Aromatic C−H Bond Activation of 2-Methylpyridine Promoted by an Osmium(VI) Complex: Formation of an $\eta^2(N,C)$-Pyridyl Derivative

Miguel A. Esteruelas,* Elena Forcén, Montserrat Oliván, and Enrique Oñate

Departamento de Química Inorgánica-Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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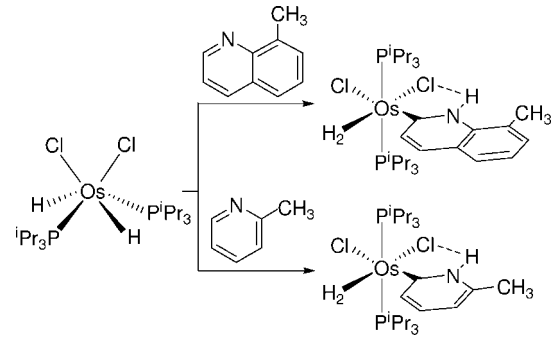
The complex $OsH_6(P^iPr_3)_2$ (**1**) activates the NC−H bond of 2-methylpyridine to afford the $\eta^2(C,N)$-pyridyl derivative $OsH_3\{\eta^2(C,N)\text{-}[NC_5H_3Me]\}(P^iPr_3)_2$ (**2**), which in dichloromethane undergoes the selective chlorination of one of the hydride ligands to give $OsH_2Cl\{\eta^2(C,N)\text{-}[NC_5H_3Me]\}(P^iPr_3)_2$ (**4**). In solution the hydride ligands of **2** exchange their positions through two different processes, which have been analyzed by ^1H NMR spectroscopy and DFT calculations. The X-ray structures of **2** and **4** are also reported.

Introduction

Pyridines, which are extensively used in the pharmaceutical industry,[1] have a ubiquitous presence in transition-metal chemistry.[2] Their more classical mode of coordination is κN via the lone pair of the nitrogen atom. Several alternative metal ligand interactions, including η^2(C,N)-, η^2(C,C)-, and η^6-bound pyridine, have been also documented.[3] Recently, Carmona and coworkers have observed that some iridium complexes promote a 1,2-hydrogen shift from carbon to nitrogen to afford compounds with the heterocycle coordinated by the atom adjacent to nitrogen.[4] We have concurrently found that osmium and ruthenium promote the tautomerization not only of pyridines[5] but also of quinolines.[6] Thus, we have reported that the complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with 8-methylquinoline and 2-methylpyridine to give derivatives containing the corresponding NH tautomers (Scheme 1).

Scheme 1



One of the most interesting reactions of these heterocycles is aromatic C−H bond activation, due to its connection with the functionalization of these substrates at the α-position.[7] There can be two major cases of bonding: κC- and $\eta^2(C,N)$-pyridyl. The first of them has been mainly observed with platinum-group metals,[8] while the second one has been reported for early metals, including scandium,[9] ytrium,[10] luthetium,[11] thorium and uranium,[12] titanium,[13] zirconium,[14] niobium,[15] molybdenum,[16] and

* To whom correspondence should be addressed. E-mail: maester@unizar.es.

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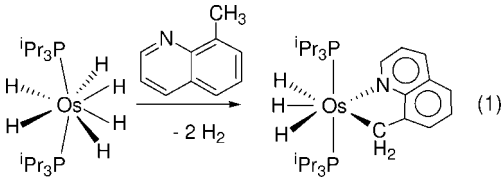
rhenium.[17] However, $\eta^2(C,N)$-pyridyl complexes of platinum-group metals are unknown.

The C−H bond activation reactions are promoted by low-valent metal complexes.[18] The use of high-valent metal compounds is rare, in particular hydride derivatives. In spite of this, as a part of the work of our group on the chemistry of polyhydride and dihydrogen osmium species,[19] we have reported that the osmium(VI) complex $OsH_6(P^iPr_3)_2$ (**1**) activates C−H bonds of activated olefins,[20] imines,[21] ketones,[22] aldehydes,[23] and imidazolium salts.[24] In contrast to $OsH_2Cl_2(P^iPr_3)_2$, it also activates a C(sp^3)−H bond of the methyl group of 8-methylquinoline to give a five-membered heterometalated species (eq 1).[25]



Results and Discussion

We now show that this hexahydride compound is able to produce the aromatic activation of 2-methylpyridine to afford an $\eta^2(C,N)$-pyridyl derivative of a platinum-group metal. Treatment of toluene solutions of **1** with 2.0 equiv of 2-methylpyridine under reflux leads after 6 h to a yellow solution, which affords a yellow residue. The addition of acetone and the subsequent cooling of the resulting solution at −20 °C yields the $\eta^2(C,N)$-pyridyl derivative $OsH_3\{\eta^2(C,N)\text{-}[NC_5H_3Me]\}(P^iPr_3)_2$ (**2**) as yellow crystals suitable for an X-ray diffraction analysis, in 49% yield (Scheme 2).

Scheme 2

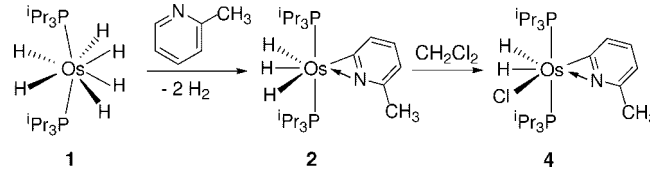


Figure 1 shows a drawing of the new compound. The structure proves that the aromatic C−H bond activation of the heterocycle gives an $\eta^2(C,N)$-pyridyl ligand, which acts with a C(1)−Os−N bite angle of 36.10(15)°. Thus, the coordination geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the two phosphorus atoms of the triisopropylphosphine ligands occupying axial positions (P(1)−Os−P(2) = 172.12(4)°). The osmium sphere is completed by the heterocycle and the hydride ligands, in the base, which are separated by 1.84(4) Å (H(01)−H(02)) and 1.69(4) Å (H(02)−H(03)), whereas the H(01)−Os−H(02) and H(02)−Os−H(03) angles are 70(1) and 65(1)°, respectively.

The hydride positions obtained from X-ray diffraction data are, in general, imprecise.[26] However, DFT calculations have been shown to provide useful accurate data for the hydrogen positions in both classical polyhydride and dihydrogen complexes.[19a,b,21,22a,25] Thus, to confirm the positions of H(01), H(02), and H(03), the structure of the model compound $OsH_3\{\eta^2(C,N)\text{-}[NC_5H_3Me]\}(PMe_3)_2$ (**2t** in Chart 1) has been optimized by DFT calculations (B3PW91). In agreement with the X-ray results, the H(01)−H(02) and H(02)−H(03) separations are 1.852 and 1.769 Å, and the H(01)−Os−H(02) and H(02)−Os−H(03) angles are 68.3 and 65.8°, respectively.

The $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^1H NMR spectra of **2** are consistent with the structure shown in Figure 1. In the $^{13}C\{^1H\}$ NMR spectrum in acetone-d_6 at room temperature, the most noticeable resonance is a triplet at 162.4 ppm with a C−P

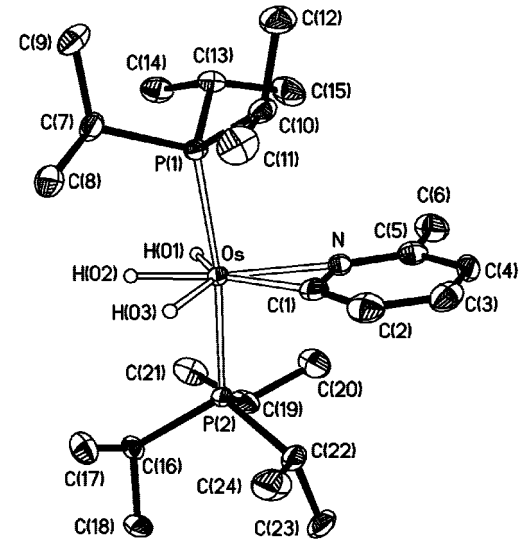


Figure 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Os−C(1) = 2.045(4), Os−N = 2.170(3), C(1)−N = 1.312(5), H(01)···H(02) = 1.84(4), H(02)···H(03) = 1.69(4); P(1)−Os−P(2) 172.12(4), C(1)−Os−N = 36.10(15), H(01)−Os−H(02) = 70(1), H(02)−Os−H(03) = 65(1).

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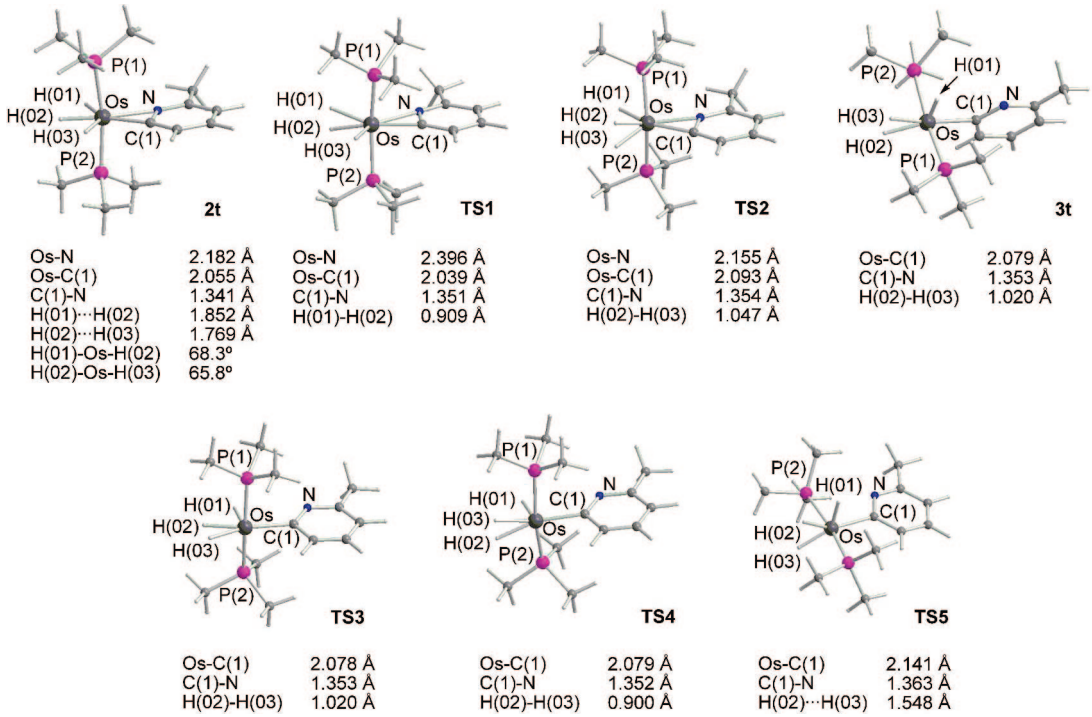
Chart 1



coupling constant of 7.5 Hz, due to the metalated carbon atom C(1) of the heterocycle. In agreement with the equivalence of the phosphine ligands the $^{31}P\{^{1}H\}$ NMR spectrum in toluene-d_8 shows a singlet at 36.6 ppm, which is temperature invariant between 373 and 243 K. As expected for three inequivalent hydride ligands, the ^{1}H NMR spectrum in toluene-d_8 between 253 and 198 K contains three hydride resonances at −4.89 (H_A), −11.50 (H_B), and −14.13 ppm (H_C). The H_A and H_B signals appear as double triplets with a H−H coupling constant of 1.5 Hz and H−P coupling constants of 14.5 and 15.0 Hz, respectively, while the H_C resonance is observed as a triplet with a H−P coupling constant of 13.0 Hz. In this temperature range, the T_1 values of these signals decrease in the sequence H_A (580−223 ms) > H_C (463−173 ms) > H_B (333−118 ms). Since the main contribution to the relaxation rate of a hydride ligand is the relaxation rate due to the hydride dipole−dipole interactions,[27] the H−H separations obtained from the X-ray diffraction analysis and DFT calculations, together with these T_1 values, unambiguously indicate that the resonances H_A, H_B, and H_c correspond to the hydrides H(01), H(02), and H(03), respectively. The assignment of H_B to H(02) was confirmed by means of monodimensional NOESY experiments. In addition it should be noted that, in contrast to H(03), H(01) shows a small coupling with H(02) in agreement with a H(01)−Os−H(02) angle larger than H(02)−Os−H(03). At 333 K, coalescence between the resonances H_A and H_B takes place. Thus, at 373 K, two broad signals centered at −8.4 and −14.4 ppm are observed (Figure 2). This behavior indicates that in toluene solution the H(01) and H(02) hydride ligands of **2** undergo a thermally activated position exchange. A $\Delta G^{\ddagger}_{333}$ value of 14 kcal mol^{-1} can be estimated for the process.

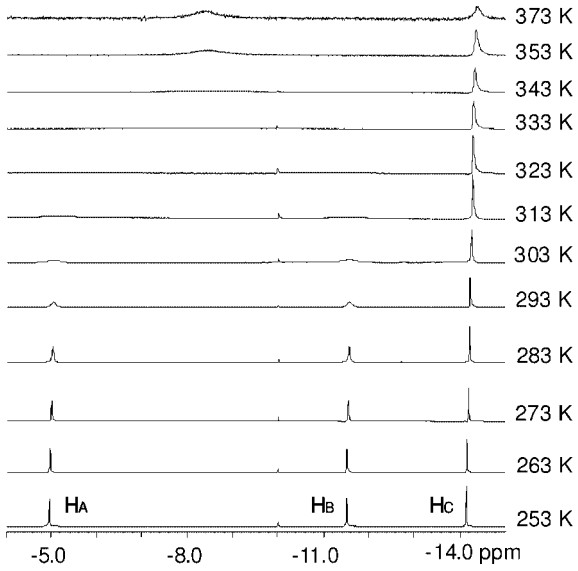


Figure 2. Variable-temperature $^{1}H\{^{31}P\}$ NMR spectra (400 MHz, toluene-d_8) of **2** (hydride region).

The change in free energy for the position exchange between the H(01) and H(02) hydride ligands of **2t** has been computed at 298.15 K and $P = 1$ atm. The process takes place through the transition state **TS1** (Chart 1), which in agreement with the $\Delta G^{\ddagger}_{333}$ value lies 16.6 kcal mol^{-1} above **2t**. It is a hydride−dihydrogen species with the hydrogen molecule H(01)−H(02) disposed cisoid to the nitrogen atom of the

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(27) See for example: Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 4498, and references therein.

heterocycle and parallel to the P−Os−P direction. The H(01)−H(02) separation is 0.909 Å.

Figure 2 shows that, at temperatures higher than 333 K, the H_C resonance broadens. This suggests that the H(02) and H(03) hydride ligands undergo a thermally activated position exchange process, which has an activation energy higher than the H(01)−H(02) exchange. Not only is the energy higher but also the exchange mechanism is more complex. The hydride−dihydrogen **TS2** transition state, related to **TS1**, with the hydrogen molecule disposed cisoid to the carbon atom of the heterocycle, lies 25.3 kcal mol^{-1} above **2t**, an energy value that is too high. As a consequence of this, the $\eta^2(C,N)$- to κC-pyridyl transformation of the heterocycle is favored with regard to the formation of **TS2**. The transformation in the coordination mode of the heterocycle leads to **3t**, which is 17.2 kcal mol^{-1} less stable than **2t**. Complex **3t** is a hydride (H(01))−elongated dihydrogen (H(02)−H(03)) compound. Its structure can be rationalized as a square pyramid with H(01) in the apical position. The base is formed by the phosphines disposed trans (P−Os−P = 171.5°), the coordinated hydrogen molecule perpendicular to the P−Os−P direction, and the heterocycle parallel to the H(02)−H(03) bond. The H(02)−H(03) distance is 1.020 Å. The transition state **TS3** connecting **2t** ant **3t** results from the dissociation of the nitrogen atom and the approach of the hydride ligands, which give rise to a hydride-elongated dihydrogen species with H(01)−H(02) and H(02)−H(03) separations of 1.602 and 1.431 Å, respectively. It lies 19.1 kcal mol^{-1} above **2t**. In **3t**, the H(02) and H(03) atoms exchange their positions via the transition state **TS4**, where the H(02)−H(03) dihydrogen ligand (d_{H-H} = 0.900 Å) is disposed perpendicular to the heterocycle. It lies 22.8 kcal mol^{-1} above **2t** and 2.5 kcal mol^{-1} below **TS2**. The rotation of the heterocycle around the Os−C(1) bond occurs through the transition state **TS5** and has an activation barrier (23.4 kcal mol^{-1}) slightly higher than that of **TS4**.

The relatively low energy required for the release of the nitrogen atom from the metal center appears to be responsible for the high instability of **2** in dichloromethane solutions. In this solvent, complex **2** rapidly undergoes selective chlorination at the H(01) position to give the orange derivative $OsH_2Cl\{\eta^2(C,N)$-$[NC_5H_3Me]\}(P^iPr_3)_2$ (**4**) in quantitative yield, after 5 min at room temperature (Scheme 2). The reaction should involve the C−Cl bond activation of the solvent by a six-coordinate intermediate related to **3t**. Thus, the resulting Cl−$[OsH_3]$−CH_2Cl species could eliminate CH_3Cl to afford **4**.

Complex **4** has been also characterized by X-ray diffraction analysis. Figure 3 shows a drawing of this compound. The structure proves that the chloride ligand occupies the same position as the H(01) hydride of **2**. Thus, the coordination geometry around the metal center can be described as a distorted pentagonal bipyramid with the two phosphorus atoms of the phosphines in axial positions (P(1)−Os−P(2) = 168.44(7)°). The base of the pyramid is formed by the $\eta^2(C,N)$-pyridyl ligand, which acts with a bite angle C(1)−Os−N of 35.4(3)°, the hydride ligands separated by 1.64(7) Å, and the chloride disposed cisoid to the nitrogen atom.

The substitution of H(01) by chloride produces a slight perturbation in the structural parameters of the three-membered OsCN cycle. The Os−C(1) bond length is shortened from 2.045(4) Å in **2** to 1.995(7) Å in **4**, while the Os−N distance increases from 2.170(3) Å in **2** to 2.274(5) Å in **4**. The C(1)−N distances of 1.312(5) (**2**) and 1.323(9) Å (**4**) are statistically identical.

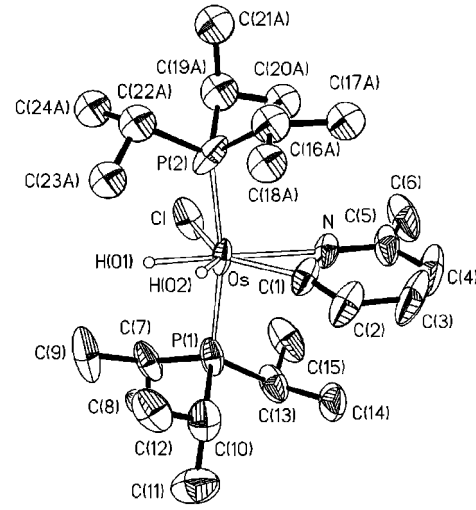

Figure 3. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Os−C(1) = 1.995(7), Os−N = 2.274(5), C(1)−N = 1.323(9), H(01)···H(02) = 1.64(7); P(1)−Os−P(2) = 168.44(7), C(1)−Os−N = 35.4(3).

The $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^1H NMR spectra of **4** in acetone-d_6 are in agreement with the structure shown in Figure 3. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance corresponding to the metalated carbon atom C(1) of the heterocycle appears at 155.8 ppm, as a triplet with a C−P coupling constant of 6.2 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 23.3 ppm, as expected for equivalent phosphines. In accord with the presence of two inequivalent hydride ligands in the complex, the ^1H NMR spectrum shows triplets at −8.53 and −12.00 ppm with H−P coupling constants of 14.0 and 11.7 Hz, respectively.

Concluding Remarks

In conclusion, there are marked differences in reactivity between the osmium(IV) complex $OsH_2Cl_2(P^iPr_3)_2$ and the osmium(VI) derivative $OsH_6(P^iPr_3)_2$, toward 8-methylquinoline and 2-methylpyridine. While the former tautomerizes and stabilizes the resulting NH tautomers of both heterocycles (Scheme 1), the latter promotes direct reactions of C−H bond activation. The hexahydride compound activates a $C(sp^3)$−H bond of the methyl substituent of 8-methylquinoline to generate a five-membered heterometallacycle (eq 1). However, 2-methylpyridine undergoes aromatic C−H bond activation to afford the $\eta^2(C,N)$-pyridyl derivative $OsH_3\{\eta^2(C,N)$-$[NC_5H_3Me]\}$-$(P^iPr_3)_2$, which in dichloromethane is unstable and evolves into $OsH_2Cl\{\eta^2(C,N)$-$[NC_5H_3Me]\}(P^iPr_3)_2$ by selective chlorination of one of the hydride ligands.

Experimental Section

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Toluene was obtained oxygen- and water-free from a MBraun solvent purification apparatus, while acetone was dried and distilled under argon. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ 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 (^1H, $^{13}C\{^1H\}$) or to external 85% H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants J and N are given in hertz. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer as neat solids. C, H, and N analyses were carried out with a Perkin-Elmer 2400

CHNS/O analyzer. $OsH_6(P^iPr_3)_2$ (**1**) was prepared according to published methods.[28]

Reaction of $OsH_6(P^iPr_3)_2$ with 2-Methylpyridine: Preparation of $OsH_3\{\eta^2(C,N)\text{-}[NC_5H_3Me]\}(P^iPr_3)_2$ (2). A colorless solution of **1** (150 mg, 0.26 mmol) in toluene (15 mL) was treated with 2 equiv of 2-methylpyridine (54.0 μL, 0.52 mmol). The resulting solution was refluxed for 6 h. The resulting yellow solution was cooled to room temperature, and the solvent was evaporated. The yellow residue obtained was dissolved in acetone (5 mL) and cooled at 253 K overnight, giving yellow crystals that were washed with cold acetone (2 × 2 mL) and dried in vacuo. Yield: 86 mg (49%). Anal. Calcd for $C_{24}H_{51}NOsP_2$: C, 47.57; H, 8.48; N, 2.31. Found: C, 47.49; H, 8.31; N, 2.26. IR (neat compound, cm^{-1}): ν(Os−H) 2119 (w), 2084 (w); ν(C═C) 1579 (m). ^1H NMR (300 MHz, acetone-d_6, 293 K): δ 7.14 (t, J_{H-H} = 7.2, 1H, NC_5H_3), 6.91 (d, J_{H-H} = 7.2, 1H, NC_5H_3), 6.24 (d, J_{H-H} = 7.2, 1H, NC_5H_3), 2.33 (s, 3H, CH_3), 1.81 (m, 6H, PC*H*$(CH_3)_2$), 1.19 (dvt, J_{H-H} = 7.2, N = 12.6, 18H, PCH(C*H*$_3)_2$), 1.18 (dvt, J_{H-H} = 6.9, N = 12.6, 18H, PCH(C*H*$_3)_2$), −5.20 (br, 1H, OsH), −11.72 (br, 1H, OsH), −14.35 (t, J_{H-P} = 1H, OsH). ^1H NMR (300 MHz, toluene-d_8, 243 K, high-field region): δ −4.89 (td, J_{H-P} = 14.5, J_{H-H} = 1.5, 1H, OsH), −11.50 (td, J_{H-P} = 15, J_{H-H} = 1.5, 1H, OsH), −14.13 (t, J_{H-P} = 13.0, 1H, OsH). $^{13}C\{^1H\}$ NMR (75.4 MHz, acetone-d_6, 293 K): δ 162.4 (t, J_{P-C} = 7.5, Os−C), 150.3 (s, *C*−CH_3), 137.3, 123.1, 119.2 (all s, NC_5H_3), 28.6 (vt, N = 24, P*C*H$(CH_3)_2$), 23.0 (s, CH_3), 21.7, 21.5 (both s, PCH(*C*$H_3)_2$). $^{31}P\{^1H\}$ NMR (121.42 MHz, acetone-d_6, 293 K): δ 36.6 (s).

Reaction of 2 with Dichloromethane: Preparation of $OsH_2Cl\{\eta^2(C,N)\text{-}[NC_5H_3Me]\}(P^iPr_3)_2$ (4). Complex **2** (70 mg, 0.12 mmol) was dissolved in CH_2Cl_2 (5 mL) and the solution stirred for 5 min at room temperature. The resulting orange solution was evaporated to dryness and the residue dissolved in acetone (1 mL) and cooled to 253 K over 24 h. A small amount of yellowish orange crystals were isolated after removal of the supernatant solution. ^1H and $^{31}P\{^1H\}$ NMR spectra show that the reaction is quantitative, but the obtained yield is very low due to the high solubility of the complex in acetone. Anal. Calcd for $C_{24}H_{50}ClNOsP_2$: C, 45.02; H, 7.87; N, 2.19. Found: C, 45.36; H, 7.51; N, 1.96. IR (neat compound, cm^{-1}): ν(Os−H) 2154 (w); ν(C═C) 1537 (m). ^1H NMR (300 MHz, acetone-d_6, 293 K): δ 7.22 (t, J_{H-H} = 7.4, 1H, NC_5H_3), 6.68 (d, J_{H-H} = 7.4, 1H, NC_5H_3), 6.32 (d, J_{H-H} = 7.4, 1H, NC_5H_3), 2.50 (s, 3H, CH_3), 2.25 (m, 6H, PC*H*$(CH_3)_2$), 1.23 (dvt, J_{H-H} = 5.7, N = 12.0, 18H, PCH(C*H*$_3)_2$), 1.21 (dvt, J_{H-H} = 6.9, N = 13.5, 18H, PCH(C*H*$_3)_2$), −8.53 (t, J_{H-P} = 14.0, 1H, OsH), −12.00 (t, J_{H-P} = 11.7, 1H, OsH). $^{13}C\{^1H\}$ NMR (75.4 MHz, acetone-d_6, 293 K): δ 155.8 (t, J_{P-C} = 6.2, Os−*C*) 150.7 (s, *C*−CH_3), 137.9, 123.9, 117.9 (all, NC_5H_3), 24.4 (vt, N = 30, P*C*H$(CH_3)_2$), 21.9 (s, CH_3), 20.0, 19.7 (both s, PCH(*C*$H_3)_2$). $^{31}P\{^1H\}$ NMR (121.42 MHz, acetone-d_6, 293 K): δ 23.3 (s).

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Supporting Information Available: Text, tables, figures, and CIF files giving details of the X-ray analysis and crystal structure determinations, including bond lengths and angles of compounds **2** and **4**, orthogonal coordinates, and absolute energies of the optimized theoretical structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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