Preparation and Structure of Alkylidene−Osmium and Hydride−Alkylidyne−Osmium Complexes Containing an N-Heterocyclic Carbene Ligand

Ricardo Castarlenas, Miguel A. Esteruelas,* 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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*Summary: The complex [(η^6-p-cymene)OsCl(=CHPh)(IPr)]OTf (**1**) releases the arene in acetonitrile at 40 °C. The resulting 12-valence-electron metallic fragment is trapped by the solvent to afford the tris(solvento) compound [OsCl(=CHPh)(NCCH$_3$)$_3$(IPr)]OTf (**2**), which reacts with AgOTf in acetonitrile at room temperature to give the tetrakis(solvento) derivative [Os(=CHPh)(NCCH$_3$)$_4$(IPr)](OTf)$_2$ (**3**). In dichloromethane at 40 °C, the treatment of **1** with triisopropylphosphine and triphenylphosphine yields the unsaturated five-coordinate mixed phosphine−NHC hydride−alkylidyne−osmium species [OsHCl(≡CPh)(IPr)(PR$_3$)]OTf (R = ^{i}Pr (**4**), Ph (**5**)).*

Octahedral half-sandwich osmium(II) complexes show ligand substitution activation energies higher than those of their ruthenium analogues, as a consequence of the dependence of the crystal field activation energy on Δ_0.[1] Thus, while arene substitution by solvent molecules or monodentate ligands easily occurs for half-sandwich ruthenium(II) complexes,[2] it requires photochemical conditions in the osmium chemistry.[3]

Osmium is also more reducing than ruthenium and prefers coordination saturation and redox isomers with more metal−carbon bonds.[4] A clear example are the hydride−carbyne complexes OsHCl$_2$(≡CR)(PR′$_3$)$_2$.[5] They are oxidized isomers of the unknown compounds OsCl$_2$(=CHR)(PR′$_3$)$_2$, which should be the osmium counterparts to the metathesis precursors RuCl$_2$(=CHR)(PR′$_3$)$_2$.[6]

The second generation of alkylidene−ruthenium initiators involves the substitution of one phosphine by a bulky N-heterocyclic carbene ligand (NHC). This modification has produced mixed phosphine−NHC compounds, RuCl$_2$(=CHR)(NHC)(PR′$_3$), which display dramatically improved metathesis activity, thermal stability, and inertness toward oxygen and moisture in comparison to RuCl$_2$(=CHR)(PR′$_3$)$_2$. This success has given rise to an active area based on mixed phosphine−NHC ruthenium complexes.[7] However, the findings with ruthenium have not awakened research interest in the third-row counterparts, although osmium has provided catalysts for C−C bond formation[8] and affords stable models of reactive intermediates proposed in catalytic transformations with ruthenium.[9] Thus, NHC−osmium complexes are extremely rare,[10] and the mixed phosphine−NHC systems remain unknown.[11]

As a part of our work on half-sandwich transition-metal compounds,[12] we have recently reported the preparation of the alkylidene−osmium complex [(η^6-*p*-cymene)OsCl(=CHPh)(IPr)]OTf (**1**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene, OTf = CF$_3$SO$_3$) which is an efficient catalyst precursors for olefin metathesis.[13] Despite the high kinetic inertia of the octahedral half-sandwich osmium(II) compounds, *p*-cymene was detected in the catalytic solutions, suggesting that the precursor is activated by means of the arene decoordination.

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

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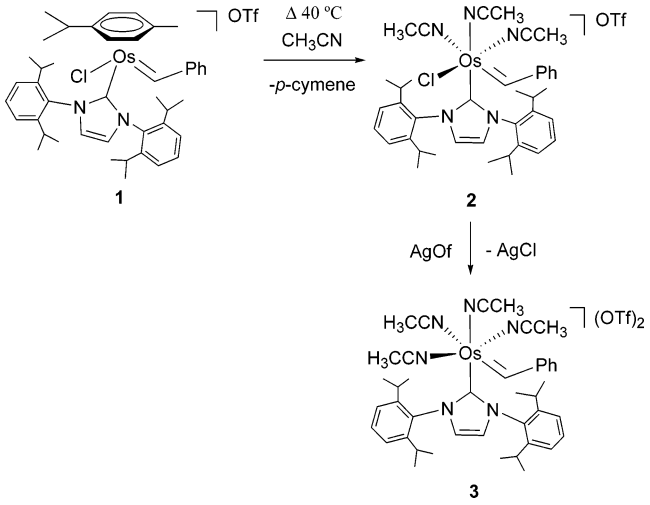
Scheme 1



In order to open a synthetic route toward mixed phosphine−NHC complexes containing Os−C multiple bonds, we have now investigated the displacement of the arene ligand from **1**.

In acetonitrile at 40 °C, complex **1** releases *p*-cymene and the resulting 12-valence-electron metallic fragment is trapped by the solvent to afford the tris(solvento) complex [OsCl(=CHPh)($NCCH_3$)$_3$(IPr)]OTf (**2**; Scheme 1). The presence of the alkylidene ligand in **1** certainly facilitates the dissociation of the arene from the coordination sphere of the osmium atom. In this context, it should be mentioned that, in contrast to **1**, the complexes [(η^6-*p*-cymene)OsCl(L)(IPr)]OTf (L = CO, CH_3CN) are stable in acetonitrile, even under reflux for 16 h. They are prepared in about 90% yield by reaction of the unsaturated compound [(η^6-*p*-cymene)OsCl(IPr)]OTf with carbon monoxide and acetonitrile, respectively.

Complex **2** is isolated as a blue solid in 86% yield. In the ^{1}H NMR spectra in dichloromethane-d_2, the resonance due to the H_α alkylidene proton appears as a singlet at 21.11 ppm, shifted between 2.0 and 3.6 ppm toward low field with regard to those found in the half-sandwich complexes **1** (δ 17.95), [(η^6-*p*-cymene)OsCl(=CHPh)(IMes)]OTf (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolylidene; δ 17.50),[13] Os(η^5-C_5H_5)Cl(=CHPh){P^iPr_2[$C(CH_3)$=CH_2]} (δ 18.50),[14] and Os(η^5-C_5H_5)Cl(=CHPh)(P^iPr_3) (δ 19.17).[15] The coordinated acetonitrile molecules display three singlets at 3.08, 2.38, and 2.22 ppm. Since in general the activation enthalpy for the rotation of an organic fragment around an Os−C double bond is small,[16] we assume that in **2** the rotation of the alkylidene ligand is fast. Thus, the presence of three acetonitrile signals is consistent with a *fac* disposition of these ligands. In the ^{13}C{^{1}H} NMR spectrum, the C_α resonance due to the alkylidene appears at 279.5 ppm, shifted slightly toward high field with regard to **1** (δ 288.9) and [(η^6-*p*-cymene)OsCl(=CHPh)(IMes)]OTf (δ 285.2)[13] and about 45 ppm toward low field with regard to the cyclopentadienyl derivatives Os(η^5-C_5H_5)Cl(=CHPh){P^iPr_2-[$C(CH_3)$=CH_2]} (δ 234.2)[14] and Os(η^5-C_5H_5)Cl(=CHPh)(P^i-Pr_3) (δ 235.0).[15] The C_α atom of the NHC ligand gives rise to a singlet at 157.9 ppm. In agreement with the ^{1}H NMR spectrum, six singlets between 128 and 121 ppm (CN) and between 5 and 3 ppm (CH_3) for the acetonitrile ligands are also observed in the ^{13}C{^{1}H} NMR spectrum.

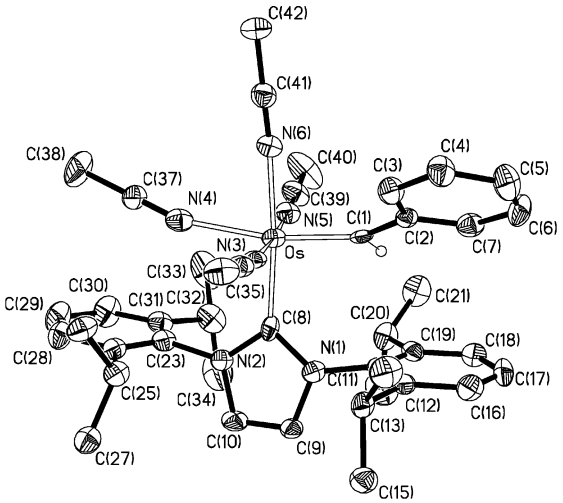


Figure 1. Molecular diagram of cation of **3**. Selected bond lengths (Å) and angles (deg): Os−C(1) = 1.926(6), Os−C(8) = 2.069(6), Os−N(3) = 2.015(5), Os−N(4) = 2.161(6), Os−N(5) = 2.024(6), Os−N(6) = 2.079(5); C(8)−Os−N(6) = 173.6(2), Os−C(1)−C(2) = 134.3(5), C(8)−Os−C(1) = 94.5(2), Os−N(3)−C(35) = 173.0(5), Os−N(4)−C(37) = 164.1(6), Os−N(5)−C(39) = 171.9(6), Os−N(6)−C(41) = 175.0(6).

Complex **2** is moderately stable in acetonitrile. At temperatures higher than 60 °C, it decomposes to a complex mixture of unidentified compounds. At room temperature, in the presence of 1.1 equiv of AgOTf the abstraction of the chloride ligand and the subsequent formation of the tetrakis(solvento) derivative [Os(=CHPh)($NCCH_3$)$_4$(IPr)]($OTf)_2$ (**3**) takes place (Scheme 1). This compound is isolated as a blue solid in 75% yield.

Complex **3** is a rare example of a dicationic species containing an Os−C double bond.[17] It has been characterized by elemental analysis, by IR and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and by an X-ray crystallographic study. A view of the structure of the cation is shown in Figure 1. The geometry around the osmium atom can be described as a distorted octahedron with the alkylidene and N-heterocyclic carbene ligands mutually cis disposed (C(1)−Os−C(8) = 94.5(2)°). The separation of 1.926(6) Å between the osmium atom and the alkylidene, which

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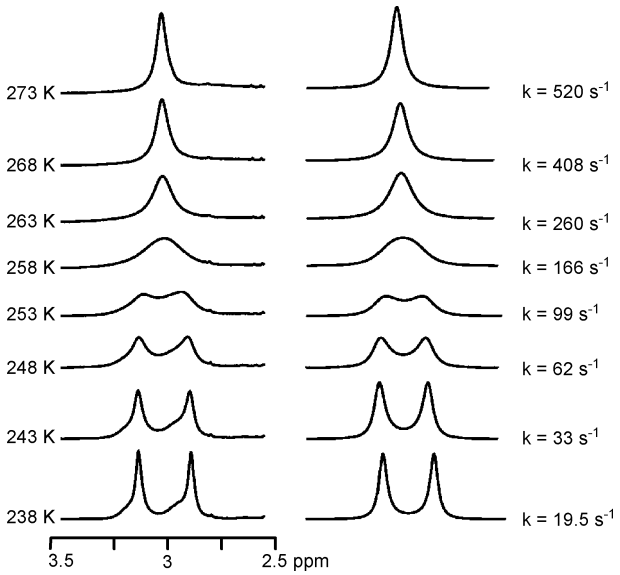
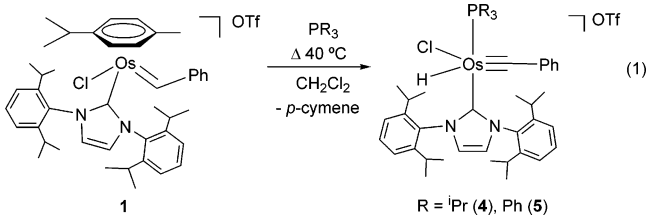


Figure 2. Variable-temperature ^{1}H NMR spectra in the acetonitrile region of [Os(=CHPh)(NCCH$_3$)$_4$(IPr)](OTf)$_2$ (**3**): (left) experimental; (right) calculated.

supports the Os−C(1) double-bond formulation,[13,14,18] is about 0.14 Å shorter than that between the metal and the N-heterocyclic carbene ligand (Os−C(8) = 2.069(6) Å). In agreement with the sp^2 hybridization at C(1), the Os−C(1)−C(2) angle is 134.3(5)°.

The ^{1}H and ^{3}C{^{1}H} NMR spectra of **3** are consistent with Figure 1. In the ^{1}H NMR spectrum in acetonitrile-d_3, the H$_\alpha$ alkylidene resonance appears as a singlet at 19.87 ppm. As expected for a low rotational energy barrier of the alkylidene ligand, at room temperature, the four inequivalent acetonitrile molecules display three signals at 2.88, 2.40, and 1.99 ppm. At −30 °C, the rotation of the alkylidene around the Os−C double bond is blocked. As a result, the signal at 2.88 ppm is split into two singlets at 2.98 and 2.78 ppm. Line shape analysis of the temperature-dependent acetonitrile signals between 0 and −35 °C (Figure 2) allows the calculation of the rate constants for the rotation process. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\ddagger} = 11.9 \pm 0.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -1.9 \pm 1.8$ cal K^{-1} mol^{-1}. In the ^{13}C{^{1}H} NMR spectrum, the C$_\alpha$ alkylidene resonance is observed at 284.5 ppm, whereas that due to the C$_\alpha$ atom of the NHC ligand appears at 156.4 ppm. In accordance with Figure 1 and the ^{1}H NMR spectrum at −30 °C, at this temperature, the ^{13}C{^{1}H} NMR spectrum contains eight singlets for the acetonitrile ligands between 127 and 119 ppm (CN) and between 5 and 1 ppm (CH$_3$).

In dichloromethane, in addition to the dissociation of the arene, the migration of the hydrogen atom from the α-carbon of the alkylidene to the metal center takes place, and the resulting hydride-alkylidyne metal fragment can be trapped by phosphines. Thus, the heating at 40 °C of dichloromethane solutions of **1** in the presence of triisopropylphosphine and triphenylphosphine affords the 16-electron five-coordinate mixed phosphine−NHC hydride−alkylidyne compounds [OsHCl(≡CPh)(IPr)(P^{i}R$_3$)]OTf (R = ^{i}Pr (**4**), Ph (**5**)), which are isolated as orange solids in about 85% yield, according to eq 1.



Complexes **4** and **5** were characterized by elemental analysis and IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. Complex **4** was further characterized by an X-ray crystallographic study. A view of the structure of the cation is shown in Figure 3. The geometry around the osmium atom can be rationalized as a distorted trigonal bipyramid with the phosphine and N-heterocyclic carbene ligands in the apical positions (P−Os−C(8) = 164.63(6)°) and inequivalent angles within the Y-shaped equatorial plane. The angles C(1)−Os−Cl, Cl−Os−H(01), and C(1)−Os−H(01) are 140.83(7), 130.9(10), and 88.2(10)°, respectively. The very short Os−C(1) bond length of 1.717(2) Å is fully consistent with an Os−C triple-bond formulation.[19] Similar to the case for other metal carbyne compounds,[5a,16c,d,20] a slight bending in the Os−C(1)−C(2) moiety is also present (Os−C(1)−C(2) = 173.76(18)°).

In agreement with the presence of a hydride ligand in **4** and **5**, their ^{1}H NMR spectra in dichloromethane-d_2 show doublets at −9.34 (**4**) and −8.68 ppm (**5**) with H−P coupling constants

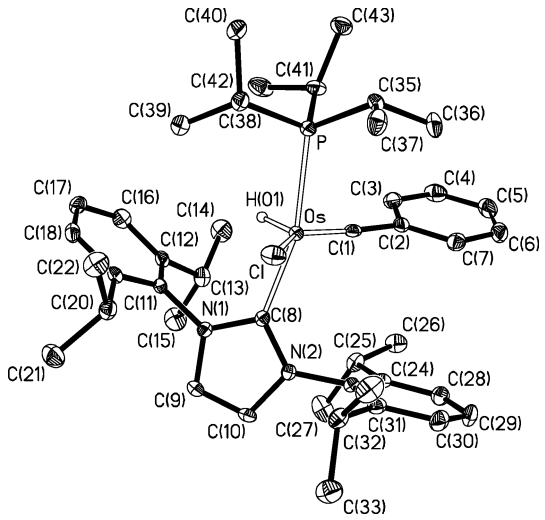


Figure 3. Molecular diagram of cation of **4**. Selected bond lengths (Å) and angles (deg): Os−C(1) = 1.717(2), Os−C(8) = 2.108(2), Os−P = 2.4056(6), Os−H(01) = 1.32(2); P−Os−C(8) = 164.63(6), C(1)−Os−Cl = 140.83(7), Cl−Os−H(01) = 130.9(10), C(1)−Os−H(01) = 88.2(2)°, Os−C(1)−C(2) = 173.76(18).

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of 14.1 and 15.6 Hz, respectively. In the $^{13}C\{^1H\}$ NMR spectra, the resonances corresponding to the C_α alkylidyne atom appear at 271.5 (**4**) and 276.8 ppm (**5**), as doublets with C−P coupling constants of 10.5 and 9.0 Hz, respectively. In accordance with the trans disposition of the phosphine and NHC ligands, the C_α resonances of the latter are observed as doublets with C−P coupling constants of 83.0 (**4**) and 85.3 Hz (**5**), at 185.4 and 184.7 ppm, respectively. The $^{31}P\{^1H\}$ NMR spectra contain singlets at 49.6 (**4**) and 28.7 ppm (**5**).

In conclusion, these results show that an alkylidene ligand favors the dissociation of the arene from octahedral half-sandwich arene osmium derivatives. Thus, the complexes $[(\eta^6\text{-arene})OsCl(=CHPh)(NHC)]^+$ are useful starting materials to prepare tris- and tetrakis(solvento) alkylidene−osmium complexes, and five-coordinate mixed phosphine−NHC hydride−alkylidyne−osmium derivatives.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Organic solvents were dried by standard procedures and distilled under argon prior to use. The starting material **1** was prepared as previously described in the literature.[13] Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) or external H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants, *J*, are given in hertz.

Preparation of [OsCl(=CHPh)(NCCH$_3$)$_3$(IPr)]OTf (2). A dark green solution of **1** (200 mg, 0.203 mmol) in 10 mL of acetonitrile was heated at 40 °C for 1 h. The resulting blue solution was filtered through Celite, and the filtrate was evaporated to dryness. Addition of diethyl ether caused the precipitation of a blue solid, which was washed with diethyl ether (3 × 2 mL) and dried in vacuo. Yield: 170 mg (86%). Anal. Calcd for $C_{41}H_{51}N_5SClF_3O_3Os$: C, 50.42; H, 5.26; N, 7.17; S, 3.28. Found: C, 50.38; H, 5.37; N, 6.99; S, 3.47. IR (Nujol, cm^{-1}): $\nu(CH_3CN)$ 2327 (w); $\nu_a(SO_3)$ 1266 (s); $\nu_s(CF_3)$ 1224 (m); $\nu_a(CF_3)$ 1151 (s); $\nu_s(SO_3)$ 1033 (s); $\delta_a(SO_3)$ 638 (s). MS: *m*/*z* 704 $[M - 3(CH_3CN)]^+$. ^1H NMR (300 MHz, CD_2Cl_2, 243 K): δ 21.11 (s, 1H, Os=CH), 7.7−7.2 (11H, H_{Ph}), 6.93 (s, 2H, =CHN), 3.08, 2.38, and 2.22 (all s, 9H, CH_3CN), 2.92 (m, 4H, CH), 1.2−1.1 (24H, CH_3). $^{13}C\{^1H\}$ APT NMR plus HSQC and HMBC (75.4 MHz, CD_2Cl_2, 243 K): δ 279.5 (s, Os=C), 158.2, 147.3, and 137.6 (all s, C_q), 157.9 (s, Os−C), 133.6, 133.0, 133.1, 128.7, and 124.6 (all s, C_{Ph}), 127.9, 123.2, and 121.0 (all s, CN), 126.5 (s, =CHN), 121.2 (q, J_{C-F} = 320.4, CF_3), 28.2 (s, CH), 25.8 and 23.0 (both s, CH*C*H$_3$), 4.8, 3.7, and 3.5 (all s, *C*H$_3$CN).

Preparation of [Os(IPr)(NCCH$_3$)$_4$(=CHPh)](OTf)$_2$ (3). A blue solution of **2** (200 mg, 0.205 mmol) in 10 mL of acetonitrile, protected from light, was treated with AgOTf (60 mg, 0.233 mmol), and this mixture was stirred at room temperature for 16 h. The resulting blue suspension was filtered through Celite, and the filtrate was evaporated to dryness. Addition of diethyl ether caused the precipitation of a blue solid, which was washed with diethyl ether (3 × 2 mL) and dried in vacuo. Yield: 175 mg (75%). Anal. Calcd for $C_{44}H_{54}N_6S_2F_6O_6Os$: C, 46.71; H, 4.81; N, 7.42; S, 5.67. Found: C, 46.37; H, 5.11; N, 7.53; S, 5.38. IR (Nujol, cm^{-1}): $\nu(CH_3CN)$ 2314 and 2286 (w); $\nu_a(SO_3)$ 1274 (s); $\nu_s(CF_3)$ 1225 (m); $\nu_a(CF_3)$ 1161 (s); $\nu_s(SO_3)$ 1030 (s); $\delta_a(SO_3)$ 639 (s). ^1H NMR (300 MHz, CD_3CN, 243 K): δ 19.87 (s, 1H, Os=CH), 7.8−7.2 (11H, H_{Ph}), 6.81 (s, 2H, =CHN), 2.98, 2.78, 2.40, and 1.99 (all s, 12H, CH_3CN), 3.00, 2.80, 2.27, and 1.87 (all m, 4H, CH), 1.6−0.5 (24H, CH_3). $^{13}C\{^1H\}$ APT NMR plus HSQC and HMBC (75.4 MHz, CD_3CN, 243 K): δ 284.5 (s, Os=C), 156.4 (s, Os−C), 155.0, 146.8, 137.0, and 135.8 (s, C_q), 134.9, 132.5, 132.1, 129.9, 127.6, 127.4, 125.3 (all s, C_{Ph}), 124.7 (s, =CHN), 126.3, 123.4, 120.5, and 119.4 (all s, CN), 121.4 (q, J_{C-F} = 320.2, CF_3), 29.5, 29.1, and 28.5 (all s, CH), 25.6, 25.2, and 22.6 (all s, CH*C*H$_3$), 4.7, 4.3, 3.2, and 1.7 (all s, *C*H$_3$CN).

Preparation of [OsHCl(≡CPh)(IPr)(P^{i}Pr$_3$)]OTf (4). A dark green solution of **1** (200 mg, 0.203 mmol) in 10 mL of CH_2Cl_2 was treated with P^iPr_3 (100 μL, 0.512 mmol), and it was heated at 40 °C for 2 h. The resulting orange solution was filtered through Celite, and the filtrate was evaporated to dryness. Addition of diethyl ether caused the precipitation of an orange solid, which was washed with diethyl ether (3 × 2 mL) and dried in vacuo. Yield: 170 mg (83%). Anal. Calcd for $C_{44}H_{63}N_2SClF_3O_3OsP$: C, 52.13; H, 6.26; N, 2.76; S, 3.16. Found: C, 52.46; H, 6.30; N, 2.98; S, 3.21. IR (Nujol, cm^{-1}): ν(Os−H) 2222 (w); $\nu_a(SO_3)$ 1269 (s); $\nu_s(CF_3)$ 1224 (m); $\nu_a(CF_3)$ 1161 (s); $\nu_s(SO_3)$ 1028 (s); $\delta_a(SO_3)$ 637 (s). MS: *m*/*z* 865 $[M]^+$. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.7−6.9 (11H, H_{Ph}, =CHN), 3.35 and 2.64 (sept, J_{H-H} = 6.5, 4H, CH), 2.64 (sept, J_{H-H} = 7.2, 3H, PCH), 1.51, 1.13, 1.12, and 1.01 (both d, J_{H-H} = 6.5, 24H, CH_3), 0.99 and 0.84 (both dd, J_{H-P} = 14.8, J_{H-H} = 7.2, 18H, PCHC*H*$_3$), −9.34 (d, J_{H-P} = 14.1, 1H, OsH). $^{13}C\{^1H\}$ APT NMR plus HSQC and HMBC (75.4 MHz, CD_2Cl_2, 293 K): δ 271.5 (d, J_{C-P} = 10.5, Os=C), 185.4 (d, J_{C-P} = 83.0, Os−C), 146.9, 146.1, 141.7, and 133.9 (all s, C_q), 134.3, 132.1, 130.3, 129.1, 126.6, 125.2, and 125.0 (s, C_{Ph}, =CHN), 121.5 (q, J_{C-F} = 322.5, CF_3), 29.5 and 29.2 (both s, CH), 26.5, 26.2, 22.7, and 22.6 (all s, CH_3), 26.3 (d, J_{C-P} = 16.6, PCH), 20.0 and 19.6 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ (121.4 MHz, CD_2Cl_2, 293 K): δ 49.6 (s).

Preparation of [OsHCl(≡CPh)(IPr)(PPh$_3$)]OTf (5). This product was prepared as described for **4** by starting from **1** (200 mg, 0.203 mmol) and PPh_3 (150 mg, 0.571 mmol). Yield: 190 mg (84%). Anal. Calcd for $C_{53}H_{57}N_2SClF_3O_3OsP$: C, 57.05; H, 5.15; N, 2.51; S, 2.87. Found: C, 56.86; H, 5.19; N, 2.68; S, 3.03. IR (Nujol, cm^{-1}): $\nu_a(SO_3)$ 1270 (s); $\nu_s(CF_3)$ 1223 (m); $\nu_a(CF_3)$ 1149 (s); $\nu_s(SO_3)$ 1027 (s); $\delta_a(SO_3)$ 637 (s). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.5−6.5 (28H, H_{Ph}, =CHN), 3.30 and 2.70 (both m, 4H, CH), 1.4−1.1 (24H, CH_3), −8.68 (d, J_{H-P} = 15.6, 1H, OsH). $^{13}C\{^1H\}$ APT NMR plus HSQC and HMBC (75.4 MHz, CD_2Cl_2, 293 K): δ 276.8 (d, J_{C-P} = 9.0, Os=C), 184.7 (d, J_{C-P} = 85.3, Os−C), 146.9, 146.2, 140.4, 133.7, and 130.0 (all s, C_q), 134.7, 134.3, 134.1, 132.2, 131.9, 130.5, 129.3, 129.2, 128.5, 126.4, 125.1, and 125.0 (all s, C_{Ph}, =CHN), 121.5 (q, J_{C-F} = 320.4, CF_3), 29.5 and 29.3 (both s, CH), 26.2, 26.0, 22.6, and 22.5 (all s, CH_3). $^{31}P\{^1H\}$ (121.4 MHz, CD_2Cl_2, 293 K): δ 28.7 (s).

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Supporting Information Available: Text and figures giving details of the preparation of complexes, determination of the rotational barrier of carbene ligand on complex **3**, and crystal structure determinations and CIF files giving crystal data for compounds **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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