C-C Bond Activation of the NHC Ligand of an Osmium-Amido Complex

Tamara Bolaño, María L. Buil, Miguel A. Esteruelas, Susana Izquierdo, Ralte Lalrempuia, Montserrat Oliván, and Enrique Oñate*

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

E-mail: maester@unizar.es (M. A. E.)

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Summary: *Treatment of (η^6-p-cymene)$OsCl_2$(IPr) (**1**, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene) with $AgBF_4$ in acetonitrile leads to [(η^6-p-cymene)$Os(CH_3CN)_2$(IPr)]$[BF_4]_2$ (**2**) which reacts with aniline and cyclohexylamine to afford [(η^6-p-cymene)Os(=NHR)(IPr)]BF_4 (R = Ph (**3**), Cy (**4**)). Complexes **3** and **4** have been also prepared by addition of ^{n}BuLi to tetrahydrofuran solutions of the amine compounds [(η^6-p-cymene)$OsCl(NH_2R)$(IPr)]BF_4 (R = Ph (**6**), Cy (**7**)). Complex **4** decomposes in tetrahydrofuran at 100ºC and in the presence of H_2O, to give cyclohexanone, propane, and [(η^6-p-cymene)Os{$CCHCHCHC(^iPr)CNCHCHN(C_6H_3{}^iPr_2)C$}$(NH_3)$]$BF_4$ (**8**). In dichloromethane at 50ºC, **4** evolves to [(η^6-p-cymene)$OsH(NH{=}C\overline{CH_2CH_2CH_2CH_2CH_2}$)(IPr)]$BF_4$ (**9**), which also gives **8** in tetrahydrofuran at 100 ºC and in the presence of H_2O. On the basis of these transformations, a*

*mechanism for the formation of **8** is proposed.*

Introduction

Metal-amido complexes, $L_nM(NRR')$, are proposed as key intermediates in hydroamination reactions of unsaturated organic substrates.[1] The stability of the amido ligands decreases as the electrophilicity of the metal center also decreases. Thus, while stable Os(IV)-amido complexes are well known,[2] the Os(II)-amido species are very rare.[3]

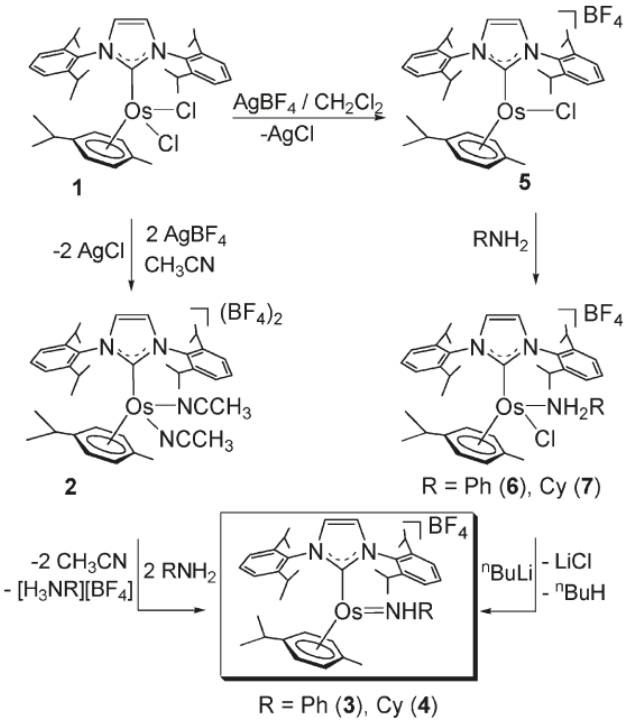
N-Heterocyclic carbenes (NHCs) are cyclic "Fischer-type" ligands bearing at least one α-amino substituent.[4] Although there are significant differences between them, NHCs were initially introduced as analogues to phosphines.[5] During the past few years, their chemistry has experienced explosive development due to the design of diverse homogeneous catalytic systems comprising such carbene ligands.[6] However, a number of recent reports have shown that NHC ligands can undergo degradation via a range of NHC-based reactions.[7] They include dissociation,[8] reductive elimination of imidazolium salts,[9] migratory insertion,[10] N-substituent cleavage,[11] ring expansion involving heterocyclic N-C bond cleavage,[12] C-H bond activation of N-alkyl and N-aryl substituents,[13] and ruthenium promoted methyl abstraction from an aryl N-substituent.[14]

In 2005, as a part of our work on NHC-osmium complexes,[15] we reported that the dimer $[(\eta^6\text{-}p\text{-cymene})OsCl_2]_2$ reacts with 1,3-bis(2,6-diisopropylphenyl)imidazolylidene (IPr) to give the mononuclear derivative $(\eta^6\text{-}p\text{-cymene})OsCl_2(IPr)$. By treatment with AgOTf (OTf = CF_3SO_3) and subsequent addition of phenyldiazomethane, this complex affords the alkylidene derivative $[(\eta^6\text{-}p\text{-cymene})OsCl(=CHPh)(IPr)]OTf$, which is an efficient initiator for olefin CM, RCM, and ROMP reactions.[16] We have now prepared related amido species $[(\eta^6\text{-}p\text{-cymene})Os(=NHR)(IPr)]BF_4$ and observed that the cyclohexyl derivative (R = Cy) undergoes IPr degradation by abstraction of an isopropyl group of one of the phenyl substituents.

Results and Discussion

1. Preparation of [(η^6-*p*-cymene)Os(=NHR)(IPr)]BF_4. These compounds have been prepared according to Scheme 1.

Scheme 1



Treatment of acetonitrile solutions of (η^6-*p*-cymene)$OsCl_2$(IPr) (**1**) with 2.5 equiv of $AgBF_4$ under reflux for 12 hours produces the precipitation of AgCl and the formation of the bis(solvento) compound [(η^6-*p*-cymene)Os($CH_3CN)_2$(IPr)][BF_4]$_2$ (**2**). This compound, which is isolated as a yellow solid in 74% yield, has been characterized by X-ray diffraction analysis (Figure 1). The geometry around the osmium center can be described as a distorted octahedron with the six-membered ring of the *p*-cymene ligand occupying the three sites of a face. The angles N(3)-Os-N(4), N(3)-Os-C(1), and N(4)-Os-C(1) are 82.0(2)º, 83.6(2)º, and 91.6(2)º, respectively. The separation between the metal and the IPr ligand, Os-C(1) = 2.096(7) Å, agrees well with those previously reported for Os-NHC compounds with normal coordination of the NHC unit.[15,16] In the $^{13}C\{^1H\}$ NMR spectrum, in dichloromethane-d_2 at room

temperature, the acetonitrile resonances appear at 126.7 (CN) and 5.2. (CH_3) ppm whereas the OsC signal of the IPr ligand is observed at 145.7 ppm.

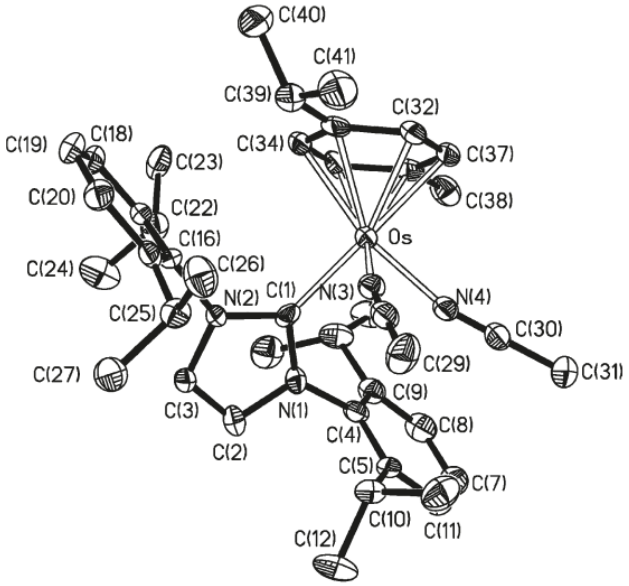


Figure 1. Molecular diagram of complex **2**. Selected bond lengths (Å) and angles (deg): Os-C(1) 2.096(7), Os-N(3) 2.028(6), Os-N(4) 2.040(6), N(3)-C(28) 1.161(8), N(4)-C(30) 1.149(7); N(3)-Os-N(4) 82.0(2), N(3)-Os-C(1) 83.6(2), N(4)-Os-C(1) 91.6(2).

Complex **2** reacts with aniline and cyclohexylamine. The addition of 10 equiv of the amines to the dichloromethane solutions of this compound leads after 5 days at 50ºC to the amido derivatives [(η^6-*p*-cymene)Os(=NHR)(IPr)]BF_4 (R = Ph (**3**), Cy (**4**)), which are isolated as red solids in about 60% yield (44% from **1**). Both compounds have been characterized by X-ray diffraction analysis (Figure 2). The geometry around the osmium atoms are the typical two-legged piano stool for five-coordinated half-sandwich complexes of this type[15,16j,17] with N(1)-Os-C(1) angles of 82.7(2)º (**3**) and 89.67(11)º (**4**). The amido nitrogen atoms N(1) are trigonal planar with angles C(28)-N(1)-Os, C(28)-N(1)-H(1), and Os-N(1)-H(1) of 137.2(4)º, 106(4)º, and 117(4)º, respectively, for **3** and 130.7(2)º, 113(2)º, and 116(2)º, respectively, for **4**. They are positioned for optimum dative $p_\pi(N) \rightarrow d_\pi(Os)$ bonding, which is sensitive to the donor power of the phenyl and cyclohexyl groups. Thus, in agreement with a donor power lower

for phenyl than for cyclohexyl, the Os-N(1) distance in the phenylamido complex **3** (1.924(5) Å) is about 0.04 Å longer than that in the cyclohexylamido derivative **4** (1.882(3) Å). However, the separations between the metal and the IPr ligand (2.078(6) Å (**3**) and 2.095(3) Å (**4**)) are statistically identical. In the ^{1}H NMR spectra of these compounds the most noticeable feature is the NH resonance. That of **3** appears at 11.69 ppm as a singlet, whereas that of **4** is observed at 11.67 ppm as a doublet with a H-H coupling constant of 7.8 Hz. In the ^{13}C{^{1}H} NMR spectra, the OsC resonances of the IPr ligands appear at 172.8 (**3**) and 169.7 (**4**) ppm.

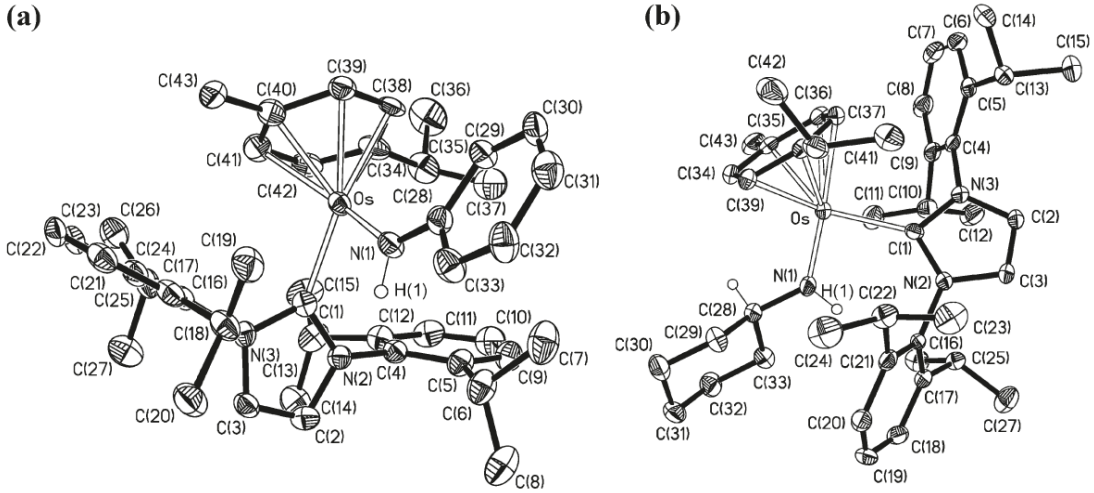


Figure 2. (a) Molecular diagram of complex **3**. Selected bond lengths (A˚) and angles (deg): Os-C(1) 2.078(6), Os-N(1) 1.924(5), N(1)-C(28) 1.416(7); N(1)-Os-C(1) 82.7(2), Os-N(1)-C(28) 137.2(4), C(28)-N(1)-H(1) 106(4), Os-N(1)-H(1) 117(4). (b) Molecular diagram of complex **4**. Selected bond lengths (A˚) and angles (deg): Os-C(1) 2.095(3), Os-N(1) 1.882(3), N(1)-C(28) 1.470(4); C(1)-Os-N(1) 89.67(11), Os-N(1)-C(28) 130.7(2), C(28)-N(1)-H(1) 113(2), Os-N(1)-H(1) 116(2).

Complexes **3** and **4** can be also prepared via amine intermediates by a three step procedure. Complex **1** reacts with $AgBF_4$ in dichloromethane to give the 16-valence-electron complex [(η^6-*p*-cymene)OsCl(IPr)]BF_4 (**5**).[15] The addition of 2.0 equiv of aniline and cyclohexylamine to the dichloromethane solutions of **5** affords the six-coordinate derivatives [(η^6-*p*-

cymene)OsCl(NH_2R)(IPr)]BF_4 (R = Ph (**6**), Cy (**7**)), which react with *n*-butyllithium to give the corresponding amido complexes **3** and **4** in 50-54% yield from **1**.

Complexes **6** and **7** are isolated as yellow solids in 91% and 95% yield, respectively. Complex **6** was also characterized by X-ray diffraction analysis (Figure 3). The geometry around the osmium center is close to octahedral, with the arene occupying three sites of a face. The angles C(1)-Os-N(1), C(1)-Os-Cl, and N(1)-Os-Cl are 91.5(3)º, 81.7(2)º, and 79.3(2)º, respectively. The separation between the aniline ligand and the metal (2.199(6) Å) is about 0.27 Å longer than that between the osmium atom and the amido group in **3**. Interestingly, the separation between the chloride ligand and the hydrogen atom H(1A) of the amine (2.506 Å) is shorter than the sum of the van der Waals radii of hydrogen and chlorine,[18] suggesting that there is an intramolecular Cl···H-N hydrogen bond between these atoms. The Os-C(1) bond length of 2.112(7) Å agrees well with the Os-IPr separations in **2**-**4**. In the ^{1}H NMR spectra of **6** and **7** in dichloromethane at -20 ºC, the most noticeable resonances are those due to the NH_2 groups. In the spectrum of **6**, they appear at 5.10 and 4.06 ppm, whereas in that of **7** they are observed at 3.05 and 2.73 ppm. In the ^{13}C{^{1}H} NMR spectra, the OsC resonances of the IPr ligands appear at 150.2 (**6**) and 169.1 (**7**) ppm.

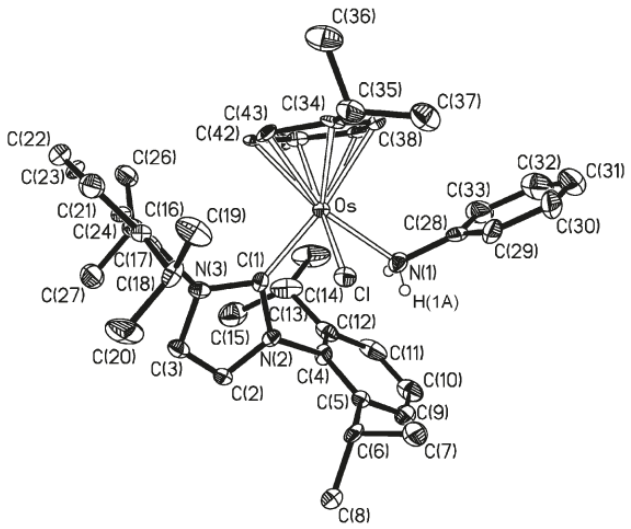
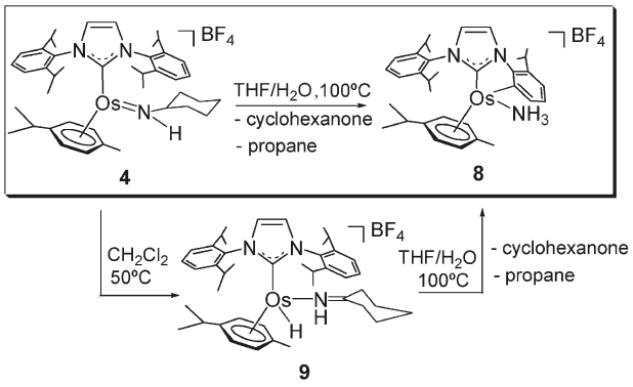


Figure 3. Molecular diagram of complex **6**. Selected bond lengths (A˚) and angles (deg): Os-Cl

2.4225(19), Os-C(1) 2.112(7), Os-N(1) 2.199(6), N(1)-C(28) 1.443(10), Cl 3 3 3 H-(1A) 2.506; C(1)-Os-Cl 81.7(2), N(1)-Os-Cl 79.3(2), C(1)-Os-N(1) 91.5(3), Os-N(1)-C(28) 116.9(5).

2. Degradation of [(η^6-*p*-cymene)Os(=NHCy)(IPr)]BF_4. This complex decomposes in tetrahydrofuran at 100 ºC and in the presence of traces of water (2.0 equiv) to give cyclohexanone, which was identified by GC-MS, propane, and the organometallic compound [(η^6-*p*-cymene)Os{CCHCHCHC(^{i}Pr)CNCHCHN($C_6H_3{}^iPr_2$)C}(NH_3)]BF_4 (**8**), which is isolated after 4 days as a yellow solid in 57% yield, according to Scheme 2. This complex has been also characterized by X-ray diffraction analysis (Figure 4). The structure proves the abstraction of an isopropyl group from one of the phenyl substituents of the IPr ligand of **7**, to form a polycyclic system of three fused rings, and the presence of an ammonia molecule coordinated to the metal center. The geometry around the osmium center is close to octahedral, with the arene ligand occupying three sites of a face. The angles formed by the ammonia molecule and the metalated carbon atoms are 89.24(18)º (C(1)-Os-N(5)) and 81.1(2)º C(5)-Os-N(5), whereas the C(1)-Os-C(5) angle is 76.1(2)º. The metalatricycle core is almost planar (maximum deviation 0.0762(46) Å for C(5)). The metalation of the aromatic substituent produces the shortening of the metal-carbene separation. Thus, the Os-C(1) bond length of 2.023(5) Å, which is about 0.05 Å shorter than the Os-C(5) distance of 2.072(5) Å, is also between 0.02 and 0.09 Å shorter than the Os-carbene separations in **2**, **3**, **4**, and **6**. The Os-N(5) bond length of 2.153(5) Å agrees well with the Os-aniline separation in **6**. The NH_3 resonance in the ^{1}H NMR spectrum of **8** in dichloromethane-d_2 at room temperature is observed at 2.59 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the metalated carbon atoms appear at 171.2 (C(1)) and 146.9 (C(5)) ppm.

Scheme 2



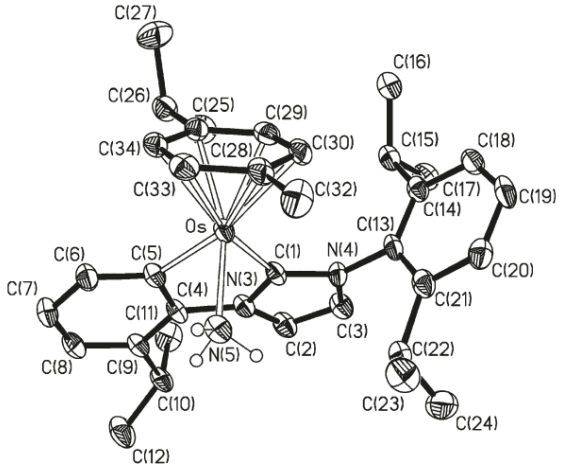
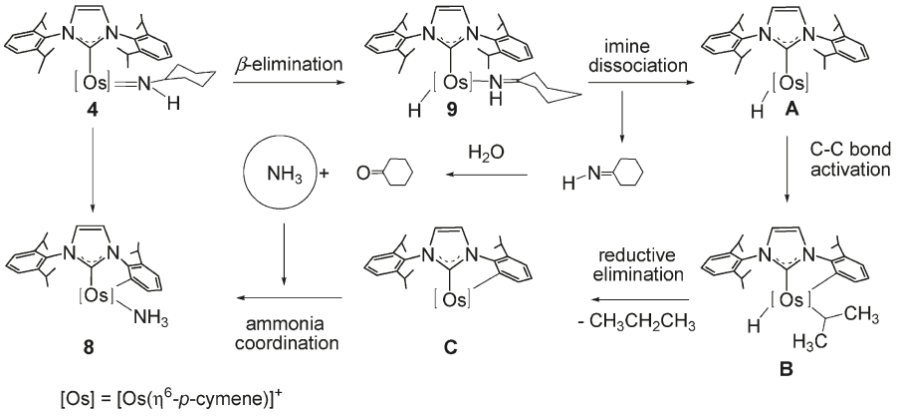


Figure 4. Molecular diagram of complex **8**. Selected bond lengths (A˚) and angles (deg): Os-C(1) 2.023(5), Os-C(5) 2.072(5), Os-N(5) 2.153(5); C(1)-Os-C(5) 76.1(2), C(1)-Os-N(5) 89.24(19), C(5)-Os-N(5) 81.1(2).

Complex **4** undergoes a hydrogen β-elimination reaction in dichloromethane at 50ºC to give after 12 h the hydride-imine derivative $[(\eta^6\text{-}p\text{-cymene})OsH(NH{=}\overline{CCH_2CH_2CH_2CH_2CH_2})(IPr)]BF_4$ (**9**) which is isolated as an orange solid in 77% yield. The presence of a hydride ligand in this compound is strongly supported by its ^1H NMR spectrum in dichloromethane-d_2 at room temperature, which shows a singlet at -8.75 ppm. In the $^{13}C\{^1H\}$ NMR spectrum the most noticeable resonances are two singlets at 169.5 and 79.3 ppm corresponding to the OsC and NC carbon atoms of the IPr and imine ligands, respectively. Complex **9** is an intermediate species in the transformation of **4** to **8**. In agreement with this, we have

observed that **9** gives **8** in tetrahydrofuran at 100 ºC and in the presence of 2 equiv of water. The formation of **8** can be rationalized according to Scheme 3. The dissociation of the imine ligand from **9** should give the unsaturated hydride intermediate **A**, which could promote the C-C cleavage of an isopropyl-aryl bond of one of the substituents of the IPr ligand. uents of the IPr ligand. A direct C-C cleavage has been proposed by Whittlesey for the methyl abstraction from an aryl substituent of 1,3-bis(2,4,6-trimethylphenyl)-imidazolylidene (IMes) in complex $RuH_2(CO)(IMes)_2$-(PPh_3).[14] The process should lead to a hydride-isopropyl intermediate **B**, containing a metalated NHC ligand. The reductive elimination of propane from **B** should give **C**. It is well known that compounds containing carbon-nitrogen double bonds are hydrolyzed to the corresponding aldehydes or ketones. For alkyl imines the hydrolysis is easy and can occur with water. Thus, the coordination to the osmium atom of **C** of the ammonia molecule, generated from the hydrolysis of the released cyclohexylimine ligand, should yield **8**.

Scheme 3



Splitting of the C-C single bonds of hydrocarbons is a scarcely observed reaction.[19] Usually such C-C bond activation requires either the attainment of the aromaticity [20] or the use of a coordination auxiliary that brings the transition metal to the C-C bond,[21] as occurs in this case. Specific C-C activations have also been achieved under photochemical conditions.[22] Although one should expect that the C-H bond activation of the abstracted isopropyl group were more accessible in **A** than the C-C

cleavage, it should be taken into account that the former process is expected to be reversible, and so the irreversible C-C bond activation becomes possible at elevated temperature.

Concluding Remarks

Phenyl- and cyclohexylamido complexes of osmium stabilized by the IPr ligand can be prepared via amine intermediates and by reaction of the bis(solvento) cation $[(\eta^6\text{-}p\text{-cymene})Os(CH_3CN)_2(IPr)]^+$ with amines. At 100 ºC in tetrahydrofuran and in the presence of traces of water the IPr ligand of the cyclohexylamido derivative undergoes degradation, by C-C bond activation of an isopropyl-aryl bond of one of its substituents, to afford a polycyclic system of three fused rings with an Os-NHC core.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents (except acetonitrile, which was dried and distilled under argon) were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker ARX 300 or a Bruker AVANCE 400 instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$). Coupling constants, *J*, are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer (Nujol mulls on polyethylene sheets). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a Micro TOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). The starting materials $(\eta^6\text{-}p\text{-cymene})OsCl_2(IPr)$ (**1**) and $[(\eta^6\text{-}p\text{-cymene})\text{-}OsCl(IPr)]BF_4$ (**5**) were prepared as previously described in the literature.[15]

Preparation of $[(\eta^6\text{-}p\text{-cymene})Os(CH_3CN)_2(IPr)][BF_4]_2$ (2). A light-protected mixture of $(\eta^6\text{-}p\text{-cymene})OsCl_2(IPr)$ (**1**) (1 g, 1.276 mmol) and $AgBF_4$ (620 mg, 3.19 mmol) in 15 mL of acetonitrile was heated under reflux overnight. After this time the suspension was filtered through Celite and the solution was evaporated to dryness. The residue was treated with 15 mL of dichloromethane and filtered again

through Celite. After evaporation of the solvent, the addition of diethyl ether caused the formation of a very pale yellow solid. Yield: 920 mg (74%). Anal. Calcd for $C_{41}H_{56}B_2F_8N_4Os$: C, 50.83; H, 5.82; N, 5.78. Found: 50.78; H, 5.68; N, 5.69. IR (cm^{-1}): ν(CH_3CN) 2323 and 2294 (w); ν(BF_4) 1055 (s). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.63 (t, J_{H-H} = 7.2, 2H, H_p-2,6-^{i}Pr$_2$Ph), 7.48 (d, J_{H-H} = 7.2, 4H, H_m-2,6-^{i}Pr$_2$Ph), 7.24 (s, 2H, NCH), 5.65 (d, J_{H-H} = 5.4, 2H, Ph-*p*-cymene), 5.49 (d, J_{H-H} = 5.4, 2H, Ph-*p*-cymene), 2.56 (sept, J_{H-H} = 6.9, 4H, C*H*(CH_3)$_2$-2,6-^{i}Pr$_2$Ph), 2.51 (br s, 6H, CH_3CN), 2.02 (s, 3H, C*H*$_3$-*p*-cymene), 1.44 (d, J_{H-H} = 6.9, 12H, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.19 (sept, J_{H-H} = 6.6, 1H, C*H*(CH_3)$_2$-*p*-cymene), 1.14 (m, 18H, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph + CH(C*H*$_3$)$_2$-*p*-cymene). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 146.2 (s, C_o-2,6-^{i}Pr$_2$Ph), 145.7 (s, OsC), 137.1 (s, C_{ipso}-2,6-^{i}Pr$_2$Ph), 132.7 (s, C_p-2,6-^{i}Pr$_2$Ph), 128.7 (s, NCH), 126.7 (s, CH_3*C*N), 125.5 (s, C_m-2,6-^{i}Pr$_2$Ph), 105.6 (s, C_{ipso}-*p*-cymene), 97.5 (s, C_{ipso}-*p*-cymene), 84.2 (s, Ph-*p*-cymene), 82.4 (s, Ph-*p*-cymene), 31.4 (s, *C*H(CH_3)$_2$-*p*-cymene), 29.7 (s, *C*H(CH_3)$_2$-2,6-^{i}Pr$_2$Ph), 26.4 and 22.8 (both s, CH(*C*H$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 22.9 (s, CH(*C*H$_3$)$_2$-*p*-cymene), 19.1 (s, *C*H$_3$-*p*-cymene), 5.2 (s, *C*H_3CN).

Preparation of [(*η*^{6}-*p*-cymene)Os(dNHPh)(IPr)][BF$_4$] (3). *Method a*: A mixture of [(η^6-*p*-cymene)Os(CH_3CN)$_2$(IPr)][BF_4]$_2$ (100 mg, 0.103 mmol) and aniline (143 μL, 1.030 mmol) in 10 mL of dichloromethane was heated at 50 ºC for 5 days. After this time the suspension was filtered through Celite and the resulting solution evaporated to dryness. The addition of diethyl ether caused the formation of a dark red solid, which was then washed with diethyl ether (4 x 5 mL). Yield: 55 mg (60%). *Method b*: A yellow suspension of [(η^6-*p*-cymene)OsCl(NH_2Ph)(IPr)][BF_4] (**6**) (150 mg, 0.162 mmol) and ^{n}BuLi (71 μL, 0.178 mmol) in 8 mL of THF was placed into an ice bath and stirred for 30 min. After this time the mixture was allowed to reach room temperature slowly and then filtered through Celite and evaporated to dryness. The residue was treated with 10 mL of dichloromethane filtered again through Celite. After evaporation of the solvent, the addition of diethyl ether caused the formation of a dark red solid, which was washed with diethyl ether (3 x 2 mL) and dried in vacuo. Yield: 95 mg (66%). Anal. Calcd for $C_{43}H_{56}BF_4N_3Os$: C, 57.90; H, 6.33; N, 4.71. Found: C, 57.97; H, 6.47; N, 4.40. IR (cm^-

^{1}): ν(NH) 3317 (w); ν(BF_4) 1049 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 243 K): δ 11.69 (s, 1H, NH), 7.55 (t, J_{H-H} = 7.8, 2H, H_p-2,6-$^{i}Pr_2Ph$), 7.39 (d, J_{H-H} = 7.8, 4H, H_m-2,6-$^{i}Pr_2Ph$), 7.31 (s, 2H, NCH), 7.3-7.1 (m, 5H, aniline), 6.0 (d, J_{H-H} = 4.2, 2H, Ph-*p*-cymene), 5.78 (d, J_{H-H} = 5.1, 2H, Ph-*p*-cymene), 2.61 (sept, J_{H-H} = 6.6, 4H, C*H*$(CH_3)_2$-2,6-$^{i}Pr_2Ph$), 2.13 (br, 1H, C*H*$(CH_3)_2$-*p*-cymene), 1.27 and 1.20 (both d, J_{H-H} = 6.6, 24H, CH(C*H*$_3$)$_2$-2,6-$^{i}Pr_2Ph$), 1.12 (s, 3H, C*H*$_3$-*p*-cymene), 0.84 (d, J_{H-H} = 6.9, 6H, CH(C*H*$_3$)$_2$-*p*-cymene). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 172.8 (s, OsC), 161.0 (s, C_{ipso}-aniline), 146.4 (s, C_o-2,6-$^{i}Pr_2Ph$), 135.6 (s, C_{ipso}-2,6-$^{i}Pr_2Ph$), 132.7 (s, C_p-2,6-$^{i}Pr_2Ph$), 131.0 (s, C_m-aniline), 127.5 (s, NCH), 125.5 (s, C_m-2,6-$^{i}Pr_2Ph$), 125.2 (s, C_p-aniline), 121.7 (s, C_o-NH_2-Ph), 91.3 (s, C_{ipso}-*p*-cymene), 80.1 (s, C_{ipso}-*p*-cymene), 79.8 (s, Ph-*p*-cymene), 77.0 (s, Ph-*p*-cymene), 32.7 (s, *C*H$(CH_3)_2$-*p*-cymene), 30.3 (s, *C*H$(CH_3)_2$-2,6-$^{i}Pr_2Ph$), 27.1 and 22.9 (both s, CH(*C*H$_3$)$_2$-2,6-$^{i}Pr_2Ph$), 23.6 (s, CH(*C*H$_3$)$_2$-*p*-cymene), 19.5 (s, *C*H$_3$-*p*-cymene).

Preparation of [(*η*^{6}-*p*-cymene)Os(dNHCy)(IPr)][BF_4] (4). *Method a*: A mixture of [(η^{6}-*p*-cymene)Os$(CH_3CN)_2$(IPr)][BF_4]$_2$ (**1**) (380 mg, 0.392 mmol) and cyclohexylamine (224 μL, 1.96 mmol) in 10 mL of dichloromethane was heated at 50 ºC for 5 h After this time the suspension was filtered through Celite and the resulting solution evaporated to dryness. The addition of diethyl ether caused the formation of a red solid, which was then washed with diethyl ether (4 x 5 mL). Yield: 220 mg (63%). *Method b*: A yellow suspension of [(η^{6}-*p*-cymene)OsCl(NH_2Cy)(IPr)][BF_4] (**7**) (200 mg, 0.214 mmol) and ^{n}BuLi (95 μL, 0.237 mmol) in 8 mL of THF was placed into an ice bath and stirred for 30 min. After this time the mixture was allowed to reach room temperature slowly and then filtered through Celite and evaporated to ca. 0.1 mL. The residue was treated with 10 mL of dichloromethane and filtered again through Celite. After evaporation of the solvent to ca. 0.1 mL, the addition of diethyl ether caused the formation of a red solid, which was washed with diethyl ether (3 x 2 mL) and dried in vacuo. Yield: 111.2 mg (58%). Anal. Calcd for $C_{43}H_{62}BF_4N_3Os{\cdot}0.5CH_2Cl_2$: C, 55.55; H, 6.75; N, 4.47. Found: C, 56.03; H, 6.24; N, 4.01. IR (cm^{-1}): ν(NH) 3323 (w); ν(BF_4) 1049 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 243 K): δ 11.67 (d, J_{H-H} = 7.8, 1H, N*H*), 7.59 (t, J_{H-H} = 7.6, 2H, H_p-2,6- Pr_2Ph), 7.41 (d, J_{H-H} = 7.6, 4H,

H$_m$-2,6- Pr$_2$Ph), 7.21 (s, 2H, NCH), 5.4-5.3 (m, 4H, Ph-*p*-cymene), 2.8-2.6 (m, 1H, Cy), 2.60 (sept, J = 6.8, 4H, C*H*(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.99 (sept, $J_{H\text{-}H}$ = 6.9, 1H, C*H*(CH$_3$)$_2$-*p*-cymene), 1.80 (s, 3H, C*H*$_3$-*p*-cymene), 1.7-1.5 (m, 5H, Cy), 1.40 and 1.15 (both d, $J_{H\text{-}H}$ = 6.8, 24H, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.04 (d, $J_{H\text{-}H}$ = 6.9, 6H, CH(C*H*$_3$)$_2$-*p*-cymene), 0.76-0.61 (m, 6H, Cy). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 169.7 (s, OsC), 146.5 (s, C$_o$-2,6-^{i}Pr$_2$Ph), 136.3 (s, C$_{ipso}$-2,6-^{i}Pr$_2$Ph), 131.8 (s, C$_p$-2,6-^{i}Pr$_2$Ph), 126.7 (s, NCH), 125.4 (s, C$_m$-2,6-^{i}Pr$_2$Ph), 98.2 (s, C$_{ipso}$-*p*-cymene), 85.7 (s, C$_{ipso}$-*p*-cymene), 79.6 (s, *C*$_\infty$-Cy), 77.2 (s, Ph-*p*-cymene), 74.6 (s, Ph-*p*-cymene), 35.6 (s, Cy), 32.5 (s, CH(*C*H$_3$)$_2$-*p*-cymene), 29.7 (s, *C*H(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 26.7 and 23.0 (both s, CH(*C*H$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 25.8 and 25.7 (s, Cy), 23.8 (s, *C*H(CH$_3$)$_2$-*p*-cymene), 20.0 (s, *C*H$_3$-*p*-cymene).

Preparation of [(*η*^{6}-*p*-cymene)OsCl(NH$_2$Ph)(IPr)][BF$_4$] (6). To a green solution of [(η^6-*p*-cymene)OsCl(IPr)]BF$_4$ (**5**) (300 mg, 0.336 mmol) in 10 mL of dichloromethane was added aniline (77 μL, 0.672 mmol), and the reaction mixture was stirred at room temperature for 10 min. The resulting red solution was concentrated to ca. 0.1 mL. The subsequent addition of diethyl ether caused the precipitation of a yellow solid, which was washed with diethyl ether (3 x 2 mL) and dried in vacuo. Yield: 282.7 mg (91%). Anal. Calcd for $C_{43}H_{57}BClF_4N_3Os{\cdot}0.5CH_2Cl_2$: C, 53.81; H, 6.02; N, 4.33. Found: C, 53.77; H, 6.01; N, 3.83. IR (cm^{-1}): ν(NH$_2$) 3319 and 3249 (w); ν(BF$_4$) 1060 (s). ^{1}H NMR (500 MHz, CD_2Cl_2, 253 K): δ 7.62 (t, $J_{H\text{-}H}$ = 7.6, 2H, H$_p$-2,6-^{i}Pr$_2$Ph), 7.50 and 7.42 (both d, $J_{H\text{-}H}$ = 7.6, 2H each, H$_m$-2,6-^{i}Pr$_2$Ph), 7.28 (t, $J_{H\text{-}H}$ = 7.6, 2H, H$_m$-aniline), 7.17 (s, 2H, NCH), 7.16 (t, $J_{H\text{-}H}$ = 7.6, 1H, H$_p$-aniline), 6.78 (d, $J_{H\text{-}H}$ = 7.6, 2H, H$_o$-aniline), 5.58, 5.11, 4.05, and 3.95 (all br, 1H each, Ph-*p*-cymene), 5.10 and 4.06 (both br, 1H each, NH$_2$), 3.21 and 2.79 (both br, 2H each, C*H*(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 2.36 (br, 1H, C*H*(CH$_3$)$_2$-*p*-cymene), 2.33 (s, 3H, C*H*$_3$-*p*-cymene), 1.44 (br, 12H, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.21 and 1.06 (d, $J_{H\text{-}H}$ = 6.8, 6H each, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.00 and 0.93 (both d, $J_{H\text{-}H}$ = 6.8, 3H each, CH(C*H*$_3$)$_2$-*p*-cymene). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (125.7 MHz, CD_2Cl_2, 253 K): δ 150.2 (s, OsC), 145.9 (s, C$_{ipso}$-aniline), 145.8 (s, C$_o$-2,6-^{i}Pr$_2$Ph), 144.9 (s, C$_{ipso}$-2,6-^{i}Pr$_2$Ph), 132.1 (s, C$_p$-2,6-^{i}Pr$_2$Ph), 129.5 (s, C$_m$-aniline), 126.9 (s, NCH), 126.5 (s, C$_p$-aniline), 125.1 and 124.8 (s, C$_m$-2,6-

^{i}Pr$_2$Ph), 119.7 (s, C$_o$-aniline), 115.6 (s, C$_{ipso}$-*p*-cymene), 82.2 (s, C$_{ipso}$-*p*-cymene), 86.2, 77.2, 73.9, and 59.5 (all s, Ph-*p*-cymene), 30.5 (s, *C*H(CH$_3$)$_2$-*p*-cymene), 29.1 and 28.7 (s, *C*H(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 27.3, 26.5, and 22.8 (all s, CH(*C*H$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 24.3 and 18.0 (both s, CH(*C*H$_3$)$_2$-*p*-cymene), 19.8 (s, C*H*$_3$-*p*-cymene).

Preparation of [(*η*^{6}-*p*-cymene)OsCl(NH$_2$Cy)(IPr)][BF$_4$] (7). To a green solution of [(η^6-*p*-cymene)OsCl(IPr)]BF$_4$ (**5**) (250 mg, 0.280 mmol) in 8 mL of dichloromethane was added cyclohexylamine (64 μL, 0.560 mmol), and the mixture was stirred at room temperature for 10 min. The resulting orange-red solution was concentrated to 0.1 mL. The subsequent addition of diethyl ether caused the precipitation of a yellow solid, which was washed with diethyl ether (3 x 2 mL) and dried in vacuo. Yield: 248.3 mg (95%). Anal. Calcd for C$_{43}$H$_{63}$BClF$_4$N$_3$Os·CH$_2$Cl$_2$: C, 51.84; H, 6.43; N, 4.12. Found: C, 51.57; H, 6.48; N, 3.97. IR (cm^{-1}): ν(NH$_2$) 3316 and 3252 (w); ν(BF$_4$) 1059 (s). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 233 K): δ 7.65 (t, J_{H-H} = 7.5, 2H, H$_p$-2,6-^{i}Pr$_2$Ph), 7.48 and 7.44 (both d, J_{H-H} = 7.5, 2H each, H$_m$-2,6-^{i}Pr$_2$Ph), 7.14 and 6.93 (both s, 1H each, NCH), 5.85 and 5.16 (both d, J_{H-H} = 5.4, 1H each, Ph-*p*-cymene), 5.57 and 3.92 (both d, J_{H-H} = 5.0, 1H each, Ph-*p*-cymene), 3.24 (m, 1H, C*H*$_α$-Cy), 3.22, 2.99, 2.72, and 2.61 (all m, 1H each, C*H*(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 3.05 and 2.73 (both s br, 1H each, NH$_2$), 2.39 (m, 1H, C*H*(CH$_3$)$_2$-*p*-cymene), 2.27 (s, 3H, C*H*$_3$-*p*-cymene), 1.95, 1.54, 1.51, 1.44, 1.20, 1.13, 1.05, 0.95, 0.46, and 0.27 (m, 10H, Cy), 1.26, 1.17, 1.10, and 0.95 (d, J_{H-H} = 6.8, 6H each, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.4-0.9 (m, 30H, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph + CH(C*H*$_3$)-*p*-cymene). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (75.4 MHz, CD$_2$Cl$_2$, 243 K): δ 169.1 (s, OsC), 147.3, 145.9, 145.0, and 143.1 (all s, C$_o$-2,6-^{i}Pr$_2$Ph), 135.2 and 129.2 (both s, C$_{ipso}$-2,6-^{i}Pr$_2$Ph), 132.0 and 131.9 (s, C$_p$-2,6-^{i}Pr$_2$Ph), 127.5 and 126.9 (both s, NCH), 126.8, 124.9, 124.8, and 124.0 (all s, C$_m$-2,6-^{i}Pr$_2$Ph), 114.7 and 81.1 (both s, C$_{ipso}$-*p*-cymene), 84.2, 78.4, 70.6, and 61.4 (all s, Ph-*p*-cymene), 64.9 (s, C$_α$-Cy), 35.8 (s, Cy), 33.1 (s, Cy), 30.2 (s, *C*H(CH$_3$)$_2$-*p*-cymene), 29.2, 28.5, 28.1, and 27.8, (all s, *C*H(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 29.4, 28.9, 28.0, 26.7, 26.1, 25.8, 25.6, and 24.2 (all s, CH(*C*H$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 24.7, 24.4, and 24.3 (s, Cy), 19.2 (s, C*H*$_3$-*p*-cymene), 18.0, and 15.1 (both s, CH(*C*H$_3$)$_2$-*p*-cymene).

Preparation of [(η^6-*p*-cymene)Os{CCHCHCHC(^{i}Pr)CNCHCHN($C_6H_3{}^iPr_2$)C}(NH_3)]BF_4 (8). A suspension of [(η^6-*p*-cymene)Os(=NHCy)(IPr)]BF_4 (**4**) (350 mg, 0.392 mmol) and H_2O (14 μL, 0.783 mmol) in 10 mL of THF was heated at 100 ºC for 4 days in a Schlenk flask equipped with a Teflon closure. After this time the suspension was filtered through Celite and the solution concentrated to ca. 0.1 mL. The addition of diethyl ether caused the formation of a yellow solid, which was washed with diethyl ether (4 x 5 mL) and dried in vacuo. Yield: 170 mg (57%). Anal. Calcd for $C_{34}H_{46}BF_4N_3Os$: C, 52.77; H, 5.99; N, 5.43. Found: C, 52.32; H, 5.59; N, 5.13. IR (cm^{-1}): ν(NH_3) 3258. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.95 (d, $J_{H\text{-}H}$ = 2.2, 1H, NCH), 7.79 (d, $J_{H\text{-}H}$ = 7.6, 1H, H$_m$-2,6-^{i}Pr$_2$Ph), 7.66 (t, $J_{H\text{-}H}$ = 7.6, 1H, H$_p$-2,6-^{i}Pr$_2$Ph), 7.48 (d, $J_{H\text{-}H}$ = 7.2, 1H, H$_m$-2,6-^{i}Pr$_2$Ph), 7.46 (d, $J_{H\text{-}H}$ = 7.6, 1H, H$_m$- 2,6-^{i}Pr$_2$Ph), 7.15 (d, $J_{H\text{-}H}$ = 2.2, 1H, NCH), 7.11 (d, $J_{H\text{-}H}$ = 7.2, 1H, H$_m$-2,6-^{i}Pr$_2$Ph), 6.98 (t, $J_{H\text{-}H}$ = 7.2, 1H, H$_p$-2,6-^{i}Pr$_2$Ph), 5.73 and 5.30 (both d, $J_{H\text{-}H}$ = 6.0, 1H each, Ph-*p*-cymene), 4.48 and 4.26 (both d, $J_{H\text{-}H}$ = 5.2, 1H each, Ph-*p*-cymene), 3.59 (sept, $J_{H\text{-}H}$ = 6.6, 1H, C*H*(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 2.59 (br, 3H, NH_3), 2.60 (m, 1H, C*H*(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 2.25 (sept, $J_{H\text{-}H}$ = 6.3, 1H, C*H*(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 2.07 (m, 1H, C*H*(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 2.01 (s, 3H, C*H*$_3$-*p*-cymene), 1.47, 1.42, 1.38, and 1.04 (all d, 3H each, $J_{H\text{-}H}$ = 6.6, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.26 and 1.24 (both d, 3H each, $J_{H\text{-}H}$ = 6.3, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 0.94 and 0.43 (both d, 3H each, $J_{H\text{-}H}$ = 6.9, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 171.2 (s, OsC(1)), 146.9 (s, OsC(5)), 146.8, 146.6, and 145.4 (all s, C$_o$-2,6-^{i}Pr$_2$Ph), 139.9 (s, C$_m$-2,6-^{i}Pr$_2$Ph), 131.2 and 126.7 (both s, C$_p$-2,6-^{i}Pr$_2$Ph), 124.6, 124.3, and 122.3 (all s, C$_m$-2,6-^{i}Pr$_2$Ph), 124.2 and 119.4 (both s, NCH), 98.4 and 90.6 (s, C$_{ipso}$-*p*-cymene), 89.7, 82.9, 82.1, and 68.4 (all s, Ph-*p*-cymene), 30.9 (s, *C*H(CH$_3$)$_2$-*p*-cymene), 28.9, 28.8, 28.7 (all s, *C*H-(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 26.5, 24.6, 23.9, 23.7, 23.2, and 22.4 (all s, CH(*C*H$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 24.5 and 20.4 (both s, CH(*C*H$_3$)$_2$-*p*-cymene), 18.4 (s, *C*H$_3$-*p*-cymene).

Preparation of [(η^6-*p*-cymene)OsH(NH=CCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$)(IPr)]BF_4 (9). A solution of [(η^6-*p*-cymene)Os(=NHCy)(IPr)]BF_4 (**4**) (260 mg, 0.2895 mmol) in 10 mL of dichloromethane was

heated at 50 ºC overnight. It was filtered through Celite and concentrated to ca. 0.1 mL. The addition of diethyl ether caused the formation of an orange solid, which was washed with diethyl ether (4 x 5 mL). Yield: 201 mg (77%). Anal. Calcd for $C_{43}H_{62}BF_4N_3Os$: C, 57.51; H, 6.96; N, 4.68. Found: C, 57.85; H, 6.67; N, 4.41. IR (cm^{-1}): ν(NH) 3319 (w); ν(H) 2159 (w); ν(BF_4) 1048 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 11.65 (br, 1H, NH), 7.59 (t, J_{H-H} = 7.7, 2H, H$_p$-2,6-^{i}Pr$_2$Ph), 7.40 (d, J_{H-H} = 7.7, 4H, H$_m$-2,6-^{i}Pr$_2$Ph), 7.22 (s, 2H, NCH), 5.42 and 5.39 (both br, 4H, Ph-*p*-cymene), 2.60 (sept, J_{H-H} = 6.8, 4H, C*H*(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.99 (sept, J_{H-H} = 6.9, 1H, C*H*(CH$_3$)$_2$-*p*-cymene), 1.80 (s, 3H, C*H*$_3$-*p*-cymene), 2.05, 2.03, 1.79, 1.61, and 1.59 (br, 5H, NH$_2$-C*H*$_2$-cy), 1.39 and 1.14 (both d, J_{H-H} = 6.8, 12H each, CH(C*H*$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 1.03 (d, J_{H-H} = 6.9, 6H, CH(C*H*$_3$)$_2$-*p*-cymene), 1.36, 1.30, 1.15, 0.92, and 0.68 (br, 5H, NH$_2$-C*H*$_2$-cy), -8.75 (s, 1H, OsH). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 169.5 (s, OsC), 145.8 (s, C$_o$-2,6-^{i}Pr$_2$Ph), 136.0 (s, C$_{ipso}$-2,6-^{i}Pr$_2$Ph), 131.5 (s, C$_p$-2,6-^{i}Pr$_2$Ph), 126.5 (s, NCH), 125.2 (s, C$_m$-2,6-^{i}Pr$_2$Ph), 97.8 (s, C$_{ipso}$-*p*-cymene), 85.5 (s, C$_{ipso}$-*p*-cymene), 79.3 (s, C$_α$-Cy), 76.8 (s, Ph-*p*-cymene), 74.3 (s, Ph-*p*-cymene), 35.3, 30.9, 25.5, 24.9 and 24.6 (s, Cy), 32.3 (s, CH(*C*H$_3$)$_2$-*p*-cymene), 29.4 (s, *C*H(CH$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 26.5 and 22.8 (both s, CH(*C*H$_3$)$_2$-2,6-^{i}Pr$_2$Ph), 23.5 (s, CH(*C*H$_3$)$_2$-*p*-cymene), 19.9 (s, *C*H$_3$-*p*-cymene).

Structural Analysis of Complexes 2, 3, 4, 6, and 8. X-ray data were collected on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 A˚) operating at 50 kV and 40(**2, 3, 4, 8**)/ 30(**6**) mA. Data were collected over the complete sphere. Each frame exposure time was 10 or 20 s covering 0.3º in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[23] The structures were solved by direct methods. Refinement of complexes was performed by full-matrix least-squares on F^2 with SHELXL97,[24] including isotropic and subsequently anisotropic displacement parameters.

Crystal data for **2**: $C_{41}H_{56}N_4Os{\cdot}2BF_4{\cdot}0.5NC_2H_3$, M_w 989.24, irregular block, brown (0.14 x 0.08 x 0.04), monoclinic, space group $P2_1/c$, a = 11.288(3) A˚, b = 19.507(5) A˚, c = 20.839(6) A˚, β =

99.531(7)º, V = 4526(2) A˚3, Z = 4, D_{calc} = 1.452 g cm^{-3}, F(000) = 1996, T = 100(2) K, μ = 2.884 mm^{-1}; 45 816 measured reflections (2θ: 3-58º, ω scans 0.3º), 11 151 unique (R_{int} = 0.1308); min./max. transm factors 0.710/0.831. Final agreement factors were R_1 = 0.0494 (5669 observed reflections, $I > 2\sigma(I)$) and wR_2 = 0.0951; data/restraints/parameters 11 151/2/ 531; GoF = 0.719. Largest peak and hole: 1.815 and -1.080 e/A˚3.

Crystal data for **3**: $C_{43}H_{56}BF_4N_3Os \cdot BF_4 \cdot 0.2CH_2Cl_2 \cdot 0.2C_4H_{10}O$, M_w 923.73, irregular block, red (0.06 x 0.06 x 0.04), triclinic, space group $P\bar{1}$, a = 11.905(3) A˚, b = 12.513(3) A˚, c = 16.552(3) A˚, R = 108.329(4)º, β = 92.278(5)º, γ = 112.821(4)º, V = 2120.1(8) A˚3 Z = 2, D_{calc} = 1.447 g cm^{-3}, F(000) = 938, T = 100(2) K, μ = 3.084 mm^{-1}; 23 930 measured reflections (2θ: 3-58º, ω scans 0.3º), 10 028 unique (R_{int} = 0.0591); min./max. transm factors 0.674/0.887. Final agreement factors were R_1 = 0.0529 (8296 observed reflections, $I > 2\sigma(I)$) and wR_2 = 0.1145; data/restraints/parameters 10 028/22/515; GoF = 1.010. Largest peak and hole: 1.560 and -2.088 e/A˚3.

Crystal data for **4**: $C_{43}H_{62}N_3Os \cdot BF_4$, M_w 897.97, irregular prism, brown (0.14 x 0.12 x 0.08), monoclinic, space group $P2_1/c$, a = 11.875(3) A˚, b = 16.183(4) A˚, c = 21.160(6) A˚, β = 94.704(5)º, V = 4052.7(19) A˚3, Z = 4, D_{calc} = 1.472 g cm^{-3}, F(000) = 1832, T = 100(2) K, μ = 3.198 mm^{-1}; 50 399 measured reflections (2θ: 3-58º, ω scans 0.3º), 10 080 unique (R_{int} = 0.0649); min./max. transm factors 0.539/0.766. Final agreement factors were R_1 = 0.0295 (7439 observed reflections, $I > 2\sigma(I)$) and wR_2 = 0.0503; data/restraints/parameters 10 080/21/478; GoF = 0.886. Largest peak and hole: 1.534 and -0.867 e/A˚3.

Crystal data for **6**: $C_{43}H_{57}ClN_3Os \cdot BF_4$, M_w 928.38, irregular block, yellow (0.20 x 0.06 x 0.03), monoclinic, space group $P2_1$, a = 10.2084(15) A˚, b = 19.096(3) A˚, c = 1.1508(17) A˚, β = 110.698(3)º, V = 2033.4(5) A˚3, Z = 2, D_{calc} = 1.516 g cm^{-3}, F(000) = 940, T = 100(2) K, μ = 3.254 mm^{-1}; 25 433 measured reflections (2θ: 3-58º, ω scans 0.3º), 9639 unique (R_{int} = 0.0689); min./max. transm factors 0.691/0.909. Final agreement factors were R_1 = 0.0494 (8162 observed reflections, $I > 2\sigma(I)$) and wR_2 =

0.1027; Flack parameter 0.004(9); data/restraints/ parameters 9639/13/496; GoF = 0.995. Largest peak and hole: 2.045 and -2.279 e/A˚3.

Crystal data for **8**: $C_{34}H_{46}N_3Os{\cdot}BF_4{\cdot}CH_2Cl_2$, M_w 858.67, irregular block, yellow (0.14 x 0.04 x 0.04), monoclinic, space group $P2_1/c$, a = 12.6290(11) A˚, b = 12.2917(11) A˚, c = 23.440(2) A˚, β = 101.2130(10)º, V = 3569.1(5) A˚3, Z = 4, D_{calc} = 1.598g cm^{-3}, F(000) = 1720, T = 100(2) K, μ = 3.772 mm^{-1}; 40 471 measured reflections (2θ: 3-58º, ω scans 0.3º), 8498 unique (R_{int} = 0.0688); min./max. transm factors 0.484/ 0.746. Final agreement factors were R_1 = 0.0385 (6525 observed reflections, $I > 2\sigma(I)$) and wR_2 = 0.1001; data/restraints/ parameters 8498/3/434; GoF = 1.025. Largest peak and hole: 1.507 and -1.252 e/A˚3.

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Supporting Information Available. Experimental details for the synthesis, characterization and crystallographic data for **2**, **3**, **4**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675. (b) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104. (c) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673. (d) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079. (e) Severin, R.; Doye, S. *Chem. Soc. Rev.* **2007**, *36*, 1407. (f) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795. (g) Roesky, P. W. *Angew. Chem. Int. Ed.* **2009**, *49*, 4892.

(2) See for example: (a) Crevier, T. J.; Mayer, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5595. (b) Soper, J. D.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 5594. (c) Crevier, T. J.; Bennett, B. K.;

Soper, J. D.; Bowman, J. A.; Dehestani, A.; Hrovat, D. A.; Lovell, S.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 1059. (d) Soper, J. D.; Bennet, B. K.; Lovell, S.; Mayer, J. M. *Inorg. Chem.* **2001**, *40*, 1888. (e) Soper, J. D.; Mayer, J. M.; *J. Am. Chem. Soc.* **2003**, *125*, 12217. (f) Soper, J. D.; Rhile, I. J.; DiPascuale, A. G.; Mayer, J. M. *Polyhedron* **2004**, *23*, 323. (g) Soper, J. D.; Saganic, E.; Weinberg, D.; Hrovat, D. A.; Benedict, J. B.; Kaminsky, W.; Mayer, J. M. *Inorg. Chem.* **2004**, *43*, 5804.

(3) (a) Daniel, T.; Mahr, N.; Werner, H. *Chem. Ber.* **1993**, *126*, 1403. (b) Clapham, S. E.; Morris, R. H. *Organometallics*, **2005**, *24*, 479.

(4) (a) Arduengo, A. J. III *Acc Chem. Res.* **1999**, *32,* 913. (b) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (c) de Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009***, 253*, 862.

(5) (a) Arnold, P. L. Pearson, S. *Coord. Chem. Rev.* **2007,** *251*, 596. (b) Schuster, O.; Yang, L.; Raubenheimer, H. G., Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445.

(6) (a) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem. Int. Ed.* **2007**, *46*, 2768. (b) Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440. (c) Samojlowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev*. **2009**, *109*, 3708. (d) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612.

(7) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247.

(8) See for example: (a) Titcomb, L. R.; Caddick, S.; Cloke, F. G. N.; Wilson, D. J.; McKerrecher, D. *Chem. Commun* **2001**, 1388. (b) Simms, R. W.; Drewitt, M. J.; Baird, M. C. *Organometallics* **2002**, *21*, 2958. (c) Lewis, A. K.; de, K; Caddick, S.; Cloke, F. G. N.; Billingham, N. C.; Hitchcock., P. B.; Leonard, J. *J. Am. Chem. Soc.* **2003**, *125*, 10066. (d) Trmka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546. (e) Allen, D. P.; Crudden, C. M.; Calhoun, L. A.; Wang, R. Y. *J. Organomet. Chem.* **2004,**

689, 3203.

(9) See for example: (a) Nielsen, D. J.; Magill, A. M.; Yates, B. F.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Chem. Commun.* **2002**, 2500. (b) Clement, N. D.; Cavell, K. J. *Angew. Chem. Int. Ed.* **2004**, *43*, 3845. (c) Bacciu, D.; Cavell, K. J.; Fallis, I. A.; Ooi, L. *Angew. Chem. Int. Ed.* **2005**, *44*, 5282. (d) Graham, D. C.; Cavell, K. J.; Yates, B. F. *Dalton Trans.* **2005**, 1093. (e) Graham, D. C.; Cavell, K. J.; Yates, B. F. *Dalton Trans.* **2006**, 1768.

(10) (a) Danopoulos, A. A., Tsoureas, N.; Green, J. C.; Hursthouse, M. B. *Chem. Commun.* **2003**, 756. (b) Hu, X.; Meyer, K. *J. Am. Chem. Soc.* **2004**, *127*, 16322. (c) Galan, B. R.; Gembicky, M.; Dominiak, P. M.; Keister, J. B.; Diver, S. T. *J. Am. Chem. Soc.* **2005**, *126*, 15702. (d) Becker, E.; Stingl, V.; Daringer, G.; Puchberger, M.; Mereiter, K.; Kirchner, K. *J. Am. Chem. Soc.* **2006**, *128*, 6572. (e) Becker, E.; Stingl, V.; Dazinger, G.; Mereiter, K.; Kirchner, K. *Organometallics* **2007**, *26*, 1531. (f) Fantasia, F.; Jacobsen, H.; Cavallo, L.; Nolan, S. P. *Organometallics* **2007**, *26*, 3286.

(11) (a) Caddick, S.; Cloke, F. G. N.; Hitchock, P. B.; Lewis, A. K.; de, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5824. (b) Burling, S.; Mahon, M. F.; Powell, R. E.; Whittlesey, M. K.; Williams, J. M. J. *J. Am. Chem. Soc.* **2006**, *128*, 13702.

(12) Waltman, A. W. W.; Ritter, T.; Grubbs, R. H. *Organometallics* **2006**, *25*, 4238.

(13) See for example: (a) Burling, S.; Mahon, M. F.; Paine, B. M.; Whittlesey M. K.; Williams, J. M. J. *Organometallics* **2004**, *23*, 4537. (b) Dorta, R.; Stevens, E. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5054. (c) Abdur-Rashid, K.; Fedorkiw, T.; Lough, A. J.; Morris, R. H. *Organometallics* **2004**, *23*, 86. (d) Cabeza, J. A.; del Río, I.; Miguel, D.; Sánchez-Vega, M. G. *Chem. Commun* **2005**, 3956. (e) Scott, N. M.; Pons, V.; Stevens, E. D.; Heinekey, D. M.; Nolan, S. P. *Angew. Chem. Int. Ed.* **2005**, *44*, 2512. (f) Corberán, R.; Sanaú, M.; Peris, E. *Organometallics* **2006**, *25*, 4002. (g) Hanasaka, F.; Tanabe, Y.; Fujita, K.; Yamaguchi, R. *Organometallics* **2006**, *25*, 826. (h) Spencer, L. P.; Beddie, C.; Hall, M.

B.; Fryzuk, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 12531. (i) Corberán, R.; Sanaú, M.; Peris, E. *J. Am. Chem. Soc.* **2006**, *128*, 3974. (j) Cariou, R.; Fischmeister, C.; Toupet, L.; Dixneuf, P. H. *Organometallics* **2006**, *25*, 2126. (k) Tanabe, Y.; Hanasaka, F.; Fujita, K.; Yamaguchi, R. *Organometallics* **2007**, *26*, 4618. (l) Hong, S. H.; Chlenov, A.; Day, M. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2007**, *46*, 5148. (m) Ellul, C. E.; Mahon, M. F.; Saker, O.; Wittlesey, M. K. *Angew. Chem. Int. Ed.* **2007**, *46*, 6343.

(14) (a) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Wittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944. (b) Diggle, R. A.; Macgregor, S. A.; Wittlesey, M. K. *Organometallics,* **2008**, *27*, 617.

(15) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 4343.

(16) (a) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 13044. (b) Esteruelas, M. A.; López, A. M.; Oliván, M. *Coord. Chem. Rev.* **2007**, *251*, 795. (c) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 2129. (d) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 3082. (e) Esteruelas, M. A.; Fernández-Alvarez, F.; Oñate, E. *Organometallics* **2007**, *26*, 5239. (f) Baya, M.; Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 6556. (g) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oliván, M.; Oñate, E. *J. Am. Chem. Soc.* **2007**, *129*, 10998. (h) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Puerta, M. *Organometallics* **2008**, *27*, 445. (i) Castarlenas, R.; Esteruelas, M. A.; Lalrempuia, R.; Oliván, M. Oñate, E. *Organometallics* **2008**, *27*, 795. (j) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2008**, *27*, 3240. (k) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 4680. (l) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oñate, E. *Organometallics* **2008**, *27*, 6236. (m) Buil, M. L.; Castarlenas, R.; Esteruelas, M. A.; Izquierdo, S.; Lalrempuia, R.; Oñate, E. *Organometallics* **2010**, *29*, 876.

(17) See for example: (a) Jiménez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *J. Am. Chem.*

Soc. **2000**, *122*, 11230. (b) Carbó, J. J.; Crochet, P.; Esteruelas, M. A.; Jean, Y.; Lledós, A.; López, A. M.; Oñate, E. *Organometallics* **2002**, *21*, 305. (c) Sapunov, V. N.; Schmid, R.; Kirchner, K.; Nagashima, H. *Coord. Chem. Rev.* **2003**, *238-239*, 363.

(18) (a) Castarlenas, R.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Oñate, E. *Organometallics* **2001**, *20*, 1545. (b) Barrio, P.; Esteruelas, M. A.; Lledós, A.; Oñate, E.; Tomàs, J. *Organometallics* **2004**, *23*, 3008.

(19) (a) Tipper, C. F. H. *J. Chem. Soc.* **1955**, 2045. (b) Adams, D. M.; Chatt, J.; Guy, R. G.; Shepperd, N. *J. Chem. Soc.* **1961**, 738. (c) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392. (d) Jones, W. D. *Nature* **1993**, *364*, 676. (e) Yang, X.; Seyam, A. M.; Fu, P.-F.; Marks, T. J. *Macromolecules* **1994**, *27*, 4625. (f) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241. (g) Jia, L.; Yang, X. Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 1547. (h) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, *16*, 2016. (i) Wick, D. D.; Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4484. (j) Edelbach, B.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843. (k) Murakami, M.; Ito, Y. *Top. Organomet. Chem.* **1999**, *3*, 97-129. (l) Rybtchinski, B.; Milstein, D. *Angew. Chem. Int. Ed.* **1999**, *38*, 870. (m) Jun, C.-H. *Chem. Soc. Rev.* **2004**, *33*, 610. (n) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; López, F.; Mascareñas, J. L.; Oliván, M.; Oñate, E.; Saya, L.; Villariño, L. *J. Am. Chem. Soc.* **2010**, *132*, 454.

(20) (a) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (b) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222.

(21) (a) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054. (b) Nishimura, T.; Uemura, S. *J. Am. Chem. Soc.* **1999**, *121*, 11010. (c) Rybtchinski, B.; Oevers, S.; Montag, M.; Vigalok, A.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 9064. (d) Jun, C.-H.; Moon, C. W.; Lee, H.; Lee, D.-Y. *J. Mol. Catal. A: Chem.* **2002**, *189*, 145. (e) Gandelman, M.; Shimon, L. J.

W.; Milstein, D. *Chem. Eur. J.* **2003**, *9*, 4295.

(22) (a) Müller, C.; Iverson, C. N.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 9718. (b) Gunay, A.; Jones, W. D. *J. Am. Chem. Soc.* **2007**, *129*, 8729.

(23) Blessing, R. H. *Acta Crystallogr.* **1995,** *A51*, 33. *SADABS: Area-Detector Absorption Correction*; Bruker-AXS: Madison, WI, 1996.

(24) *SHELXTL* Package v. 6.10; Bruker-AXS: Madison, WI, 2000. Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

TOC Entry

C-C Bond Activation of the NHC Ligand of an Osmium-Amido Complex

Tamara Bolaño, María L. Buil, Miguel A. Esteruelas, Susana Izquierdo, Ralte Lalrempuia, Montserrat Oliván, and Enrique Oñate*

The NHC ligand 1,3-bis(2,6-diisopropylphenyl)imidazolylidene of complex **I** undergoes degradation by means of a C-C bond cleavage of one of its isopropyl substituents to afford **II**, that contains a polycyclic system with three fused rings with an Os-NHC core.