh_4$ (**3a**), $BF_4$ (**3b**), Br (**3c**)) isomers are obtained. The formation rate of the abnormal isomer and the abnormal to normal ratio decrease as the coordinating power of the anion of the used salt increases. Treatment of **2b** with either $HBF_4 \cdot OEt_2$ or $LiBF_4$ gives rise to its isomerization to **3b**. The X-ray structure of **2a** and $T_1$(min) values of the $OsH_3$ resonances of the cations support the hydride-elongated dihydrogen nature of these compounds. The nonclassical interaction between the hydrogen atoms of the $OsH_3$ unit is more important in the normal isomer than in the abnormal. Treatment of **1** with 2.0 equiv of 1-(2-pyridylmethyl)-3-methylimidazolium bromide yields the bis(normal-NHC) complex $[OsH\{\kappa C^2,N\text{-}[1\text{-}(2\text{-pyridylmethyl})\text{-}3\text{-methylimidazol-}2\text{-ylidene}]\}_2(P^iPr_3)]Br$ (**4**), which has been also characterized by X-ray diffraction analysis.

## Introduction

N-heterocyclic carbenes (NHC) are an emergent class of versatile ancillary ligands, which are receiving increased attention due to their ability to stabilize a variety of transition-metal complexes, some of which are very active in catalytic reactions.[1] The common coordination of these types of ligands takes place through the C-2 atom to the heterocycle. However, there are also a few reports on NHC−metal complexes that show the ligand bound through a backbone C-4 or C-5 carbon atom (Chart 1).[2]

The free normal and abnormal NHC species are tautomers. Theoretical calculations have predicted that the first of them is 20.0 kcal $mol^{-1}$ more stable than the second one.[3] This is consistent with the scarce number of reported complexes containing the abnormal tautomers. However, it should be taken into account that in both biological[4] and catalytic[5] processes the energetically less stable tautomer is often an active intermediate that dictates the mechanism and the formed products. Thus, it is of great interest to know the factors determining the formation of the less favored tautomers and the influence of their coordination on the behavior of the other coligands of the complexes.

The abnormal coordination is mainly determined by the steric requirement of the substituents at the N atoms. By varying their size, it is possible to control whether abnormal binding will occur or not.[2f] For reactions of the pentahydride $IrH_5(PPh_3)_2$ with 1-(2-pyridylmethyl)-3-methylimidazolium salts,[6] it has been observed that the coordination mode of the NHC ligand in the

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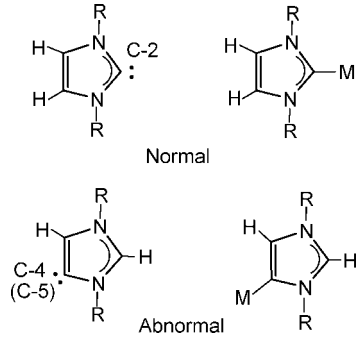
**Chart 1**




products also depends upon the counterion of the used salt. This surprising and interesting fact certainly needs additional studies with other systems where abnormal binding also occurs to establish how often it takes place.

The complex $OsH_6(P^iPr_3)_2$ is a $d^2$ polyhydride which is obtained in high yield from the known compound $OsH_2Cl_2(P^iPr_3)_2$,[7] via the trihydride tetrahydrideborate intermediate $OsH_3(\eta^2\text{-}H_2BH_2)(P^iPr_3)_2$.[8] This hexahydride reacts with Lewis bases to afford $d^4$ polyhydride derivatives, where the hydride ligands undergo thermally activated site exchange processes and show quantum exchange coupling,[9] and activates C−H bonds of amines,[10] ketones,[11] and aldehydes[12] to give species reminiscent of the intermediates proposed for Murai's reactions.[13] In spite of that, Os−NHC compounds are extremely rare,[14] in particular those containing abnormal tautomers, and we have now studied the reactions of the hexahydride $OsH_6(P^iPr_3)_2$ with 1-(2-pyridylmethyl)-3-methylimidazolium salts.

In this paper, we report the following: (i) the formation and X-ray structure of an osmium complex containing an NHC ligand with abnormal coordination, (ii) the influence of the counterion of the used salt on the coordination mode of the NHC ligand in the reaction products, and (iii) the preparation and X-ray structure of a novel bis(normal NHC)Os compound.

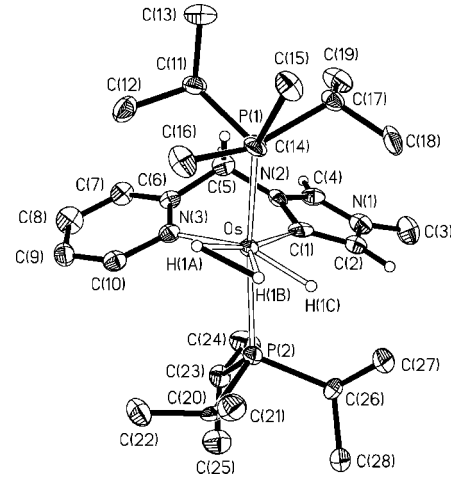
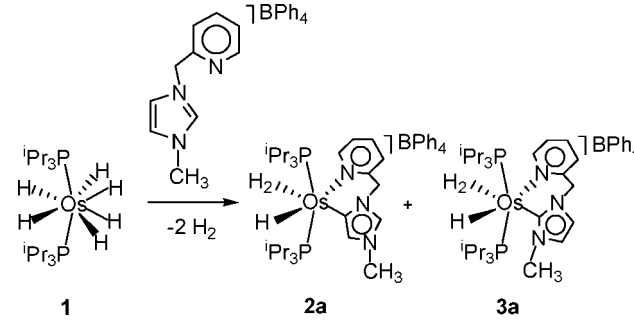



**Figure 1.** Molecular structure of the cation of **2a**. Selected bond lengths (Å) and angles (deg): Os−P(1) = 2.3605(14), Os−P(2) = 2.3683(14), Os−N(3) = 2.213(4), Os−C(1) = 2.123(6), H(1A)−H(1B) = 1.44(5); P(1)−Os−P(2) = 164.39(5), P(1)−Os−N(3) = 99.70(11), P(2)−Os−N(3) = 93.44(11), P(1)−Os−C(1) = 98.58(14), P(2)−Os−C(1) = 90.78(14), N(3)−Os−C(1) = 85.40(18).

## Results and Discussion

**1. Preparation and Characterization of an Abnormal Os−NHC Complex.** Treatment under reflux of tetrahydrofuran solutions of $OsH_6(P^iPr_3)_2$ (**1**) with 1.1 equiv of 1-(2-pyridylmethyl)-3-methylimidazolium tetraphenylborate, over 6 h, produces the release of 2.0 equiv of molecular hydrogen and the formation of an 84:16 mixture of the abnormal- and normal-NHC complexes **2a** and **3a**, according to eq 1.




(1)

The major product, the abnormal complex **2a**, was separated from its normal isomer **3a** as yellow crystals suitable for an X-ray diffraction analysis, by crystallization in dichloromethane–diethyl ether. Figure 1 shows a view of the cation of the salt. The structure proves the abnormal coordination of the imidazolium ring and suggests that this complex is a hydride-elongated dihydrogen species.[15]

The geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the phosphine ligands occupying axial positions (P(1)−Os−P(2) = 164.39(5)°). The metal coordination sphere is completed by the pyridinic nitrogen atom N(3) and the abnormal carbon atom C(1) of the chelate group and the hydrogen atoms H(1A), H(1B), and H(1C) of

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the hydride-elongated dihydrogen unit. The chelate ligand acts with a C(1)−Os−N(3) bite angle of 85.40(18)° and forms a six-membered ring with the metal center. As a result of the boat conformation of the ring, the phosphines are inequivalent. Thus, at 143 K, the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_2F$ shows an AB spin system centered at 22.1 ppm and defined by $J_{AB} = 240$ Hz and $\Delta\nu = 860$ Hz. At temperatures higher than 143 K, the interconversion of the conformers produces the equilibration of the phosphine ligands. Thus, at 293 K in $CD_2Cl_2$, the spectrum contains a singlet at 23.6 ppm.

The Os−C(1) bond length of 2.123(6) Å is between 0.01 and 0.05 Å longer than the Os−NHC distances found in the normal 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) complexes $[(\eta^6\text{-}p\text{-cymene})OsCl(IPr)]^+$ (2.078(2) Å), $[(\eta^6\text{-}p\text{-cymene})OsCl(=CHPh)(IPr))]^+$ (2.090(3) Å),[14d] $[OsCl(=CHPh)(CH_3CN)_4(IPr)]^+$ (2.069(6) Å), $[OsHCl(\equiv CPh)(IPr)(P^iPr_3)]^+$ (2.108(2) Å),[14g] and $[OsCl\{\kappa^3C,N,O\text{-}[=CHC(O)pyC(CH_3)O]\}(NCCH_3)(IPr)]^+$ (2.074(5) Å),[14h] and about 0.12 Å longer than the separation between the metal and the NH tautomer of 8-methylquinoline in the complex $OsCl_2(\eta^2\text{-}H_2)\{\kappa\text{-}C\text{-}(HNC_8H_6Me)\}(P^iPr_3)_2$ (2.005(6) Å),[16] where the joint with the metal also implies a carbon atom in an α-position with regard to only one nitrogen atom. In agreement with the abnormal nature of C(1), its resonance in the $^{13}C\{^1H\}$ NMR spectrum in $CD_2Cl_2$ at room temperature appears as a triplet at 153.8 ppm, with a C−P coupling constant of 1.2 Hz. Singlets at 133.5 and 127.9 ppm were assigned to the carbon atoms C(4) and C(2), respectively, on the basis of the HSQC spectrum. In the $^1H$ NMR spectrum the resonance of the normal C(4)−H proton appears at 5.95 ppm, in accordance with the chemical shift found in the free salt ($\delta$ 5.37), whereas the abnormal C(2)−H resonance is observed at 6.22 ppm.

The separation between the hydrogen atoms H(1A) and H(1B), which are disposed transoid to C(1), of 1.44(5) Å lies within the range of distances found in the so-called elongated dihydrogen complexes,[15] and it is about 0.14 Å shorter than that between H(1B) and H(1C) (1.58(5) Å). The separation between H(1A) and H(1C) is 2.65(4) Å. Although the three hydrogen atoms are inequivalent, at room temperature, they give rise to only one signal centered at −10.90 ppm in the high-field region of the $^1H$ NMR spectrum. For this resonance, a $T_1$(min) value of 68 ms was obtained at 263 K in the 300 MHz scale.

The total relaxation rate for a H($n$) hydride ligand ($R(n) = 1/T_1(\text{min})_{H(n)}$) is the addition of the relaxation rate due to the hydride dipole–dipole interactions (at 300 MHz $R_{H-H} = 129.18/r_{HH}^6$) and that due to all other of the relaxation contributors ($R^*$).[17] Thus, for these types of osmium compounds, one can obtain values of $T_1$(min) converted to the 300 MHz scale for each hydride by using eqs 2−4, when one knows the separations between the hydrides ($r_{HH}$), since $R^*$ can be estimated to be 2.5 $s^{-1}$, which is the average value of those found in the osmium trihydride compounds $[OsH_3(diolefin)(P^iPr_3)_2]BF_4$.[9b]

$$R_{H(1B)} = R^* + R_{H(1B)-H(1A)} + R_{H(1B)-H(1C)} \quad (2)$$

$$R_{H(1B)} = R^* + R_{H(1B)-H(1A)} + R_{H(1B)-H(1C)} \quad (3)$$

$$R_{H(1C)} = R^* + R_{H(1B)-H(1C)} + R_{H(1A)-H(1C)} \quad (4)$$

For exchange rates higher than 100 $s^{-1}$, as in this case at 263 K (vide infra), the relaxation rate is the weighted average of the relaxation rate of each hydride (eq 5).[18]

$$R = (R_{H(1B)} + R_{H(1A)} + R_{H(1C)})/3 \quad (5)$$

Using the H−H separations obtained from the X-ray diffraction study, an $R$ value of 16.6 $s^{-1}$ is calculated by means of eqs 2−5. This value leads to a $T_1$(min) value of 60 ms, which is in very good agreement with that determined by $^1H$ NMR spectroscopy.

The presence of only one resonance for the $OsH_3$ unit in the $^1H$ NMR spectrum in $CD_2Cl_2$ at room temperature is consistent with the operation of a thermally activated site exchange process between the hydride and the elongated dihydrogen, which proceeds at a rate sufficient to lead to the single signal. Lowering the sample temperature produces broadening of the resonance. At about 248 K decoalescence occurs, and between 243 and 213 K two signals are observed at −9.25 and −14.61 ppm in a 2:1 intensity ratio. Line-shape analyses of the $^1H\{^{31}P\}$ NMR spectra in the high-field region between 213 and 283 K allow the calculation of the rate constants for the hydride-elongated dihydrogen exchange at these temperatures. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\ddagger} = 11.9 \pm 0.4$ kcal $mol^{-1}$ and $\Delta S^{\ddagger} = 3.8 \pm 1$ eu. At 203 K in both $CD_2Cl_2$ and $CDCl_2F$, the decoalescence of the elongated dihydrogen resonance takes place. Thus, at 163 K, the spectrum in $CDCl_2F$ shows resonances at −8.2 (H(1A)), −10.2 (H(1B)), and −14.6 (H(1C)) ppm (Figure 2). Line-shape analyses of the spectra in $CDCl_2F$ between 168 and 253 K allow the calculation of the rate constants for the exchange between the hydrogen atoms of the elongated dihydrogen ligand at these temperatures. In this case, the activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\ddagger} = 7.6 \pm 0.3$ kcal $mol^{-1}$ and $\Delta S^{\ddagger} = -5 \pm 1$ eu. The value of the activation enthalpy lies in the range previously reported for other blocked rotation processes in elongated dihydrogen ligands.[10a,15,19]

**2. Influence of the Anion of the Starting Salt: Tetraphenylborate versus Tetrafluoroborate.** Figure 3 shows the composition in metal compounds as a function of the time of the reaction mixture resulting from the treatment of **1** with 1.0 equiv of 1-(2-pyridylmethyl)-3-methylimidazolium tetraphenylborate, in tetrahydrofuran under reflux. The results clearly show that under the reaction conditions the formation of the salt **2a** is favored from a kinetic point of view and that, once **2a** is formed, its conversion into **3a** does not take place in a spontaneous manner.

Treatment of dichloromethane solutions of the isomeric mixture of **2a** and **3a** with 2.0 equiv of $HBF_4 \cdot OEt_2$ produces the quantitative decomposition of the tetraphenylborate anion,

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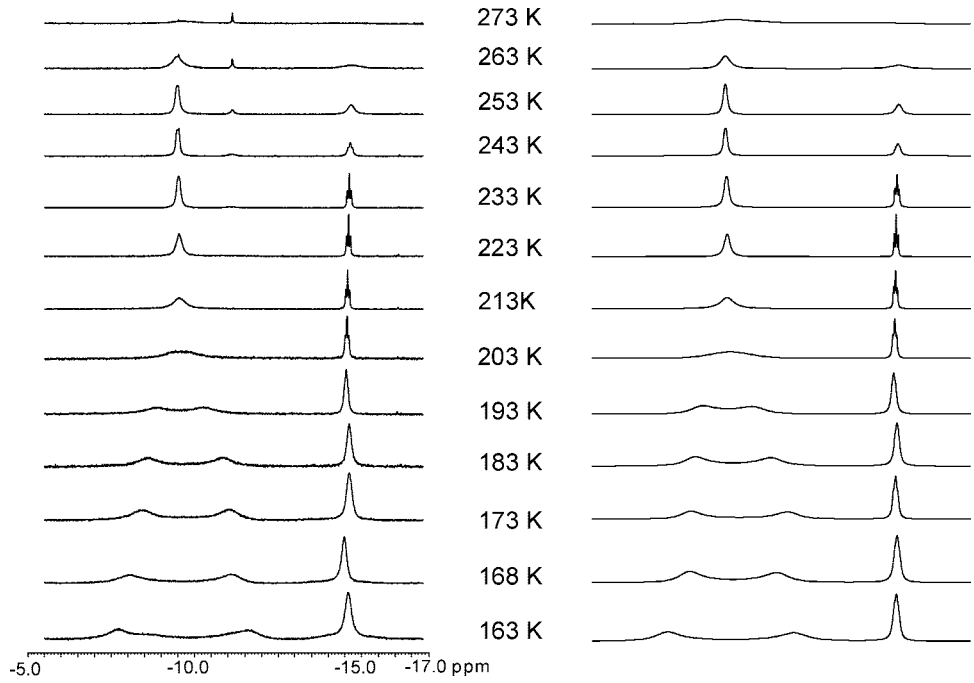



**Figure 2.** Variable-temperature $^{1}H\{^{31}P\}$ NMR spectra (400 MHz, $CDCl_2F$) in the high-field region of $[OsH(\eta^2\text{-}H_2)\{\kappa C^5,N\text{-}[1\text{-}(2\text{-pyridylmethyl})\text{-}3\text{-methylimidazol-5-ylidene}]\}(P^iPr_3)_2]BPh_4$ (**2a**): experimental (left); simulated (right).

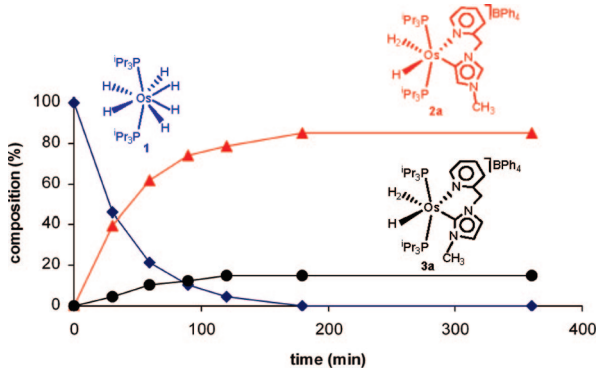
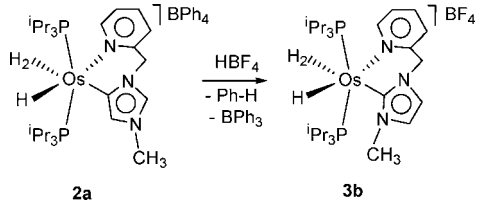



**Figure 3.** Time vs composition of the reaction mixture of **1** with 1-(2-pyridylmethyl)-3-methylimidazolium tetraphenylborate.

into benzene and triphenylborane,[20] and the isomerization of the abnormal cation to the normal one (eq 6), which is isolated as the tetrafluoroborate salt **3b**. Treatment of the latter with sodium tetraphenylborate affords **3a** as a pure yellow solid. In tetrahydrofuran under reflux, complex **3a** is stable and does not isomerize into **2a** after 6 h.




(6)

The coordination of the normal carbon atom of the five-membered ring is supported by the $^{13}C\{^{1}H\}$ NMR spectrum in $CD_2Cl_2$ at room temperature, which contains the OsC resonance at 182.0 ppm, as a triplet with a C−P coupling constant of 6.8 ppm. The $^{31}P\{^{1}H\}$ NMR spectrum shows a behavior similar to that of **2a**. At 293 K a singlet at 19.9 ppm is observed. Lowering the sample temperature produces a broadening of the resonance. At 163 K in $CDCl_2F$ the decoalescence takes place, and at 143 K the spectrum contains two broad signals corresponding to an AB spin system. In the $^{1}H$ NMR spectrum in $CD_2Cl_2$ at room temperature, the most noticeable resonance is a triplet at −10.78 ppm, with an H−P coupling constant of 13.3 Hz, corresponding to the $OsH_3$ unit. Lowering the sample temperature produces the broadening of the signal. However, decoalescence does not occur down to 143 K in $CDCl_2F$.

A variable-temperature 300 MHz study in the temperature range where the signal shape allows us to obtain accurate values, 273–223 K, gives a $T_1$ value of 89 ms at 273 K, which decreases to 55 ms at 223 K. Although this value does not correspond to the $T_1$(min) value of the resonance, it is lower than that of **2a**, which indicates that the nonclassical interaction is more important in the $OsH_3$ unit of the normal cation than in the abnormal one. In this context, it should be noted that a normal carbon atom is stabilized by two mesomeric nitrogens, while an abnormal atom is stabilized by only one. Thus, an NHC ligand should be a better $\sigma$-donor in the abnormal coordination than in the normal coordination.[21] Since the nonclassical interaction is disfavored by back-donation from filled metal orbitals of predominant d character to the $\sigma^*$ orbital of the coordinated hydrogen molecule, it appears to be clear why the abnormal coordination disfavors the nonclassical interaction with regard to the normal coordination.

Figure 4 shows the composition in metal compounds as a function of the time of the reaction mixture resulting from the treatment of **1** with 1.0 equiv of 1-(2-pyridylmethyl)-3-methylimidazolium tetrafluoroborate, in tetrahydrofuran under reflux. As is the case for the starting tetraphenylborate salt, the formation of the abnormal $BF_4$ salt **2b** is kinetically favored with regard to the normal $BF_4$ salt **3b**. However, in this case

(20) Cooper, J. N.; Powell, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 1590.

(21) Owen, J. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 8247.

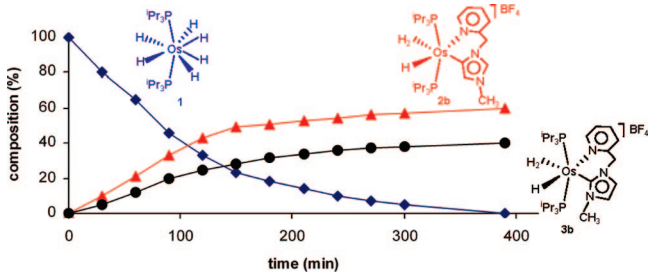



**Figure 4.** Time vs composition of the reaction mixture of **1** with 1-(2-pyridylmethyl)-3-methylimidazolium tetrafluoroborate.

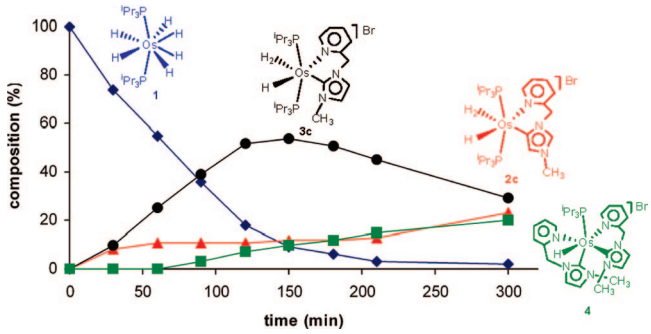



**Figure 5.** Time vs composition of the reaction mixture of **1** with 1-(2-pyridylmethyl)-3-methylimidazolium bromide.

the difference between the formation rates is significantly smaller than in the tetraphenylborate case. These results are consistent with previous observation of Crabtree's group for iridium,[6] which related the isomers ratio to the ion pairing between the normal CH proton of the starting salt and the counterions, as shown by the sensitivity of the proton NMR shift of the normal CH resonance to the nature of the anion ($\delta_{BPh4}$, 5.37; $\delta_{BF4}$, 8.98). In the starting salt the normal CH bond of the imidazolium group is weakened by a hydrogen bond with the anion. This facilitates its addition to the metal center and, therefore, the formation of the normal isomer. Thus, stronger ion pairings correspond to smaller abnormal to normal rate ratios.

The behavior of the mixture of **2b** and **3b** is similar to that of the mixture of **2a** and **3a** when it is treated with $HBF_4 \cdot OEt_2$. In agreement with the isomerization shown in eq 6, the addition of 1.0 equiv of this acid to a dichloromethane solution of the mixture of **2b** and **3b** gives rise to the quantitative transformation of **2b** to **3b**. Although this appears to support an isomerization by acidic catalysis, it must be pointed out that the same result is reached when the tetrahydrofuran solutions of the mixture are treated with lithium tetrafluoroborate.

The isomerization of **2b** to **3b** promoted by lithium tetrafluoroborate appears to rule out an acidic catalysis and opens the door to an interesting question: in solution, do the thermodynamic stabilities of the complex salts and/or the activation energy for the isomerization depend upon the nature of the anions and their concentrations? The transformation of **2b** into **3b** promoted by both $HBF_4 \cdot OEt_2$ in dichloromethane and lithium tetrafluoroborate in tetrahydrofuran certainly suggests a favorable effect of the $BF_4^-$ anion on the normal cation.

**5. Reaction with the Bromide Salt: Formation of a Bis(normal NHC) Complex.** The reaction of **1** with 1.0 equiv of 1-(2-pyridylmethyl)-3-methylimidazolium bromide is much more complex than those with the starting $BPh_4$ and $BF_4$ salts (Figure 5). In agreement with an ion pairing between the normal CH proton and the anion stronger in the starting Br salt than in those previously studied ($\delta_{Br}$, 10.49), in tetrahydrofuran under reflux, the formation of the normal Br salt **3c** is kinetically favored with regard to the formation of the abnormal Br salt **2c**. During the reaction, traces of the previously reported complexes $OsH_2Br_2(P^iPr_3)_2$[22] and $OsH_3Br(P^iPr_3)_2$[23] are also detected. Under the reaction conditions, the normal salt **3c** is unstable and evolves to the abnormal salt **2c** and the bis(normal NHC) derivative **4**. The formation of **2c** from **3c** appears to point out the idea of that both the relative stability of the normal and abnormal salts and activation energy for the isomerization depend upon the nature of the anion.

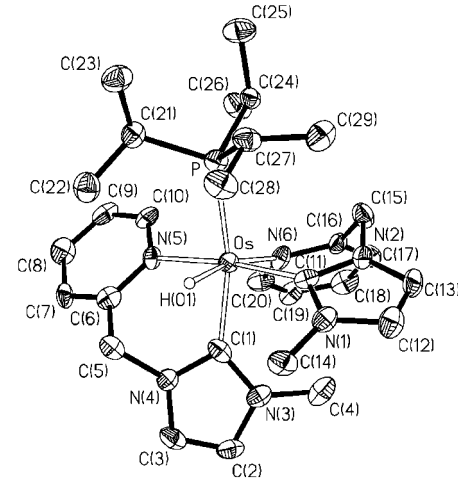
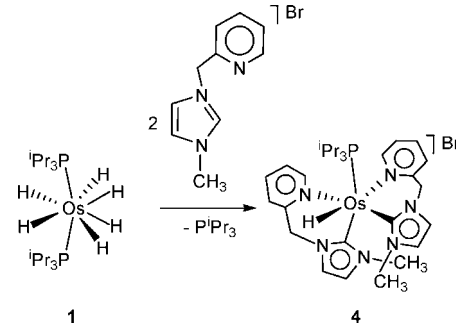



**Figure 6.** Molecular structure of the cation of **4**. Selected bond lengths (Å) and angles (deg): Os−P = 2.395(2), Os−N(5) = 2.177(6), Os−N(6) = 2.196(7), Os−C(1) = 2.035(8), Os−C(11) = 1.993(9); P−Os−N(5) = 93.09(19), P−Os−N(6) = 107.71(19), P−Os−C(1) = 163.6(2), P−Os−C(11) = 95.7(2), N(5)−Os−N(6) = 89.4(2), N(5)−Os−C(1) = 82.8(3), N(5)−Os−C(11) = 171.0(3), N(6)−Os−C(1) = 88.2(3), N(6)−Os−C(11) = 86.1(3), C(1)−Os−C(11) = 89.3(3).

The bis(normal NHC) complex **4** can be also selectively obtained as a pure red solid in 66% yield by treatment of **1** with 2.0 equiv of 1-(2-pyridylmethyl)-3-methylimidazolium bromide, in tetrahydrofuran under reflux, according to eq 7.




(7)

Figure 6 shows a view of the cation of **4**. The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with the phosphorus atom of the phosphine and the normal C(1) carbon atom of one of the chelating ligands occupying mutually *trans* positions (C(1)−Os−P = 163.6(2)°).

(22) (a) $\delta_{Os-H}$, −14.86 (t, $J_{P-H}$ = 33.3 Hz); $\delta_{PiPr3}$, 45.9. (b) Gusev, D. G.; Kuhlman, R.; Rambo, J. R.; Berke, H.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 281.

(23) (a) $\delta_{Os-H}$, −19.80 (br); $\delta_{PiPr3}$, 23.2 (223 K). (b) Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.

The nitrogen atom N(5) of this chelated group is disposed trans to the normal carbon atom C(11) of the other chelated ligand (N(5)−Os−C(11) = 171.0(3)°). The bite angles C(1)−Os−N(5) and C(11)−Os−N(6) are 82.8(3) and 86.1(3)°, respectively. In spite of the asymmetric coordination of the NHC ligands, the Os−C bond lengths of 1.993(9) (Os−C(11)) and 2.035(8) Å (Os−C(1)) are statistically identical and about 0.1 Å shorter than that of **2a**.

The asymmetry of the coordinated carbon atoms is revealed by the $^{13}C\{^1H\}$ NMR spectrum in $CD_2Cl_2$ at room temperature. The resonance due to C(1) appears at 177.4 ppm as a doublet with a C−P coupling constant of 78 Hz, while that corresponding to C(11) is observed at 172.5 ppm as a singlet. In the $^1H$ NMR spectrum, the most noticeable feature is the hydride resonance, which appears at –16.17 ppm as a doublet with a H−P coupling constant of 20.8 Hz. A singlet at 17.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also characteristic of **4**.

**Concluding Remarks.** As a new chapter of our work on the Os−C bond chemistry,[24] in this paper we describe the preparation and X-ray structure of an osmium complex containing an NHC ligand with abnormal coordination. This novel $OsH_3$ compound and its normal isomer are obtained from the reactions of the hexahydride $OsH_6(P^iPr_3)_2$ with 1-(2-pyridylmethyl)-3-methylimidazolium salts. In agreement with Crabtree's group we note that, in fact, the anion of the starting salt has a marked influence on the obtained isomer ratio.

As has been previously proposed, the anion of the starting salt interacts with the normal CH proton.[6] As a consequence of the resulting hydrogen bond, the normal CH bond is weakened. This facilitates its addition to the metal center, and therefore the formation rate of the normal isomer increases as the coordination power of the anion of the starting salt also increases ($Br^-$ > $BF_4^-$ > $BPh_4^-$).

The relative stability of the abnormal and normal salts is difficult to rationalize. It appears that $BF_4^-$ favors the normal coordination, while with $BPh_4^-$ both salts can be prepared as pure solids and none of them isomerizes in solution into the other. The anion $Br^-$ favors the decomposition of the mono(normal NHC) salt to afford a bis(normal NHC) derivative of osmium.

In conclusion, these results show that both the rates of the organometallic reactions and the stability of the formed products can have a marked dependence upon the nature of the anions of the used salts.

## Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Solvents were obtained oxygen- and water-free from an MBraun solvent purification apparatus. Infrared spectra were recorded on a Perkin-Elmer Spectrum One spectrometer as solids (Nujol mull). $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini 2000, a Bruker AXR 300, or a Bruker Avance 400 instrument. Chemical shifts are referenced to residual solvent peaks ($^1H$ and $^{13}C\{^1H\}$), external $H_3PO_4$ ($^{31}P\{^1H\}$), Coupling constants $J$ and $N$ ($N = J_{P-H} + J_{P-H}$ for $^1H$; $N = J_{P'-C} + J_{P'-C}$ for $^{13}C\{^1H\}$), are given in hertz. C, H, and N analyses were measured on a Perkin-Elmer 2400 CHNS/O analyzer. The complex $OsH_6(P^iPr_3)_2$ (**1**),[7] 1-(2-pyridylmethyl)-3-methylimidazolium bromide,[25] 1-(2-pyridylmethyl)-3-methylimidazolium tetrafluoroborate,[6c] and $CDCl_2F$[26] were prepared as previously described.

**Preparation of 1-(2-Pyridylmethyl)-3-methylimidazolium Tetraphenylborate. Anion Exchange.** A solution of 1-(2-pyridylmethyl)-3-methylimidazolium bromide (200 mg, 0.79 mmol) in acetone/MeOH (15 mL/5 mL) was treated with the stoichiometric amount of $NaBPh_4$ (269.3 mg, 0.79 mmol), and the resulting solution was stirred for 2 h at room temperature. After this time the solvent was removed and $CH_2Cl_2$ added, resulting in a suspension. The suspension was filtered through Celite and the solution concentrated to ca. 0.5 mL and diethyl ether added to afford a white solid that was washed with further portions of diethyl ether (3 × 5 mL) and dried in vacuo. Yield: 330 mg (80%). $^1H$ NMR (400 MHz, $CD_2Cl_2$, 293 K): $\delta$ 8.50 (d, $J_{H-H}$ = 5.0, 1H, $H_{py}$), 7.71 (t, $J_{H-H}$ = 7.6, 1H, $H_{py}$), 7.46 (m, 8H, *o*-$BPh_4$), 7.29 (dd, $J_{H-H}$ = 7.6, $J_{H-H}$ = 5.0, 1H, $H_{py}$), 7.15 (d, $J_{H-H}$ = 7.6, 1H, $H_{py}$), 6.97 (t, $J_{H-H}$ = 7.2, 8H, *m*-$BPh_4$), 6.84 (d, $J_{H-H}$ = 1.6, 1H, imidazole), 6.80 (t, $J_{H-H}$ = 7.2, 4H, *p*-$BPh_4$), 6.54 (d, $J_{H-H}$ = 1.6, 1H, imidazole), 5.37 (s, 1H, NC*H*N), 4.69 (s, 2H, $-CH_2-$), 3.15 (s, 3H, $-CH_3$). $^{13}C\{^1H\}$ NMR (100.56 MHz, $CD_2Cl_2$, 293 K, plus apt): $\delta$ 164.5 (q, $J_{C-B}$ = 65.6, $C_{ipso}$ $BPh_4$), 152.2 (s, $C_{py}$), 150.3 (s, $C_{py}$), 137.8 (s, $C_{py}$), 136.2 (s, N*C*HN), 136.1 (*o*-$BPh_4$), 126.4 (q, $J_{C-B}$ = 3, *m*-$BPh_4$), 124.3 (s, $C_{py}$), 122.93 (s, CH imidazole), 122.7 (s, CH imidazole), 122.6 (s, $C_{py}$), 122.5 (s, *p*-$BPh_4$), 54.1 (s, $-CH_2-$), 36.4 (s, $-CH_3$).

**Reaction of 1 with 1-(2-Pyridylmethyl)-3-methylimidazolium Tetraphenylborate.** 1-(2-Pyridylmethyl)-3-methylimidazolium tetraphenylborate (120.3 mg, 0.231mmol) was added to a solution of **1** (100 mg, 0.193 mmol) in THF (15 mL) and refluxed for 6 h. The progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which showed quantitative conversion to a 84:16 mixture of isomers **2a** and **3a** (vide infra). After this time, the solution was filtered through Celite and was taken to dryness. Subsequent addition of diethyl ether caused the precipitation of a yellow solid, which was washed with diethyl ether and dried in vacuo. Yield: 146 mg (63%). The $^1H$ and $^{31}P\{^1H\}$ NMR spectra of this solid in $CD_2Cl_2$ showed that the ratio 84:16 is maintained. Anal. Calcd for $C_{52}H_{76}BN_3OsP_2$: C, 62.07; H, 7.61; N, 4.18. Found: C, 62.19; H, 7.70; N, 4.14. Complex **2a** could be isolated in pure form by slow diffusion of diethyl ether into a concentrated solution of the isomeric mixture in dichloromethane at –30 °C.

Spectroscopic data of **2a**: IR ($cm^{-1}$): $\nu$(OsH) 2022 (w), $\nu$(N═C) 1571 (w). $^1H$ NMR (400 MHz, $CD_2Cl_2$, 293 K): $\delta$ 9.61 (d, $J_{H-H}$ = 7.0, 1H, $H_{py}$), 7.67 (t, $J_{H-H}$ = 7.0, 1H, $H_{py}$), 7.48 (br, 8H, *o*-$BPh_4$), 7.10 (d, $J_{H-H}$ = 7.0, 1H, $H_{py}$), 7.00 (t, $J_{H-H}$ = 7.2, 8H, *m*-$BPh_4$), 6.93 (t, $J_{H-H}$ = 7.0, 1H, $H_{py}$) 6.79 (t, $J_{H-H}$ = 7.2, 4H, *p*-$BPh_4$), 6.22 (s, 1H, $H_{im}$), 5.95 (s, 1H, $H_{im}$), 4.23 (s, 2H, $-CH_2-$), 3.32 (s, 3H, $-CH_3$), 1.87 (m, 6H, PC*H*$(CH_3)_2$), 0.93 (dvt, $N$ = 12.4, $J_{H-H}$ = 6.8, 18H, PCH(C*H*$_3)_2$), 0.87 (dvt, $N$ = 12.8, $J_{H-H}$ = 6.8, 18H, PCH(C*H*$_3)_2$), −10.91 (br, 3H, OsH). $^1H$ NMR (400 MHz, $CDFCl_2$, 168 K, hydride region): $\delta$ −8.19 (br, 1H, OsH), –10.24 (br, 1H, OsH), −14.55 (br, 1H, OsH). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CD_2Cl_2$, 293 K): $\delta$ 23.6 (s). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDFCl_2$, 143 K): $\delta$ 22.1 (AB spin system, $\Delta\nu$ = 860 Hz, $J_{A-B}$ = 240 Hz). $^{13}C\{^1H\}$ NMR (100.56 MHz, $CD_2Cl_2$, 293 K, plus apt): $\delta$ 164.5 (q, $J_{C-B}$ = 49.2, $C_{ipso}$ $BPh_4$), 164.5 (s, $C_{py}$), 153.8 (t, $J_{C-P}$ = 1.2, $C_{carbene}$), 137.5 (s, $C_{py}$), 136.2 (q, $J_{C-B}$ = 1.3, *o*-$BPh_4$) 133.5 (s, $C_{im}$), 127.9 (s, $C_{im}$), 126.7 (s, $C_{py}$), 126.3 (q, $J_{C-B}$ = 2.8, *m*-$BPh_4$), 124.7 (s, $C_{py}$), 122.3 (s, *p*-$BPh_4$), 55.9 (s, $-CH_2-$), 34.8 (s, $-CH_3$), 26.9 (vt, $N$ = 24.3, P*C*H$(CH_3)_2$), 20.1, 19.6 (both s, PCH(*C*H$_3)_2$). $T_1$(min) (ms, OsH, 300 MHz, $CD_2Cl_2$, 263 K): 68 ± 1 (−10.90 ppm).

Spectroscopic data of **3a**: IR ($cm^{-1}$): $\nu$(OsH) 2045 (w), $\nu$(N═C) 1580 (w). $^1H$ NMR (400 MHz, $CD_2Cl_2$, 293 K): $\delta$ 9.57 (d, $J_{H-H}$ =

(24) (a) Esteruelas, M. A.; López, A. M. *Organometallics* **2005**, *24*, 3584. (b) Esteruelas, M. A.; López, A. M.; Oliván, M. *Coord. Chem. Rev.* **2007**, *251*, 795.

(25) McGuiness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741.
(26) Siegel, J. S.; Anet, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629.

7.3, 1H, $H_{py}$), 7.70 (t, $J_{H-H}$ = 7.3, 1H, $H_{py}$), 7.37 (m, 8H, *o*-$BPh_4$), 7.14 (d, $J_{H-H}$ = 7.3, 1H, $H_{py}$), 7.06 (t, $J_{H-H}$ = 7.2, 5H, *m*-$BPh_4$, and $H_{im}$), 7.02 (t, $J_{H-H}$ = 7.2, 8H, *m*-$BPh_4$), 6.94 (d, $J_{H-H}$ = 2.0, 1H, $H_{im}$), 4.82 (s, 2H, $-CH_2-$), 3.76 (s, 3H, $-CH_3$), 1.99 (m, 6H, PC*H*$(CH_3)_2$), 0.94 (dvt, *N* = 12.8, $J_{H-H}$ = 7.2, 18H, PCH(C*H*$_3)_2$), 0.86 (dvt, *N* = 12.8, $J_{H-H}$ = 6.8, 18H, PCH(C*H*$_3)_2$), −10.78 (t, $J_{H-P}$ = 13.2, 3H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CD_2Cl_2$, 293 K): $\delta$ 19.9 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $CD_2Cl_2$, 293 K, plus apt): $\delta$ 182.0 (t, $J_{C-P}$ = 6.9, $C_{carbene}$), 164.3 (q, $J_{C-B}$ = 49.2, $C_{ipso}$ $BPh_4$), 164.3 (s, $C_{py}$), 154.1 (t, $C_{py}$), 138.2 (s, $C_{py}$),136.2 (br s, *o*-$BPh_4$) 126.7 (s, $C_{py}$), 126.1 (q, $J_{C-B}$ = 2.7, *m*-$BPh_4$), 123.1 (s, $C_{im}$), 123.0 (s, $C_{im}$), 56.7 (s, $-CH_2-$), 39.4(s, -$CH_3$), 28.6 (vt, *N* = 24.9, PC*H*$(CH_3)_2$), 19.5, 19.4, (both s, PCH(C*H*$_3)_2$). $T_1$ (ms, OsH, 300 MHz, $CD_2Cl_2$, 223 K): 55 ± 1 (−10.75 ppm).

**Treatment of the Mixture of 2a and 3a with $HBF_4$.** Two equivalents of $HBF_4 \cdot OEt_2$ (55 $\mu$L, 0.397 mmol) was added to a solution of a mixture of **2a** and **3a** (200 mg, 0.198 mmol) in $CH_2Cl_2$. After the solution was stirred for 30 min at room temperature, the color had changed from yellow to brown. The resulting solution was filtered through Celite and was taken to dryness. Addition of diethyl ether caused the precipitation of a yellow solid, which was washed with diethyl ether and dried in vacuo. Yield: 125 mg (81%). The $^1H$ and $^{31}P\{^1H\}$ NMR spectra of this solid in $CD_2Cl_2$ showed only peaks assigned to **3b**.

**Reaction of 1 with 1-(2-Pyridylmethyl)-3-methylimidazolium Tetrafluoroborate.** 1-(2-Pyridylmethyl)-3-methylimidazolium tetrafluoroborate (50.2 mg, 0.193 mmol) was added to a solution of **1** (100 mg, 0.193 mmol) in THF (15 mL) and refluxed for 5 h. The solution changed from pale to deep yellow. After the mixture was cooled to room temperature, the solvent was evaporated. Subsequent addition of diethyl ether caused the precipitation of a beige solid, which was washed with diethyl ether and dried in vacuo. Yield: 95 mg (42%). The $^1H$ and $^{31}P\{^1H\}$ NMR spectra of this solid in $CD_2Cl_2$ showed a 56:44 mixture of complexes **2b** and **3b**. Anal. Calcd for $C_{28}H_{56}BF_4N_3OsP_2$: C, 43.46; H, 7.29; N, 5.43. Found: C, 43.31; H, 7.43; N, 5.03.

Spectroscopic data of **2b**: $^1H$ NMR (500 MHz, $CD_2Cl_2$, 293 K): $\delta$ 9.67 (d, $J_{H-H}$ = 7.5, 1H, $H_{py}$), 8.74 (s, 1H, $H_{im}$), 7.74 (t, $J_{H-H}$ = 7.5, 1H, $H_{py}$), 7.62 (d, $J_{H-H}$ = 7.5, 1H, $H_{py}$), 6.97 (t, $J_{H-H}$ = 7.5, 1H, $H_{py}$), 6.47 (s, 1H, $H_{im}$), 5.22 (s, 2H, $-CH_2-$), 3.75 (s, 3H, $-CH_3$), 1.94 (m, 6H, PC*H*$(CH_3)_2$), 0.98 (dvt, *N* = 12.5, $J_{H-H}$ = 6.5, 18H, PCH(C*H*$_3)_2$), 0.92 (dvt, *N* = 13, $J_{H-H}$ = 6.0, 18H, PCH(C*H*$_3)_2$), −10.60 (very br, 3H, OsH). $^{31}P\{^1H\}$ NMR (202.34 MHz, $CD_2Cl_2$, 293 K): $\delta$ 23.6 (s).

Spectroscopic data of **3b**: $^1H$ NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 9.61 (d, $J_{H-H}$ = 6.5, 1H, $H_{py}$), 7.82 (t, $J_{H-H}$ = 6.5, 1H, $H_{py}$), 7.63 (d, $J_{H-H}$ = 6.5, 1H, $H_{py}$), 7.40 (d, $J_{H-H}$ = 1.8, 1H, $H_{im}$), 7.13 (d, $J_{H-H}$ = 1.8, 1H, $H_{im}$), 7.06 (t, $J_{H-H}$ = 6.5, 1H, $H_{py}$), 5.26 (s, 2H, $-CH_2-$), 3.81 (s, 3H, $-CH_3$) 2.02 (m, 6H, PC*H*$(CH_3)_2$), 0.95 (dvt, *N* = 12.6, $J_{H-H}$ = 6.9, 18H, PCH(C*H*$_3)_2$), 0.87 (dvt, *N* = 12.9, $J_{H-H}$ = 6.9, 18H, PCH(C*H*$_3)_2$), −10.78 (t, $J_{H-P}$ = 13.3, 3H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CD_2Cl_2$, 293 K): $\delta$ 19.9 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $CD_2Cl_2$, 293 K, plus apt): $\delta$ 182.0 (t, $J_{C-P}$ = 6.8, N*C*HC), 164.4 (s, $C_{py}$), 154.5 (t, $J_{C-P}$ = 1.2 $C_{py}$), 138.5 (s, $C_{py}$), 126.9 (s, $C_{py}$), 123.4 (s, $C_{im}$), 123.2 (s, $C_{im}$), 56.7 (s, $-CH_2-$), 39.5 (s, $-CH_3$), 28.7 (vt, *N* = 24.9, PC*H*$(CH_3)_2$), 19.7, 19.5 (both s, PCH(C*H*$_3)_2$).

**Treatment of the Mixture of 2b and 3b with $LiBF_4$.** One equivalent of $LiBF_4$ (12.1 mg, 0.129 mmol) was added to a solution of a mixture of **2b** and **3b** (100 mg, 0.129 mmol) in THF (10 mL). After the solution was stirred for 30 min at room temperature, the resulting solution was filtered through Celite and was taken to dryness. Addition of diethyl ether caused the precipitation of a yellow solid, which was washed with diethyl ether and dried in vacuo. Yield: 85 mg (85%). The $^1H$ and $^{31}P\{^1H\}$ NMR spectra of this solid in $CD_2Cl_2$ showed only peaks assigned to **3b**.

**Table 1. Crystal Data and Data Collection and Refinement Details for 2a and 4**

| | 2a | 4 |
|---|---|---|
| | Crystal Data | |
| formula | $C_{52}H_{76}BN_3OsP_2$ | $C_{30}H_{46}BrCl_2N_6OsP$ |
| mol wt | 1006.11 | 862.71 |
| color, habit | pale yellow, plate | red, irregular block |
| size, mm | 0.10,0.10,0.03 | 0.36, 0.06, 0.02 |
| sym, space group | triclinic, $P\bar{1}$ | triclinic, $P\bar{1}$ |
| *a*, Å | 11.4772(18) | 8.664(3) |
| *b*, Å | 13.186(2) | 11.597(4) |
| *c*, Å | 16.507(3) | 16.999(5) |
| α, deg | 84.376(3) | 89.303(5) |
| $\beta$, deg | 82.862(3) | 86.032(6) |
| $\gamma$, deg | 88.430(3) | 86.220(6) |
| *V*, Å$^3$ | 2466.5(7) | 1700.2(9) |
| *Z* | 2 | 2 |
| $D_{calcd}$, g cm$^{-3}$ | 1.355 | 1.685 |
| | Data Collection and Refinement | |
| diffractometer | Bruker Smart APEX | |
| $\lambda$(Mo Kα), Å | 0.710 73 | |
| monochromator | graphite oriented | |
| scan type | $\omega$ scans | |
| $\mu$, mm$^{-1}$ | 2.686 | 5.159 |
| $2\theta$ range, deg | 3−58 | 3−57 |
| temp, K | 100.0(2) | 105.0(1) |
| no. of data collected | 30 683 | 20 937 |
| no. of unique data | 11 759 ($R_{int}$ = 0.0846) | 8037 ($R_{int}$ = 0.0882) |
| no. of params/restraints | 568/3 | 382/0 |
| R1[a] ($F^2 > 2\sigma(F^2)$) | 0.0481 | 0.0620 |
| wR2[b] (all data) | 0.0806 | 0.1369 |
| S[c] (all data) | 0.752 | 0.995 |

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^2)^2]\}^{1/2}$. [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.

**Reaction of 1 with 1 Equiv of 1-(2-Pyridylmethyl)-3-methylimidazolium Bromide.** 1-(2-Pyridylmethyl)-3-methylimidazolium bromide (49 mg, 0.193 mmol) was added to a solution of **1** (100 mg, 0.193 mmol) in THF (15 mL) and heated at the reflux temperature. At regular intervals (30 min) a portion (1 mL) of the resulting mixture was transferred via cannula to a Schlenk flask and it was evaporated to dryness. A 0.5 mL portion of dichloromethane-$d_2$ was added and the solution transferred to an NMR tube. The progress of the reaction was periodically (30 min) monitored by $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopy.

Spectroscopic data of **2c**: $^1H$ NMR (400 MHz, $CD_2Cl_2$, 293 K): $\delta$ 9.50 (d, $J_{H-H}$ = 6, 1H, $H_{py}$), 8.46 (t, $J_{H-H}$ = 6, 1H, $H_{py}$), 8.20 (d, $J_{H-H}$ = 1.6, 1H, $H_{im}$), 7.75 (t, $J_{H-H}$ = 6, 1H, $H_{py}$), 7.62 (t, $J_{H-H}$ = 6, 1H, $H_{py}$), 7.04 (d, $J_{H-H}$ = 1.6, 1H, $H_{im}$), 5.07 (s, 2H, $-CH_2-$), 3.73 (s, 3H, $-CH_3$), 1.94 (m, 6H, PC*H*$(CH_3)_2$), 0.96 (dvt, *N* = 12.8, $J_{H-H}$ = 6.8, 18H, PCH(C*H*$_3)_2$), 0.89 (dvt, *N* = 12.8, $J_{H-H}$ = 6.4, 18H, PCH(C*H*$_3)_2$), −12.50 (br, 3H, OsH). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CD_2Cl_2$, 293 K): $\delta$ 23.6 (s).

Spectroscopic data of **3c**: $^1H$ NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 9.59 (d, $J_{H-H}$ = 6.5, 1H, $H_{py}$), 7.97 (d, $J_{H-H}$ = 6.5, 1H, $H_{py}$), 7.86 (t, $J_{H-H}$ = 6.5, 1H, $H_{py}$), 7.85 (s, 1H, $H_{im}$), 7.14 (s, 1H, $H_{im}$), 7.06 (t, $J_{H-H}$ = 6.5, 1H, $H_{py}$), 5.63 (s, 2H, $-CH_2-$), 3.82 (s, 3H, $-CH_3$) 2.03 (m, 6H, PC*H*$(CH_3)_2$), 0.96 (dvt, *N* = 12.9, $J_{H-H}$ = 6.9, 18H, PCH(C*H*$_3)_2$), 0.86 (dvt, *N* = 12.9, $J_{H-H}$ = 6.6, 18H, PCH(C*H*$_3)_2$), −10.79 (t, $J_{H-P}$ = 13.2, 3H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CD_2Cl_2$, 293 K): $\delta$ 19.9 (s).

**Reaction of *1* with 2 Equiv of 1-(2-Pyridylmethyl)-3-methylimidazolium Bromide: Formation of the Complex [OsH{$\kappa C^2$,*N*-[1-(2-pyridylmethyl)-3-methylimidazol-2-ylidene]}$_2$(P$^i$Pr$_3$)]Br (4).** 1-(2-Pyridylmethyl)-3-methylimidazolium bromide (147.6 mg, 0.581 mmol) was added to a solution of **1** (150 mg, 0.289 mmol) in THF (20 mL) and refluxed for 5 h. The solution changed from colorless to deep red. When the solution was cooled to room temperature, a red solid appeared. The solid was separated by decantation, washed repeatedly with diethyl ether, and dried in

vacuo. Yield: 148 mg (66%). Anal. Calcd for $C_{29}H_{44}BrN_6OsP$: C, 44.78; H, 5.70; N, 10.80. Found: C, 44.98; H, 5.87; N, 10.88. IR (Nujol, $cm^{-1}$): $\nu$(OsH) 2018 (w), $\nu$(N═C) 1594 (w), 1568 (w). $^1H$ NMR (400 MHz, $CD_2Cl_2$, 293 K): $\delta$ 8.93 (d, $J_{H-H} = 6.8$, 1H, $H_{py}$), 7.77 (t, $J_{H-H} = 6.8$, 1H, $H_{py}$), 7.66–7.63 (m, 2H, $H_{py}$), 7.58 (d, $J_{H-H} = 6.5$, 1H, $H_{py}$), 7.29 (d, $J_{H-H} = 6.5$, 1H, $H_{py}$), 7.26 (d, $J_{H-H} = 2$, 1H, $H_{im}$), 7.22 (d, $J_{H-H} = 2$, 1H, $H_{im}$), 7.04 (t, $J_{H-H} = 6.8$, 1H, $H_{py}$), 6.88 (d, $J_{H-H} = 2$, 1H, $H_{im}$), 6.69 (t, $J_{H-H} = 6.5$, 1H, $H_{py}$), 6.57 (d, $J_{H-H} = 2$, 1H, $H_{im}$), 5.31 (AB spin system, $\Delta\nu = 79.8$ Hz, $J_{AB} = 13.6$), 5.44 (d, $J_{H-H} = 2.4$, 2H, $-CH_2-$), 3.21 (s, 3H, $-CH_3$), 3.21 (s, 3H, $-CH_3$), 2.10 (m, 3H, PC*H*$(CH_3)_2$), 1.68 (s, 3H, $-CH_3$), 0.89 (m, 18H, PCH(C*H*$_3)_2$), $-16.17$ (d, $J_{H-P} = 20.8$, 1H, OsH). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CD_2Cl_2$, 293 K): $\delta$ 17.8 (s). $^{13}C\{^1H\}$ NMR (100.56 MHz, $CD_2Cl_2$, 293K, plus apt): $\delta$ 177.4 (d, $J_{C-P} = 78.0$, N*C*N), 172.5 (s, N*C*N), 161.7, 159.6, 157.8, 155.8, 135.7, 133.9, 125.2, 125.1, 125.0 (all s, $C_{py}$), 121.4, 120.6, 120.2, 120.1 (all s, $C_{im}$), 59.3 (s, $-CH_2-$), 58.3 (s, $-CH_2-$), 37.7 (s, $-CH_3$), 33.5 (s, $-CH_3$), 30.6 (d, $J_{C-P} = 19.0$, P*C*H$(CH_3)_2$), 20.8, 20.6 (both s, PCH(*C*H$_3)_2$).

**Structural Analysis of Complexes 2a and 4.** Crystals of **2a** suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a concentrated solution of the isomeric mixture of complexes **2a** and **3a** in dichloromethane and of pentane into a solution of **4** in dichloromethane. X-ray data for both complexes were collected on a Bruker Smart APEX CCD diffractometer equipped with a normal-focus, 2.4 kW sealed tube source (Mo radiation, $\lambda = 0.710\,73$ Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering 0.3° in $\omega$. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[27] The structures of both compounds were solved by the Patterson method. Refinement, by full-matrix least squares on $F^2$ with SHELXL97,[28] was similar for both complexes, including isotropic and subsequently anisotropic displacement parameters. The high quality and extended range of diffraction data allowed location of the hydride ligands of **2a** and **4** in the difference Fourier maps. However, for complex **2a** we observed short Os−H distances due to the well-known behavior of the X-ray experiments that usually show M−H distances shorter than those based on neutron diffraction, a radiation much more appropriate for the precise localization of lighter elements. Then a restrained geometry was used in the last cycles of refinement for these ligands. Hydrogen atoms were included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms. All the highest electronic residuals were observed in the close proximity of the Os centers 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 **2a** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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