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Preparation of Capped Octahedral $OsHC_6$-Complexes by Sequential Carbon-Directed C-H Bond Activation Reactions

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ABSTRACT: A synthetic procedure based on sequential C-directed C-H bond activation reactions is reported for the preparation of capped octahedral $OsHC_6$-complexes. Reactions of the dimer $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**1**) with PhMeLAgI (MePhL = 1-phenyl-3-methyl-1*H*-benzimidazolylidene (PhMeBIm), 1-phenyl-3,5,6-trimethyl-1*H*-benzimidazolylidene (PhMeBIm*)) afford $OsCl_2(\eta^6\text{-}p\text{-cymene})$(PhMeL) (L = BIm(**2**), BIm*(**3**)), which undergo cyclization to give $OsCl\{\kappa^2\text{-C,C-(MeL-}C_6H_4)\}(\eta^6\text{-}p\text{-cymene})$ (L = BIm (**4**), BIm* (**5**)) by stirring in dichloromethane suspensions of Al_2O_3. Complexes **4** and **5** exchange the anion with AgOTf (OTf = CF_3SO_3). In acetonitrile, at 75ºC, the resulting OTf-derivatives $Os(OTf)\{\kappa^2\text{-C,C-(MeL-}C_6H_4)\}(\eta^6\text{-}p\text{-cymene})$ (L = BIm (**6**), BIm* (**7**)) release the arene to yield the tetra(solvento) compounds $[Os\{\kappa^2\text{-C,C-(MeL-}C_6H_4)(CH_3CN)_4]OTf$ (L = BIm (**8**), BIm* (**9**)). Complexes **8** and **9** react with PhMeLAgI to coordinate a second NHC ligand. The generated species $Os\{\kappa^2\text{-C,C-(MeL-}C_6H_4)(PhMeL)(CH_3CN)_3]OTf$ (L = BIm (**10**), BIm* (**11**)), containing a C,C-chelate NHC-C_6H_4 ligand and a monodentated NHC group, exist as a mixture of *mer* (**a** and **b**) and *fac* (**c**) acetonitrile isomers. The X-ray diffraction structure of **10c** reveals aromatic-aromatic interactions between the N-phenyl substituent of the monodentated NHC group and aromatic rings of the chelate ligand. The π-π stacking has been analyzed by means of DFT calculations by using the AIM approach. Treatment of **10** and **11** with [PhMeLH]I, in the presence of an excess of Et_3N leads to the capped octahedral target compounds $OsH\{\kappa^2\text{-C,C-(MeL-}C_6H_4)\}_3$ (L = BIm (**12**), BIm* (**13**)), as a result of the coordination of a third NHC group and the orthometalation of the N-phenyl substituents of the second and third NHC ligands.

INTRODUCTION

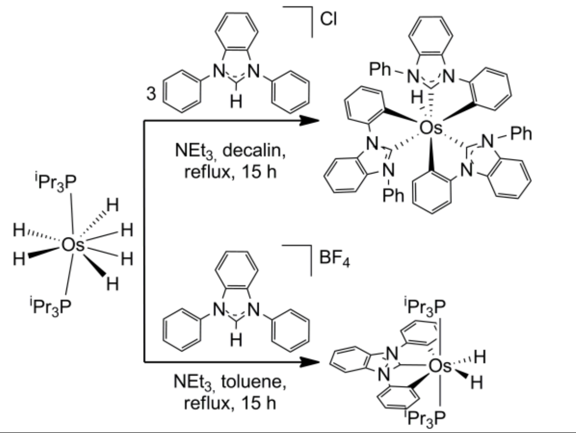
C-H Bond activation is a classical issue in organometallics by its connection with the functionalization of nonactivated organic molecules and because provides a straightforward entry to compounds that feature a metal-carbon σ-bond.[1] Among the different strategies available to stabilize the generated bond, the chelate-assistance is considered to be one of the most efficient ways.[2] The chelation gives rise to organometallic compounds with increased stability, which may result determinant for the preparation of unconventional compounds.

The chelation is produced by the coordination of a heteroatom with free electron pairs, including N, O, P, S, Se and As. Thus, the reactions are heteroatom-assisted and heteroatom directed when the heteroatom coordinates before the C-H bond activation process.[3] Carbon is an excellent directing atom. However, the carbon-assisted activation reactions are rare, in comparison with those assisted by heteroatoms. In this context, it should be noted that the previous C-coordination often requires the use of specific procedures. Regarding this, N-heterocyclic carbenes (NHCs) are the best C-assistant groups.[4]

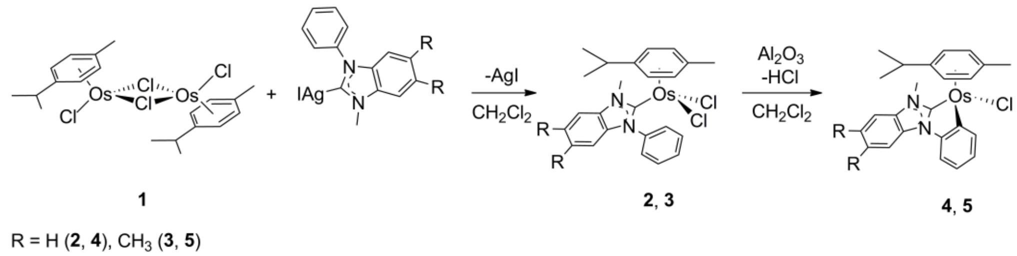
We have recently found, during the study of the reactivity of the hexahydride-osmium(VI) complex $OsH_6(P^iPr_3)_2$ toward imidazolium and benzimidazolium salts,[5] that the treatment of decaline solutions of this d^2-species with 3.0 equiv of N,N'-diphenylbenzimidazolium chloride ($[Ph_2BImH]Cl$) and 3.0 equiv of Et_3N, under reflux, leads to the MHC_6-compound $OsH\{\kappa^2\text{-C,C-(PhBIm-}C_6H_4)\}_3$ as a result of the C-assisted *ortho*-CH bond activation of a phenyl substituent and the direct metalation of the benzimidazolium group of 3 equiv of salt (Scheme 1).[6]

Transition-metal complexes containing only carbon and hydrogen atoms at the metal coordination sphere have played

Scheme 1. Reactions of $OsH_6(P^iPr_3)_2$ with $[Ph_2BImH]^+$.



Scheme 2. Coordination and Cyclization of the First NHC Ligand.



a determinant role in the conceptual development of the current chemistry. Furthermore, in the last years, some of them have proven to have notable applications in material science.[7] These blue-blood organometallic compounds are stabilized by metal centers in low oxidation states and have usually coordination numbers lower than six.[8] Complex OsH{κ^2-C,C,(PhBIm-C_6H_4)}$_3$ is notable because is the first seven-coordinate blue-blood organometallic complex of a platinum group metal and has the metal center in high oxidation state. Previously, seven-coordinate blue-blood organometallic compounds were known for 5 and 6 group metals.[9] In contrast to the osmium species, they have a MC_7 core and were stabilized by using linear isocyanide ligands. Interestingly, although for coordination number seven the most common polyhedron is the pentagonal bipyramid,[10] in particular for osmium(IV),[11] the MHC_6 core of OsH{κ^2-C,C-(PhBIm-C_6H_4)}$_3$ has the form of a capped octahedron.[6]

The unexpected formation of OsH{κ^2-C,C-(PhBIm-C_6H_4)}$_3$ is a clear case of serendipity, since the use of the BF_4-salt instead of the chloride gave rise to the expected C,C,C-pincer dihydride OsH_2{κ^3-C,C,C-(C_6H_4-BIm-C_6H_4}(P^iPr_3)$_2$ (Scheme 1). The conceptual interest of the blue-blood organometallic compounds and the novelty of the osmium(IV) complexes with a MHC_6 core prompted us to develop a rational synthetic route to the preparation of this novel type of compounds. In this paper, we describe a general procedure involving the sequential entry of three N-phenyl substituted benzimidazolylidene ligands and their subsequent C-directed orthometalation.

RESULTS AND DISCUSSION

Coordination and Cyclization of the First Ligand. All attemps to obtain $OsHC_6$ complexes starting from $OsH_6(P^iPr_3)_2$ and 1-phenyl-3-methyl-1*H*-benzimidazolium ([PhMeBImH]$^+$) or 1-phenyl-3,5,6-trimethyl-1*H*-benzimidazolium ([PhMeBIm*H]$^+$) salts were unsuccessful. In all the cases, we obtained complex mixtures of products, which were not identified, with the notable exception of the treatment of toluene solutions of the hexahydride complex with the BF_4-salts, in the presence of NEt_3, under reflux. Under these conditions, the corresponding trihydrides OsH_3{κ^2-C,C-(MeL-C_6H_4)}(P^iPr_3)$_2$ (L = BIm, BIm*) were formed in high yield.[5e] However, unfortunately, these compounds have not allowed us to introduce a second C,C-chelate ligand in the metal coordination sphere. In view of this situation, we decided to use the *p*-cymene dimer [$OsCl_2$(η^6-*p*-cymene)]$_2$ (**1**), which had previously shown to be a useful starting material to prepare osmium-NHC complexes.[12]

The first NHC ligand was introduced into the osmium coordination sphere by transmetalation from the corresponding silver species PhMeLAgI, which were generated *in situ* by the procedure previously described by Rourke and coworkers[13] and used by Wang and coworkers to prepare platinum (II) derivatives.[14] The transmetalation affords the mononuclear derivatives $OsCl_2$(η^6-*p*-cymene)(MePhL) (L = BIm (**2**), BIm* (**3**)), which were isolated as orange solids in about 80% yield (Scheme 2). The presence of a NHC ligand in **2** and **3** is strongly supported by their ^{1}H and ^{13}C{^{1}H} NMR Spectra, in dichloromethane-d_2, at room temperature. In the ^{13}C{^{1}H} NMR spectra, the most noticeable feature is a singlet at about 174 ppm corresponding to the metalated carbon atom of the carbenes.

The orthometalation of the phenyl substituent of the NHC ligand of **2** and **3** was achieved through the stirring of dichloromethane solutions of these compounds, in the presence of Al_2O_3, at room temperature, for 24h. The resulting complexes OsCl{κ^2-C,C-(MeL-C_6H_4)}(η^6-*p*-cymene) (L = BIm (**4**), BIm* (**5**)) were isolated as yellow solids, in almost quantitative yield with regard to **1**, when the reactions where performed in one-pot and complexes **2** and **3** were not isolated. The orthometalation process was confirmed by means of the X-ray diffraction structure of **4**, which has four molecules chemically equivalent but crystallographically independent in the asymmetric unit. Figure 1 shows a view of one of them. The geometry around the metal center is close to octahedral, with the arene occupying three sites of a face. The C,C-chelate ligand, which acts with C(1)-Os-C(10) bite angles

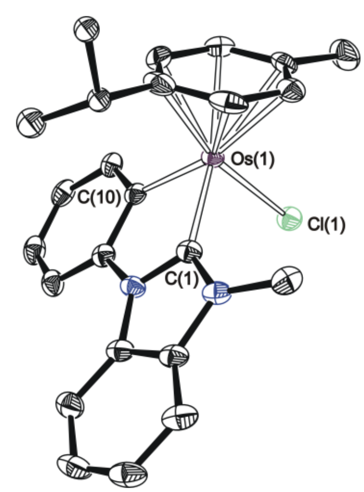
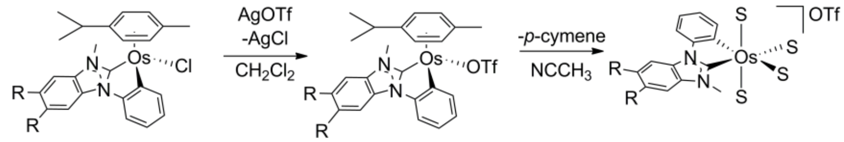


Figure 1. ORTEP diagram of complex **4** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os(1)–C(1) = 2.013(4), 2.016(4), 2.016(4) and 2.015(4), Os(1)–C(10) = 2.074(4), 2.075(4), 2.076(4) and 2.075(4), C(1)–Os(1)–C(10) = 76.62(15), 76.75(15), 76.45(15) and 76.54(15).

Scheme 3. Displacement of the *p*-Cymene Ligand.



4, **5** **6**, **7** **8**, **9**

R = H (**4**, **6**, **8**), CH_3(**5**, **7**, **9**). S = $NCCH_3$

of 76.62(15)º, 76.75(15)º, 76.45(15) and 76.54(15)º lies in the opposite site. The Os-C(1) bond lengths of 2.013(4), 2.016(4), 2.016(4) and 2.015(4) Å compare well with those reported for Os-NHC compounds with normal coordination of the NHC unit,[15] whereas the Os-C(10) distances of 2.074(4), 2.075(4), 2.076(4) and 2.075(4) Å agree well with the Os-aryl bond lengths found in other five-membered osmacycles resulting from orthometalation reactions.[16] The ^1H and $^{13}C\{^1H\}$ NMR spectra of **4** and **5**, in dichlorometane-d_2, at room temperature are consistent with the structure shown in Figure 1. In the $^{13}C\{^1H\}$ NMR spectra, the metalated carbon atoms of the chelate ligand display singlets at about 185 (NHC) and 136 (Ph) ppm.

Displacement of the *p*-Cymene Ligand. Once complexes **4** and **5** were obtained, we attempted the coordination of a second NHC ligand to the metal center, by transmetalation from the corresponding silver species again. However, the displacement of the chloride ligand by the NHC group was not observed and complexes **4** and **5** were recovered unchanged from the mixtures in high yield. Then, we decided to substitute the chloride ligand by a better leaving group as the triflate anion (OTf). The treatment of **4** and **5** with the stoichiometric amounts of AgOTf, in dichloromethane, at room temperature produces the precipitation of AgCl and the formation of the triflate derivatives Os(OTf){κ^2-C,C-(MeL-C_6H_4)}(η^6-*p*-cymene) (L = BIm (**6**), BIm* (**7**)), which were isolated as green solids in 80% (**6**) and 94% (**7**) yield (Scheme 3). In accordance with **4** and **5**, the $^{13}C\{^1H\}$ NMR spectra of **6** and **7**, in dichloromethane-d_2, at room temperature contain singlets at about 182 and 149 ppm, due to the metalated carbon atoms of the benzimidazolylidene core and the phenyl substituent, respectively. The presence of the OTf ligand in the complexes is strongly supported by a singlet about -79 ppm, in the $^{19}F\{^1H\}$ NMR spectra. In contrast to **4** and **5**, complexes **6** and **7** reacted with the PhMeLAgI. Unfortunately, the reactions gave complex mixtures of unidentified products, most probably, as a consequence of the presence of the *p*-cymene ligand at osmium coordination sphere.

Octahedral half-sandwhich osmium(II) complexes show ligand substitution activation energies very high due to the dependence of the crystal field activation energy on Δ_0.[17] As a consequence, in contrast to ruthenium[18], for osmium the displacement of the *p*-cymene ligand is a difficult problem, which usually requires photochemical conditions.[19] Nevertheless, we have observed that acetonitrile promotes the thermal displacement of the *p*-cymene ligand from NHC-osmium(II)-alkylidene complexes.[20] Although the process is certainly favored by the high *trans*-effect of the alkylidene ligand, this observation prompted us to heat acetonitrile solutions of **6** and **7** at 75ºC. Under these conditions, the stirring of the solutions afforded the tetra(solvento) complexes [Os{κ^2-C,C-(MeL-C_6H_4)($CH_3CN)_4$]OTf (L = BIm (**8**), BIm* (**9**)) in almost quantitative yield, after 9 days, as green solids. The unexpected success of the substitution was confirmed by means of the X-ray diffraction structure of **8**. Figure 2 shows a view of the cation of the salt. The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with N(3)-Os-N(6), N(4)-Os-C(1), and N(5)-Os-C(10) angles of 175.71(10)º, 171.89(11)º and 178.05(10)º, respectively. The Os-C(1) and Os-C(10) bond lengths of 1.997(3) and 2.053(3) Å, respectively, compare well with the Os-C(chelate) distances in **4**. The Os-N separations are consistent with the different *trans*-influence of the respective *trans* donor groups, decreasing in the sequence 2.109(3) Å (Os-N(5), N *trans* to Ph) > 2.088(3) Å (Os-N(4), N *trans* to BIm) > 2.015(3) ≈ 2.013(3) Å (Os-N(6) and Os-N(3), N *trans* to CH_3CN). In agreemet with **4**, the $^{13}C\{^1H\}$ NMR spectra of **8** and **9**, in acetonitrile-d_3, at room temperature show singlets at about 186 (NHC) ppm and between 136 and 149 (Ph) ppm due to the metalated carbon atoms of the C,C-chelate ligand.

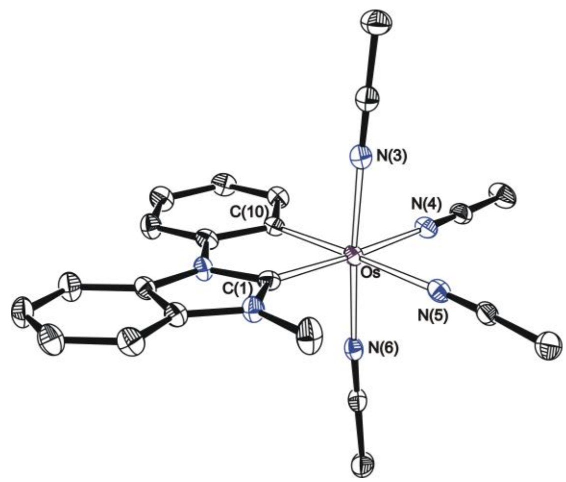
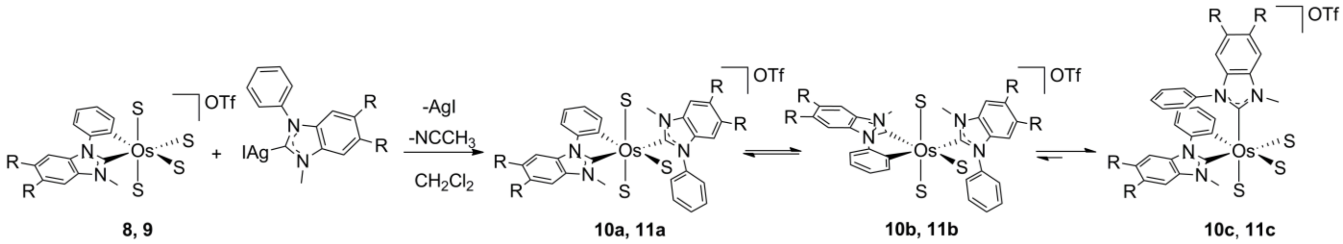


Figure 2. ORTEP diagram of the cation of complex **8** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–C(1) = 1.997(3), Os–C(10) = 2.053(3), Os–N(3) = 2.013(3), Os–N(4) = 2.088(3), Os–N(5) = 2.109(3), Os–N(6) = 2.015(3), C(1)–Os–C(10) = 78.41(12), C(1)–Os–N(4) = 171.89(11), C(10)–Os–N(5) = 178.05(10), N(3)–Os–N(6) = 175.71(10).

Coordination of the Second NHC Ligand. The absence of the arene is essential for the coordination of a new NHC ligand. In contrast to **4-7**, the tetra(solvento) complexes **8** and **9** are efficient carbene acceptors. As a consequence, the transmetalation from silver to the osmium atom of these compounds cleanly occurs at room temperature, to afford [Os{κ^2-C,C-(MeL-C_6H_4)(MePhL)($CH_3CN)_3$]OTf (L = BIm **10**), BIm* (**11**)) as a result of the replacement of an acetonitrile molecule by the NHC ligand. Complexes **10** and

Scheme 4. Coordination of the Second NHC Ligand.



R = H (**8**, **10a**, **10b**, **10c**), CH$_3$ (**9**, **11a**, **11b**, **11c**). S = NCCH$_3$

11 were isolated as green solids in 76% and 86% yield, respectively. In dichloromethane and acetonitrile, they exist as a 1:1 mixture of the two possible *mer*-acetonitrile isomers, **a** containing the L groups *trans* disposed and **b** with the L groups in *cis* position (Scheme 4). Although at first glance one should expect four resonances for the methyl group of the acetonitrile ligands in the ^{1}H NMR spectra of the mixtures, two for each isomer, the spectra contains six singlets between 1.7 and 2.3 ppm. The absence of equivalence between the acetonitrile molecules *trans* disposed suggest that the rotation of the monodentated NHC ligand around the Os-C bond is prevented as a consequence of the steric requirement of the N-substituents of the benzimidazolylidene group. The most noticeable spectroscopic differences between the isomers **a** and **b** was obtained from a ^{1}H-^{1}H NOESY experiment. The NCH$_3$-resonance assigned to the monodentate NHC ligand of isomers **a** (δ, 3.96 (**10a**); 3.90 (**11a**)) shows NOESY with the aromatic resonance corresponding to the hydrogen atom, *ortho* with regard to the metal center, of the metalated phenyl group of the chelate ligand (δ, 7.17 (**10a**); 7.13 (**11a**)). On the other hand, the NCH$_3$-resonance assigned to the monodentated NHC ligand of isomers **b** (δ, 3.90 (**10b**); 3.84 (**11b**)) gives NOESY with the NCH$_3$ resonance of the chelate group (δ, 3.65 (**10b**); 3.58 (**11b**)). The mixtures evolve into the respective *fac*-acetonitrile isomers **10c** and **11c**, in dichloromethane, acetonitrile, or even in the solid state. In acetonitrile, at 75ºC, they are the main component of the mixtures after 2 days. Under these conditions, species resulting of the orthometalation of the phenyl substituent of the new coordinated NHC ligand are not observed, although monodentated-chelate role exchange between the NHC ligands should be not rejected. Complexes **10c** and **11c** were isolated in 85% and 62% yield, respectively, also as green solids

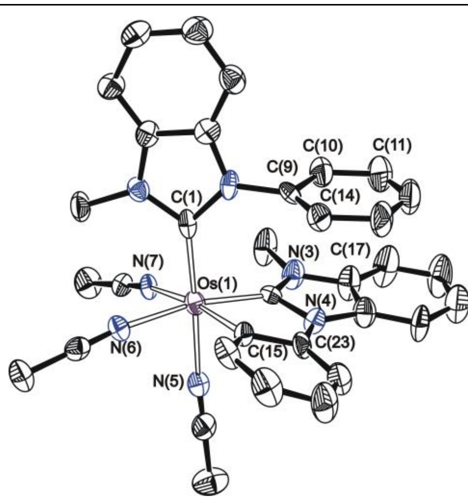


Figure 3. ORTEP diagram of the cation of complex **10c** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os(1)–C(1) = 1.978(10) and 2.020(10), Os(1)–C(15) = 1.986(9) and 1.971(11), Os(1)–C(24) = 2.062(10) and 2.042(10), C(49)–Os(1)–C(58) = 77.9(4) and 78.6(4).

Complex **10c** was characterized by X-ray diffraction analysis. The structure has two cations and two anions chemically equivalent but crystallographically independent in the asymmetric unit. Figure 3 shows a view of one of the cations. The coordination polyhedron around the osmium atom can be rationalized as a distorted octahedron with fac-acetonitriles. The chelate ligand displays Os-BIm bond lengths of 1.986(9) and 1.971(11) Å (Os(1)-C(15)) and Os-aryl distances of 2.042(10) and 2.062(10) Å (Os(1)-C(24)), which agree well with those **4** and **8**. The Os-BIm bond lengths of 2.020(10) and 1.978(10) Å (Os(1)-C(1) for the monodentated NHC ligand are statistically identical with the chelate Os-BIm distances.

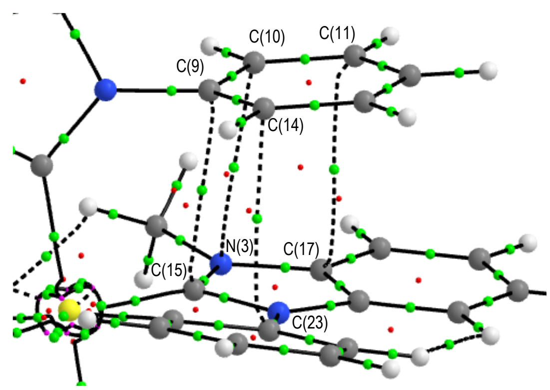


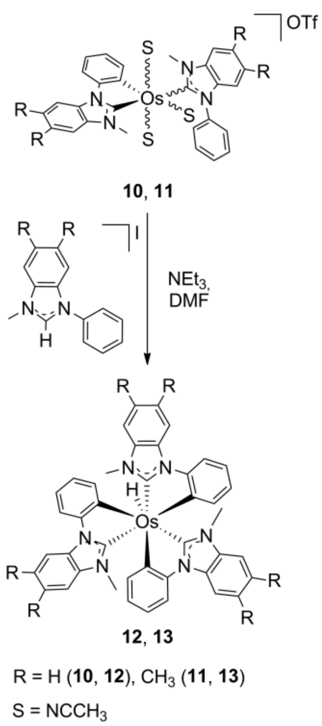
Figure 4. Molecular graphs (AIM) of complex **10c**. Green and red balls indicate BCPs and ring critical points, respectively.

The phenyl substituent of the monodentated NHC ligand stacks the aromatic rings of the chelate group with centroid-centroid separations between 3.3 and 4.4 Å, small dihedral angles between planes (2-20º), and angles between the centroid-centroid vector and the normal to the plane in the range 14-32º. This is consistent with aromatic-aromatic interactions.[21] In order to provide further information about the nature of the π-π stacking, we carried out a topological analysis of the electron density of **10c** by means of DFT calculations at the b3lyp(D3)//SDD(f)/6-31g** level, by using the AIM approach. The results revealed four interactions between the phenyl substituent of the monodentated NHC ligand and the aromatic rings of the chelate group, as shown by the critical points (BCP) detected in the graphical analysis (Figure 4). Two types of contacts were identified, C-C and C-

N. The C-C contacts include the atoms C(14) and C(23), C(9) and C(15), and C(11) and C(17). The C-N contact takes place between C(10) and N(3). The separation between the atoms linked by a bond path increases in the sequence 3.109 ((C14)-C(23)) < 3.119 (C(9)-C(15)) < 3.204 (C(10)-N((3)) < 3.399 ((C(11)-C(17)) Å. In agreement with close-shell interactions, the electron density values at the BCPs corresponding to the π-π stacking are small and increase as the separation between the involved atoms decreases; i.e., in the sequence C(11)-C(17) (0.0061) < C(10)-N(3) (0.0078) < C(9)-C(15) (0.0089) C(14)-C(23) (0.0092) a.u. The small values of the Laplacian (0.0177-0.0297 a.u.) in conjunction with the positive and small values of the total electron energy density (0.0007-0.0013 a.u.) are consistent with the no covalent character of the interactions.[22]

Coordination of the Third NHC Ligand and C-H Bond Activation of the Phenyl Substituent of the Second and Third ones. In contrast to the first and second NHC ligands, the third one was introduced into the metal coordination sphere of **10** and **11** by refluxing of dimethylformamide solutions of these compounds with the respective benzimidazolium iodide salts in the presence of an excess of Et_3N. The coordination of the third NHC ligand promotes the orthometalation of its phenyl substituent and that of the phenyl substituent of the benzimidazolylidene group coordinated in the second place, to afford the target compounds OsH{κ^2-C,C-(MeL-C_6H_4)}$_3$ (L = BIm (**12**), BIm* (**13**)). Although the order of the orthometalations is not evident, it is clear that are two different C-H bond activation processes. One of them implies an heterolytic C-H bond cleavage promoted by the external Et_3N base, while the other one is a C-H bond oxidative addition. Complexes **12** and **13** were isolated as white solids in 66% and 94% yield, respectively (Scheme 5).

Scheme 5. Coordination of the Third NHC Ligand and Metalation of the Second and Third Ones.



The formation of **12** and **13** was confirmed by means of the X-ray diffraction structure of **12**. Figure 5 shows a view of the molecule. Like in the previously reported OsH{κ^2-C,C-(PhBIm-C_6H_4)}$_3$ complex, the donor atoms around the metal center form a capped octahedral of C_3 symmetry. The hydride ligand, which is contained in the C_3 symmetry axis, lies at the center of the trigonal face defined by the carbene carbon atoms. This disposition allows the interaction between its s orbital and the formally vacant p orbitals of the carbene carbon atoms.[6] In agreement with the symmetry of the molecule, the three Os-BIm bond lengths of 2.032(3) (Os-C(1)), 2.040(3) (Os-C(15)), and 2.045(3) (Os-(C(29)) Å; as well as the three Os-aryl distances of 2.145(3) (Os-C(24)), 2.146(3) (Os-C(38)), and 2.147(3) (Os-C(10)) Å; are statistically identical. Both Os-BIm and Os-aryl bond lengths compare well with the respective distances in **4**, **8** and **10c**.

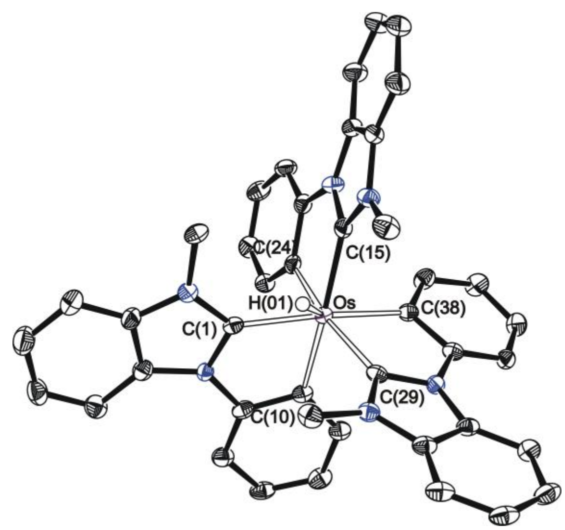


Figure 5. ORTEP diagram of complex **12** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–C(1) = 2.032(3), Os–C(10) = 2.147(3), Os–C(15) = 2.040(3), Os–C(24) = 2.145(3), Os–C(29) = 2.045(3), Os–C(38) = 2.146(3), C(1)-Os–C(10) = 75.52(11), C(15)-Os–C(24) = 75.71(12), C(29)-Os–C(38) = 75.27(11).

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **12** and **13**, in dichloromethane-d_2, at room temperature are consistent with the structure shown in Figure 5, exhibiting three equivalent NHC ligands. According to the presence of the hydride ligand in the complexes, the ^{1}H NMR spectra contain a singlet at about -9.8 ppm. In the ^{13}C{^{1}H} NMR spectra, the most noticeable resonance is that due to the metalated carbene carbon atoms, which appears at about 194 ppm.

CONCLUDING REMARKS

This study has revealed that the sequential coordination of three N-phenyl substituted NHC ligands to osmium and the subsequent C-directed C-H bond activation of the phenyl substituent afford novel capped octahedral $OsHC_6$-complexes.

The *p*-cymene dimer [$OsCl_2$(η^6-*p*-cymene)]$_2$ is a suitable starting material for carrying out the synthesic procedure, although the arene must be removed from the metal coordination sphere, after the coordination and subsequent cyclization of the first NHC ligand, in order to coordinate the second NHC group.

The addition of the first and second NHC ligands to the metal center is performed by transmetalation from silver, whereas the third one undergoes direct metalation in the presence of an excess of NEt_3.

The C-H bond activation of the N-phenyl substituent of the first NHC ligand; i.e., the cyclization of the first coordinated NHC group; is an heterolytic C-H bond cleavage promoted by an external base, which has a very low activation energy. However, the cyclization of the second one needs the previous coordination of the third NHC ligand. Once the second and third NHC ligands are coordinated, the orthometalation of their N-phenyl substituents yields the target compounds. The orthometalations are two different C-H bond activation processes: an external base-promoted heterolytic C-H bond cleavage and a C-H bond oxidative addition.

In conclusion, a rational route for the preparation of capped octahedral $OsHC_6$ complexes, involving three sequential C-directed C-H bond activation reactions, has been developed.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents (except DMF and acetonitrile that were dried and distilled under argon) were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^{1}H, ^{19}F and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker 300 ARX, Bruker Avance 300 MHz, and Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, $^{13}C\{^{1}H\}$), or external $CFCl_3$ (^{19}F). Coupling constants *J* are given in hertz. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. 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 MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**1**) was prepared according to literature.[12] 1-Phenyl-3-methyl-1*H*-benzimidazolium iodide [PhMeBImH]I and 1-phenyl-3,5,6-trimethyl-1*H*-benzimidazolium [PhMeBIm*H]I were prepared according to the published method.[5e]

$OsCl_2(\eta^6$-*p*-cymene)(PhMeBIm) (2). CH_2Cl_2 (30 mL) was added to a mixture of 1-phenyl-3-methyl-1*H*-benzimidazolium iodide ([PhMeBImH]I) (161.6 mg, 0.48 mmol), silver oxide (55.7 mg, 0.24 mmol) and molecular sieves (4 Å, 100 mg). The resulting mixture was stirred in absence of light for one hour and a white suspension was formed. The osmium dimer (190 mg, 0.24 mmol) was added and the mixture was stirred for 3 h yielding an orange solution which was extracted from the silver salts. This orange solution was concentrated in *vacuo* to Ca~ 1 mL and pentane (5 mL) was added. The resulting orange solid was washed with pentane (3x3 mL) and dried in *vacuo*. Yield: 231.0 mg (80 %). Anal. Calcd. for $C_{24}H_{26}Cl_2N_2Os$: C, 47.76; H, 4.34; N, 4.64. Found: C, 47.69; H, 4.37; N, 4.63. HRMS (electrospray, *m/z*): calcd. for $C_{24}H_{26}ClN_2Os$ $[M - Cl]^+$: 569.1399; found: 569.1384. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.60-7.40 (m, 5H, CH), 7.50-7.40 (m, 1H, CH), 7.40-7.20 (m, 1H, CH), 7.20-7.10 (m, 1H, CH), 6.80-6.70 (m, 1H, CH), 5.41 (d, $^{3}J_{H\text{-}H}$ = 5.8, 2H, CH *p*-cymene), 5.23 (d, $^{3}J_{H\text{-}H}$ = 5.8, 2H, CH *p*-cymene), 4.28 (s, 3H, NCH_3), 2.63 (hept, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 1H, C*H*$(CH_3)_2$ *p*-cymene), 2.08 (s, 3H, C-CH_3 *p*-cymene), 1.16 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$ *p*-cymene). $^{13}C\{^{1}H\}$ + HMBC + HSQC NMR (75 MHz, CD_2Cl_2, 298 K): δ 175.2 (s, N*C*N), 142.0 (s, CH), 138.5 (s, 2 C_q), 135.4 (s, C_q), 131.1 (s, CH), 129.6 (s, CH), 128.5 (s, CH), 123.9 (s, CH), 123.9 (s, CH), 111.7 (s, CH), 110.6 (s, CH), 101.1 (s, C_q), 92.2 (s, C_q), 78.4 (s, CH *p*-cymene), 75.8 (s, CH *p*-cymene), 37.5 (s, NCH_3), 31.4 (s, *C*H$(CH_3)_2$ *p*-cymene), 23.0 (s, CH(*C*H$_3$)$_2$ *p*-cymene), 19.2 (s, C*C*H$_3$ *p*-cymene).

$OsCl_2(\eta^6$-*p*-cymene)(PhMeBIm*) (3). CH_2Cl_2 (30 mL) was added to a mixture of 1-phenyl-3, 5, 6-trimethyl-1*H*-benzimidazolylidene iodide ([PhMeBIm*H]I) (185.8 mg, 0.50 mmol), silver oxide (58.6 mg, 0.25 mmol) and molecular sieves (4 Å, 100 mg). The resulting mixture was stirred in absence of light for one hour and a white suspension was formed. The osmium dimer (200 mg, 0.24 mmol) was added and the mixture was stirred for 3 h yielding an orange solution which was extracted from the silver salts. This orange solution was concentrated in *vacuo* to Ca~ 1 mL and pentane (5 mL) was added. The resulting orange solid was washed with pentane (3x3 mL) and dried in *vacuo*. Yield: 260.0 mg (76 %). Anal. Calcd. for $C_{26}H_{30}Cl_2N_2Os$: C, 49.44; H, 4.79; N, 4.44. Found: C, 49.35; H, 4.65; N, 4.67. HRMS (electrospray, *m/z*): calcd. for $C_{26}H_{30}ClN_2Os$ $[M - Cl]^+$: 597.1712; found: 597.1697. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.6-7.50 (m, 5 H, 5 CH), 7.19 (s, 1 H, CH), 6.80-6.52 (s, 1H, CH), 5.40 (d, $^{3}J_{H\text{-}H}$ = 5.6, 2H, CH *p*-cymene), 5.21 (d, $^{3}J_{H\text{-}H}$ = 5.6, 2H, CH *p*-cymene), 4.22 (s, 3 H, NCH_3), 2.62 (hept, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 1H, C*H*$(CH_3)_2$ *p*-cymene), 2.40 and 2.26 (both s, 3H each, CH_3), 2.06 (s, 3 H, C-CH_3 *p*-cymene), 1.15 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$ *p*-cymene). $^{13}C\{^{1}H\}$ + HMBC + HSQC NMR (75 MHz, CD_2Cl_2, 298 K): δ 172.8 (s, N*C*N), 141.9 (s, CH), 138.7 (s, C_q), 137.0 (s, C_q), 133.9 (s, C_q), 133.2 (s, C_q), 131.0 (s, CH), 129.4 (s, CH), 128.4 (s, CH), 111.9 (s, CH), 110.9 (s, CH), 100.7 (s, C_q), 92.1 (s, C_q), 78.2 (s, CH *p*-cymene), 75.5 (s, CH *p*-cymene), 37.3 (s, NCH_3), 31.3 (s, *C*H$(CH_3)_2$ *p*-cymene), 23.0 (s, CH(*C*H$_3$)$_2$ *p*-cymene), 20.4 and 20.2 (both s, CH_3), 19.2 (s, C*C*H$_3$ *p*-cymene).

Preparation of OsCl{κ^2-C,C-(MeBIm-C_6H_4)}(η^6-*p*-cymene) (4): CH_2Cl_2 (45 mL) was added to a mixture of [PhMeBImH]I (680.3 mg, 2.02 mmol), silver oxide (234.5 mg, 1.01 mmol) and molecular sieves (4 Å, 500 mg). The resulting mixture was stirred in absence of light for one hours and a white suspension was formed. $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (800 mg, 1.01 mmol) was added and the mixture was stirred for 3 h yielding an orange solution which was extracted with CH_2Cl_2 from the silver salts to a round bottom flask under argon atmosphere. Basic aluminium oxide (8 g) was added to the orange solution and the mixture was stirred for 24 h. The resulting orange solution was extracted and concentrated to ca~1 mL. Pentane (6 mL) was added and a yellow solid precipitated. The solid was washed with pentane (3x3 mL) and dried in *vacuo*. Yield 1119.1 mg (98 %). X-ray quality crystals were grown by layering a solution of complex **4** in CH_2Cl_2 with pentane. Anal. Calcd. for $C_{24}H_{25}ClN_2Os$ C 50.83 %; H 4.44 %; N 4.94 %. Found: C 50.91 %; H 4.72 %; N 5.08 %. HRMS (electrospray, *m/z*): calcd. for $C_{24}H_{25}ClN_2Os$ $[M]^+$: 568.1318; found: 568.1306. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.07 (m, 1H, CH), 8.0-7.90 (m, 1H, CH), 7.76 (m, 1H, CH), 7.50-7.40 (m, 1H, CH), 7.40-7.30 (m, 2H, CH), 7.08 (m, 1H, CH), 6.94 (m, 1H, CH), 5.70-5.50 (m, 2H, CH *p*-cymene), 5.48 (m, 2H, CH *p*-cymene), 4.27 (s, 3H, NCH_3), 2.22 (s, 3H, CH_3 *p*-cymene), 2.10 (m, 1H, -C*H*$(CH_3)_2$ *p*-cymene), 0.85 and 0.73 (both d, both ^{3}J = 6.9 Hz, 3H each, CH(C*H*$_3$)$_2$ *p*-cymene). $^{13}C\{^{1}H\}$ + HMBC + HSQC NMR (75 MHz, CD_2Cl_2, 298 K): δ 185.9 (s, N*C*N), 148.7 (s, CH), 148.5 (s, CH), 142.0 (s, CH), 136.9 (s, C_q), 132.0 (s, C_q), 125.0 (s, CH), 123.7 (s, CH), 123.0 (s, CH), 122.8 (s, CH), 112.6 (s, CH), 111.7 (s, CH), 110.9 (s, CH), 101.3 (s, C_q *p*-cymene), 91.3 (s, C_q *p*-cymene), 86.2 (s, CH *p*-cymene), 81.9 (s, CH *p*-cymene), 79.7 (s, CH *p*-cymene), 76.4 (s, CH *p*-cymene), 35.7 (s, NCH_3), 31.8 (s, *C*H$(CH_3)_2$ *p*-cymene), 23.3 and 22.6 (both s, CH(*C*H$_3$)$_2$ *p*-cymene), 18.8 (s, CH_3 *p*-cymene).

Preparation of OsCl{κ^2-C,C-(MeBIm*-C_6H_4)}(η^6-*p*-cymene) (5): CH_2Cl_2 (45 mL) was added to a mixture of [PhMeBImH]I (735.7 mg, 2.02 mmol), silver oxide (234.5 mg, 1.01 mmol) and molecular sieves (4 Å, 500 mg). The resulting mixture was stirred in absence of light for one hour and a white suspension was formed. $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (800 mg, 1.01 mmol) was added and the mixture was stirred in absence of light for 3 h yielding an orange solution which was extracted from the silver salts to a round bottom flask under argon atmosphere. Basic aluminium oxide (8 g) was added and the mixture was stirred for 24 h. The resulting orange solution was extracted and concentrated to ca~1 mL. Pentane (6 mL) was added and a yellow solid precipitated. The solid was washed with pentane (3x3 mL) and dried in *vacuo*. Yield 1052.1 mg (88 %). Anal. Calcd. for $C_{26}H_{29}ClN_2Os$ C 52.47 %; H 4.91 %; N 4.71 %. Found: C 52.12 %; H 5.14 %; N 4.84 %. HRMS (electrospray, *m/z*): calcd. for $C_{26}H_{29}ClN_2Os$ $[M]^+$: 596.1634; found: 596.1619. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.10-8.00 (m, 1H, CH), 7.78 (s, 1H, CH), 7.80-7.70

(m, 1H, CH), 7.21 (s, 1H, CH), 7.10-7.00 (m, 1H, CH), 7.00-6.90 (m, 1H, CH), 5.62-5.51 (m, 2H, CH *p*-cymene), 5.50-5.40 (m, 2H, CH *p*-cymene), 4.20 (s, 3H, NCH_3,), 2.45 and 2.41 (both s, 3H each, CH_3), 2.21 (s, 3H, CH_3 p-cymene), 2.15-2.02 (m, 1H, C*H*$(CH_3)_2$ *p*-cymene), 0.84 and 0.71 (both d, both $^3J_{H-H}$ = 6.9 Hz, 3H each, CH(C*H*$_3$)$_2$ *p*-cymene). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (75 MHz, CD_2Cl_2, 298 K): δ 184.4 (s, N*C*N), 148.8 (s, CH), 148.7 (s, CH), 141.9 (s, CH), 135.4 (s, C_q), 132.7 (s, C_q), 132.0 (s, C_q), 130.5 (s, C_q), 124.7 (s, CH), 122.8 (s, CH), 112.4 and 112.3 (both s, CH 2), 111.4 (s, CH), 101.1 (s, C_q *p*-cymene), 91.0 (s, C_q *p*-cymene), 85.9 (s, CH *p*-cymene), 81.6 (s, CH *p*-cymene), 79.5 (s, CH *p*-cymene), 76.4 (s, CH *p*-cymene), 35.6 (s, NCH_3), 31.8 (s, *C*H$(CH_3)_2$ *p*-cymene), 23.4 and 22.6 (both s, CH(*C*H$_3$)$_2$ *p*-cymene), 20.6 and 20.5 (both s, CH_3), 18.8 (s, CH_3 *p*-cymene).

Preparation of Os(OTf){κ²-C,C-(MeBIm-C₆H₄)}(η⁶-*p*-cymene) (6): Silver triflate (45.3 mg, 0.176 mmol) was added to a schlenk containing a dichloromethane (6 mL) solution of compound **4** (100 mg, 0.176 mmol) and acetone (3 drops) was used to sweep along the remaining silver salt. The mixture was stirred in absence of light for 45 minutes and the resulting green solution was filtered through celites to another schlenk. The green solution was concentrated to dryness yielding an oil. Cold pentane (4 mL) was added and a green solid precipitated. The solid was washed with pentane (2 x 4 mL) and dried in *vacuo*. Yield: 95.6 mg (80.0 %). Anal. Calcd. for $C_{25}H_{25}F_3N_2O_3OsS$; C 44.11 %; H 3.70 %; N 4.12 %; S 4.71. Found: C 43.83 %; H 4.07 %; N 3.98 %; S 4.76 %. HRMS (electrospray, *m/z*): calcd. for $C_{24}H_{25}N_2Os$ $[M]^+$: 533.1633; found: 533.1650. IR (ATR, cm^{-1}): (SO) 1223 (s), (SO) 1156 (s), (SO) 1027 (s). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.3-8.2 (m, 1H, CH), 8.1-8.0 (m, 1H, CH), 7.9-7.7 (m, 1H, CH), 7.7-7.6 (m, 1H, CH), 7.5-7.4 (m, 2H, CH), 7.3-7.1 (m, 1H, CH), 7.1-7.0 (m, 1H, CH), 6.0-5.8 (m, 4H, CH *p*-cymene), 4.49 (s, 3H, NCH_3), 2.22 (s, 3H, -CH_3 *p*-cymene), 2.2-1.9 (m, 1H, -C*H*$(CH_3)_2$ *p*-cymene), 0.83 and 0.78 (both d, both ^3J = 7.0 Hz, 3H each, CH(C*H*$_3$)$_2$ *p*-cymene). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (75 MHz, CD_2Cl_2, 298 K): δ 183.0 (s, N*C*N), 149.3 (s, C_q), 146.8 (s, C_q), 145.5 (s, C_q), 141.7 (s, CH), 136.9 (s, C_q), 125.5 (s, CH), 124.5 and 124.4 (both s, 2 CH), 123.5 (s, CH), 112.6 (s, CH), 112.0 (s, CH), 111.4 (s, CH), 100.3 (s, C_q *p*-cymene), 87.2 (s, C_q *p*-cymene), 85.0 (s, *C*H *p*-cymene), 82.0 (s, CH *p*-cymene), 81.3 (s, CH *p*-cymene), 77.5 (s, CH *p*-cymene), 36.6 (s, NCH_3), 31.9 (s, *C*H$(CH_3)_2$ *p*-cymene), 23.0 and 22.5 (both s, CH(*C*H$_3$)$_2$ *p*-cymene), 19.1 (s, CH_3 *p*-cymene). $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2, 298 K): δ -78.9 (s).

Preparation of Os(OTf){κ²-C,C-(MeBIm*-C₆H₄)}(η⁶-*p*-cymene) (7): Silver triflate (308.12 mg, 1.2 mmol) was added to a schlenk containing an orange dichloromethane (35 mL) solution of compound **5** (850 mg, 1.2 mmol) and acetone (10 drops) was used to sweep along the remaining silver salt. The mixture was stirred in absence of light for 45 minutes and the resulting green solution was filtered through celites to another schlenk. The green solution was concentrated to dryness yielding an oil. Cold pentane (4 mL) was added and a green solid precipitated. The solid was washed with pentane (2 x 4 mL) and dried in *vacuo*. Yield: 957.0 mg (94 %). Anal. Calcd. for $C_{27}H_{29}F_3N_2O_3OsS$; C 45.75 %; H 4.12 %; N 3.95 %; S 4.52. Found: C 45.45 %; H 4.27 %; N 3.91 %; S 4.77 %. HRMS (electrospray, *m/z*): calcd. for $C_{26}H_{29}N_2Os$ $[M]^+$: 561.1938; found: 561.1941. IR (ATR, cm^{-1}): (SO) 1226 (s), (SO) 1157 (s), (SO) 1027 (s). ^1H NMR (300 MHz CD_2Cl_2, 298 K) δ 8.3-8.2 (m, 1H, CH), 7.83 (s, 1H, CH), 7.8-7.7 (m, 1H, CH), 7.5-7.3 (m, 1H, CH), 7.34 (s, 1H, CH), 7.3-7.1 (m, 1H, CH), 5.9-5.7 (m, 4H, CH *p*-cymene), 4.44 (s, 3H, NCH_3), 2.50 and 2.47 (both s, 3H each, CH_3), 2.22 (s, 3H, -CH_3 *p*-cymene), 2.1-2.0 (m, 1H, -C*H*$(CH_3)_2$ *p*-cymene), 0.73 and 0.68 (both d, both ^3J = 6.9 Hz, 3H each, CH(C*H*$_3$)$_2$ *p*-cymene). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (75 MHz, CD_2Cl_2, 298 K): δ 181.4 (s, N*C*N), 149.5 (s, C_q), 146.8 (s, C_q), 145.6 (s, C_q), 141.6 (s, CH), 135.5 (s, C_q), 133.6 (s, C_q), 132.8 (s, C_q), 125.2 (s, CH), 124.4 (s, CH), 112.5 (s, CH), 112.4 (s, CH), 111.9 (s, CH), 100.2 (s, C_q *p*-cymene), 86.6 (s, C_q *p*-cymene), 84.7 (s, CH *p*-cymene), 81.7 (s, CH *p*-cymene), 81.1 (s, CH *p*-cymene), 77.3 (s, CH *p*-cymene), 36.3 (s, NCH_3), 31.9 (s, *C*H$(CH_3)_2$ *p*-cymene), 23.0 and 22.4 (both s, CH(*C*H$_3$)$_2$ *p*-cymene), 20.7 and 20.5 (both s, CH_3), 19.1 (s, CH_3 *p*-cymene). $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2, 298 K): δ -78.8 (s).

Preparation of [Os{κ²-C,C-(MeBIm-C₆H₄)(CH₃CN)₄]OTf (8): A green solution of compound **6** (797.3 mg, 1.17 mmol) in acetonitrile (30 mL) was heated at 75 ºC for 9 days. The resulting green solution was concentrated in vacuo to dryness and a green oil was formed. A green solid precipitated with the addition of cold Et_2O (4 mL). The green solid was washed with Et_2O (2x3 mL) and dried in *vacuo*. Yield: 776.7 mg (93 %). X-ray quality crystals were grown by layering a solution of complex **8** in CH_2Cl_2 with pentane. Anal. Calcd. for $C_{23}H_{23}F_3N_6O_3OsS$; C 38.87 %; H 3.26 %; N 11.82 %; S 4.51. Found: C 38.89 %; H 3.50 %; N 11.52 %; S 4.68 %. HRMS (electrospray, *m/z*): calcd. for $C_{18}H_{17}N_4Os$ $[M-2(NCCH_3)]^+$: 481.1064; found: 481.1064. IR (ATR, cm^{-1}): (*NC*CH$_3$) 2253 (m), (CF) 1262 (vs), (SO) 1223 (m), (SO) 1149 (s), (SO) 1029 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.1-7.9 (m, 1H, CH), 7.8-7.6 (m, 2H, CH), 7.5-7.3 (m, 1H, CH), 7.4-7.2 (m, 2H, CH), 7.0-6.8 (m, 2H, CH), 4.13 (s, 3H, NCH_3), 2.74 and 2.69 (both s, 3H each, 2 $NCCH_3$), 2.24 (s, 6H, 2 $NCCH_3$). ^1H NMR (300 MHz, $NCCD_3$, 298 K): δ 8.1-8.0 (m, 1H, CH), 7.8-7.7 (m, 2H, CH), 7.5-7.4 (m, 1H, CH), 7.3-7.2 (m, 2H, CH), 7.0-6.8 (m, 2H, CH), 4.13 (s, 3H, NCH_3). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (75 MHz, $NCCD_3$, 298 K): δ 187.1 (s, N*C*N), 153.5 (s, C_q), 148.2 (s, C_q), 138.5 (s, CH), 137.8 (s, C_q), 133.7 (s, C_q), 124.1 (s, C_q), 123.5 (s, CH), 122.6 (s, CH), 121.6 (s, CH), 111.9 (s, CH), 110.7 (s, CH), 110.4 (s, CH), 34.0 (s, NCH_3). $^{19}F\{^1H\}$ NMR (282 MHz, $NCCD_3$, 298 K): δ -79.3 (s).

Preparation of [Os{κ²-C,C-(MeBIm*-C₆H₄)(CH₃CN)₄]OTf (9): A green solution of compound **7** (400.0 mg, 0.564 mmol) in acetonitrile was heated 75ºC for 9 days. The solution was concentrated to dryness yielding a dark green oil. Cold Et_2O (3 mL) was added and a green solid precipitated. The solid was washed with Et_2O (2 x 3 mL) and dried in *vacuo*. Yield: 396.6 mg (95 %). Anal. Calcd. for $C_{25}H_{27}F_3N_6O_3OsS$; C 40.64 %; H 3.68 %; N 11.38 %; S 4.34. Found: C 40.33 %; H 3.48 %; N 11.17 %; S 4.63 %. HRMS (electrospray, *m/z*): calcd. for $C_{20}H_{21}N_4Os$ $[M - 2NCCH_3]^+$: 509.1381; found: 509.1376. IR (ATR, cm^{-1}): (*NC*CH$_3$) 2261 (m), (CF) 1259 (vs), (SO) 1222 (m), (SO) 1142 (s), (SO) 1028 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.77 (s, 1H, CH), 7.7-7.6 (m, 2H, 2 CH), 7.16 (s, 1H, CH), 7.0-6.8 (s, 2H, CH), 4.07 (s, 3H, NCH_3), 2.73 and 2.68 (both s, 3H each, 2 $NCCH_3$), 2.46 and 2.40 (both s, 3H each, CH_3), 2.23 (s, 6H, 2 $NCCH_3$). ^1H NMR (300 MHz, $NCCD_3$, 298 K): δ 7.85 (s, 1H, CH), 7.8-7.7 (m, 2H, 2 CH), 7.29 (s, CH), 7.0-6.8 (m, 2H, 2 CH), 4.09 (s, 3H, NCH_3), 2.46 and 2.41 (both s, 3H each, -CH_3), 2.20 (s, 6H 2 NCC*H*$_3$). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (75 MHz, $NCCD_3$, 298 K): δ 185.5 (s, N*C*N), 153.6 (s, CH), 148.1 (s, CH), 138.4 (s, CH), 136.2 (s, C_q), 132.1 (s, C_q), 131.3 (s, C_q), 123.8 (s, CH), 121.5 (s, CH), 120.6 (s, C_q), 118.3 (s, C_q), 115.9 (s, CH), 111.7 (s, CH), 111.4 (s, CH), 111.0 (s, CH), 33.9 (s, NCH_3), 20.2 and 20.1 (both s, -CH_3). $^{19}F\{^1H\}$ NMR (282 MHz, $NCCD_3$, 298 K): δ -79.3 (s).

Preparation of *mer*-Os{κ²-C,C-(MeBIm-C₆H₄)(PhMeBIm)(CH₃CN)₃]OTf (10a and 10b): A mixture of silver oxide (32.6 mg, 0.14 mmol) and [PhMeBImH]I (94.6 mg, 0.28 mmol) in dichloromethane (10 mL) was stirred in absence of light for one hour and a white powder precipitated. Compound **8** (200 mg, 0.28 mmol) was added and the mixture was stirred for 6 hours. The resulting green solution was extracted to another schlenck. The solution was concentrated in *vacuo* to dryness and a green oil was formed. Cold pentane (8 mL) was added and a green solid precipitated and was washed with more pentane (3x3 mL) and dried in *vacuo* yielding a mixture of two isomers in 1:1 ratio. Yield: 187.5 mg (76 %). Anal. Calcd. for $C_{35}H_{32}F_3N_7O_3OsS$; C 47.88 %; H 3.67 %; N 11.17 %; S 3.65 %. Found: C 47.53 %; H 3.83 %; N 11.41 %; S 3.98 %. HRMS (electrospray, *m/z*): calcd. for $C_{30}H_{26}N_5Os$ $[M - 2NCCH_3]^+$: 648.1799; found: 648.1791. IR (ATR, cm^{-1}): (*NC*CH$_3$) 2254 (m), (CF) 1259 (vs), (SO) 1221 (m), (SO) 1148 (s), (SO) 1028 (vs).Selected spectroscopic data for Isomer **10a**: ^1H NMR (500 MHz, $NCCD_3$, 298 K): δ 8.2-8.1 (m, 1H, CH), 7.8-7.7 (m, 1H, CH), 7.8-6.7 (13H, CH), 7.0-6.8 (m, 1H, CH), 6.8-6.7 (m, 1H, CH), 4.11 (s, 3H, NCH_3), 3.96 (s, 3H, NCH_3), 2.3-1.7 (9H, 3 NCC*H*$_3$).$^{13}C\{^1H\}$ + HMBC + HSQC NMR (125.76 MHz, $NCCD_3$, 298 K): δ 192.4 (s, NCN), 188.9 (s, NCN), 153.5 (s, C_q), 149.0 (s, C_q), 142.8 (s, CH), 140-133 (4 C_q), 137-110 (16 CH), 37.4 (s, NCH_3), 34.1 (s, NCH_3), 5-4 (2 $NCCH_3$). Note: $NCCH_3$ signals missing presumably due to coincidental overlap and exchange with the deuterated solvent. Isomer **10b**: ^{1}H NMR (500 MHz, $NCCD_3$, 298 K): δ 8.2-8.1 (m, 1H, CH), 7.9-7.8 (m, 1H, CH), 7.8-6.8 (10H, CH), 7.5-7.3 (m, 1H, CH), 7.3-7.2 (m, 2H, CH), 7.1-6.9 (m, 2H, CH), 3.90 (s, 3H, NCH_3), 3.65 (s, 3H, NCH_3), 2.3-1.7 (9H, 3$NCCH_3$). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (125.76 MHz, $NCCD_3$, 298 K): δ 189.6 (s, NCN), 188.3 (s, NCN), 157.7 (s, C_q), 153.1 (s, C_q), 140-133 (5 C_q), 137-110 (17 CH), 36.3 (s, NCH_3), 34.0 (s, NCH_3), 5-4 (2 $NCCH_3$). Note: $NCCH_3$ signals missing presumably due to coincidental overlap and exchange with the deuterated solvent. $^{19}F\{^1H\}$ NMR (282 MHz, $NCCD_3$, 298 K): δ -79.2 (s).

Preparation of *mer*-Os{κ^2-C,C-(MeBIm*-C_6H_4)(PhMeBIm*)($CH_3CN)_3$]OTf (11a and 11b): A mixture of silver oxide (62.5 mg, 0.27 mmol) and [PhMeBIm*H]I (197.2 mg, 0.54 mmol) in dichloromethane (20 mL) was stirred for one hour in the absence of light and a white powder precipitated. Compound **9** (400 mg, 0.54 mmol) was added and the mixture was stirred for 6 hours. The resulting green solution was extracted to another schlenck. The solution was concentrated in *vacuo* to dryness and a green oil was formed. Cold pentane (8 mL) was added and a green solid precipitated and was washed with more pentane (3x3 mL) and dried in *vacuo* yielding a mixture of two isomers. Yield: 434.5 mg (86 %). Anal. Calcd. for $C_{39}H_{40}F_3N_7O_3OsS$; C 50.15 %; H 4.32 %; N 10.50 %; S 3.43 %. Found: C 50.38 %; H 4.26 %; N 10.32 %; S 3.42 %. HRMS (electrospray, *m/z*): calcd. for $C_{34}H_{34}N_5Os$ [M- 2$NCCH_3$]$^+$: 704.2425; found: 704.2397. IR (ATR, cm^{-1}): (<u>NC</u>CH_3) 2254 (m), (CF) 1261 (vs), (SO) 1222 (m), (SO) 1154 (s), (SO) 1028 (vs). Isomer **11a**: ^{1}H NMR (500 MHz, $NCCD_3$, 298 K): δ 7.92 (s, 1H, CH), 7.8-7.7 (m, 1H, CH), 7.8-7.6 (5H, Ph), 7.33 (s, 1H, CH), 7.32 (s, 1H, CH), 7.2-7.1 (m, 1H, CH), 6.9-6.8 (m, 1H, CH), 6.8-6.6 (m, 1H, CH), 6.53 (s, 1H, CH), 4.05 (s, 3H, NCH_3), 3.90 (s, 3H, NCH_3), 2.5-2.3 (s, 12H, 4CH_3), 2.3-1.7 (9H, 3 $NCCH_3$). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (125 MHz, $NCCD_3$, 298 K): δ 191.0 (s, NCN), 187.4 (s, NCN), 153.6 (s, C_q), 149.0 (s, C_q), 142.6 (s, CH), 140-131 (7 C_q), 137-111 (10 CH), 136.5 (s, C_q), 135.2 (s, C_q), 124.3 (s, CH), 121.3 (s, CH), 119-116 (2 C_q $NCCH_3$), 37.2 (s, NCH_3), 33.8 (s, NCH_3), 21-20 (4 CH_3), 5-4 (2 $NCCH_3$). Note: $NCCH_3$ signals missing presumably due to coincidental overlap and exchange with the deuterated solvent. Isomer **11b**: ^{1}H NMR (500 MHz, $NCCD_3$, 298 K): δ 7.88 (s, 1H, CH), 7.9-7.8 (m, 1H, CH), 7.8-7.4 (6H, Ph), 7.31 (s, 1H, CH), 7.18 (s, 1H, CH), 7.1-6.9 (m, 2H, CH), 6.58 (s, 1H, CH), 3.84 (s, 3H, NCH_3), 3.58 (s, 3H, NCH_3), 2.5-2.2 (s, 12H, 4CH_3), 2.3-1.7 (s, 9H, 3 $NCCH_3$). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (125 MHz, $NCCD_3$, 298 K): δ 188.3 (s, NCN), 186.9 (s, NCN), 157.7 (s, C_q), 153.2 (s, C_q), 136.3 (s, C_q), 134.8 (s, C_q), 140-131 (7 C_q), 137-111 (11 CH), 124.3 (s, CH), 122.3 (s, CH), 119-116 (2 C_q $NCCH_3$) 36.2 (s, NCH_3), 33.9 (s, NCH_3), 21-20 (4 CH_3), 5-4 (2 $NCCH_3$). Note: $NCCH_3$ signals missing presumably due to coincidental overlap and exchange with the deuterated solvent. $^{19}F\{^1H\}$ NMR (282 MHz, $NCCD_3$, 298 K): δ -79.3 (s).

Preparation of *fac*-Os{κ^2-C,C-(MeBIm-C_6H_4)(PhMeBIm)($CH_3CN)_3$]OTf (10c): A solution of complexes **10a** and **10b** (347.8 mg, 0.396 mmol) in acetonitrile was stirred for two days at 75 ºC, the resulting green solution was concentrated in vacuo to dryness and Et_2O (4 mL) was added yielding a green solid which was washed with more Et_2O (3 x 4 mL). Yield 296.0 mg (85 %). X-ray quality crystals were grown by layering a solution of complex **10c** in CH_2Cl_2 with pentane. Anal. Calcd. for $C_{35}H_{32}F_3N_7O_3OsS$; C 47.88 %; H 3.67 %; N 11.17 %; S 3.65 %. Found: C 48.06 %; H 3.93 %; N 10.88 %; S 3.79 %. HRMS (electrospray, *m/z*): calcd. for $C_{28}H_{23}N_4Os$ [M-3$NCCH_3$]$^+$: 607.1538; found: 607.1533. IR (ATR, cm^{-1}): (<u>NC</u>CH_3) 2251 (m), (CF) 1258 (vs), (SO) 1222 (m), (SO) 1148 (s), (SO) 1028 (vs). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.7-7.6 (m, 1H, CH), 7.6-7.4 (m, 1H, CH), 7.4-7.2 (s, 5H, CH), 7.2-7.1 (m, 1H, CH), 7.0-6.8 (m, 2H, CH), 6.9-6.8 (s, 1H, CH), 6.8-6.6 (m, 1H, CH), 6.7-6.6 (m, 1H, CH), 6.3-6.2 (m, 1H, CH), 6.3-6.2 (m, 1H, CH), 6.1-6.0 (s, 1H, CH), 6.0-5.8 (m, 1H, CH), 4.31 (s, 3H, NCH_3), 3.85 (s, 3H, NCH_3), 2.80 (s, 3H, $NCCH_3$), 2.74 (s, 3H, $NCCH_3$), 2.16 (s, 3H, $NCCH_3$). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (75 MHz, CD_2Cl_2, 298 K): δ 189.6 (s, NCN), 178.1 (s, NCN), 152.4 (s, C_q), 151.2 (s, C_q), 138.9 (s, C_q), 137.3 (s, CH), 137.2 (s, C_q), 136.9 (s, CH), 136.1 (s, C_q), 133.6 (s, C_q), 128.6 (s, CH), 128.2 (s, CH), 127.6 (s, CH), 127.3 (s, CH), 127.2 (s, CH), 122.9 (s, CH), 122.5 (s, CH), 122.4 (s, C_q), 122.3 (s, CH), 122.2 (s, 2 $NCCH_3$), 120.5 (s, CH), 118.5 (s, $NCCH_3$), C 112.5 (s, CH), 110.6 (s, CH), 109.9 (s, CH), 108.4 (s, CH), 35.5 (s, NCH_3), 33.8 (s, NCH_3), 4.8 (s, $NCCH_3$), 4.6 (s, $NCCH_3$), 4.2 (s, $NCCH_3$). $^{19}F\{^1H\}$ NMR (282 MHz, $NCCD_3$, 298 K): δ -78.9 (s).

Preparation of *fac*-Os{κ^2-C,C-(MeBIm*-C_6H_4)(PhMeBIm*)($CH_3CN)_3$]OTf (11c): A solution of complexes **11a** and **11b** (150.0 mg, 0.165 mmol) in acetonitrile was stirred for two days at 75 ºC, the resulting green solution was concentrated in vacuo to dryness and Et_2O (4 mL) was added yielding a green solid which was washed with more Et_2O (3 x 3 mL). Yield 93.8 mg (62 %). Anal. Calcd. for $C_{39}H_{40}F_3N_7O_3OsS$; C 50.15 %; H 4.32 %; N 10.50 %; S 3.43 %. Found: C 50.15 %; H 4.26 %; N 10.34 %; S 3.74 %. $C_{32}H_{31}N_4Os$ [M-3$NCCH_3$]$^+$;: 663.2163; found: 663.2159. IR (ATR, cm^{-1}): (<u>NC</u>CH_3) 2253 (m), (CF) 1258 (vs), (SO) 1222 (m), (SO) 1147 (s), (SO) 1029 (vs). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.8-7.7 (m, 1H, CH), 7.5-7.4 (m, 1H, CH), 7.39 (s, 1H, CH), 7.3-7.2 (m, 1H, CH), 7.06 (s, 1H, CH), 7.03 (s, 1H, CH), 6.9-6.8 (m, 1H, CH), 6.8-6.7 (m, 1H, CH), 6.8-6.6 (m, H, CH), 6.7-6.6 (m, 1H, CH), 6.3-6.2 (m, 1H, CH), 6.3- 6.2 (m, 1H, CH), 6.0-5.8 (m, 1H, CH), 5.87 (s, 1H, CH), 4.18 (s, 3H, NCH_3), 3.75 (s, 3H, NCH_3), 2.75 (s, 3H, $NCCH_3$), 2.69 (s, 3H, $NCCH_3$), 2.45 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.24 (s, 3H, $NCCH_3$), 2.05 (s, 3H, CH_3). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (125.76 MHz, CD_2Cl_2, 298 K): δ 188.4 (s, NCN), 176.5 (s, NCN), 152.6 (s, C_q), 151.4 (s, C_q), 137.5 (s, C_q), 137.4 (s, C_q), 137.3 (s, CH), 135.4 (s, C_q), 134.5 (s, C_q), 132.1 (s, C_q), 131.3 (s, C_q), 131.2 (s, C_q), 130.8 (s, C_q), 130.2 (s, C_q), 128.6 (s, CH), 128.1 (s, CH), 127.5 (s, CH), 127.4 (s, CH), 127.3 (s, CH), 122.6 (s, CH), 122.0 (s. $NCCH_3$), 121.8 (s, $NCCH_3$), 120.3 (s, CH), 118.1 (s, $NCCH_3$), 112.2 (s, CH), 111.5 (s, CH), 110.4 (s, CH), 109.9 (s, CH), 109.2 (s, CH), 35.3 (s, NCH_3), 33.6 (s, NCH_3), 20.5 (s, CH_3), 20.4 (s, CH_3), 20.2 (s, CH_3), 19.9 (s, CH_3), 4.7 (s, $NCCH_3$), 4.6 (s, $NCCH_3$), 4.2 (s, $NCCH_3$). $^{19}F\{^1H\}$ NMR (282 MHz, $NCCD_3$, 298 K): δ -79.0 (s).

Preparation of OsH{κ^2-C,C-(MeBIm-C_6H_4)}$_3$ (12): A solution of complexes **10a** and **10b** (200.0 mg, 0.227 mmol), [PhMeBimH]I (76.6 mg, 0.227 mmol) and NEt_3 (317.1 µL, 0.91 mmol) in DMF (5 mL) was stirred for 3 hours at 95 ºC. The resulting solution was concentrated to dryness and toluene (8 mL) was added. The dark yellow solution was extracted and concentrated in *vacuo* to ca~1 mL and MeOH (5 mL) was added. A pale solid precipitated and the solution was filtered off. The resulting white solid was washed with MeOH (3x3 mL). Yield 122.0 mg (66 %). X-ray quality crystals were grown by adding acetonitrile to **12**. Anal. Calcd. for $C_{42}H_{34}N_6Os$; C 62.05 %; H 4.22 %; N 10.34 %. Found: C 62.35 %; H 4.08 %; N 10.61 %. HRMS (electrospray, *m/z*): calcd. for $C_{42}H_{34}N_6Os$ [M]$^+$: 814.2457; found: 814.2500. IR (ATR, cm^{-1}): (Os-H) 2166 (vw). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.3-8.1 (m, 3H, CH), 8.1-8.0 (m, 3H, CH), 7.4-7.2 (m, 3H, CH), 7.3-7.1 (m, 6H, CH), 7.1-7.0 (m, 3H, CH), 6.6-6.5 (m, 3H, CH), 6.3-6.2 (m, 3H, CH), 3.30 (s, 9H, NCH_3), -9.73 (s, 1H, Os-H). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (125.76 MHz, CD_2Cl_2, 298 K): δ 194.9 (s, NCN), 155.2 and 149.5 (both s, 2 C_q), 137.2 (s, C_q), 137.1 (s, CH), 132.7 (s, C_q), 123.7 (s, C_q), 122.4 (s, CH), 122.4 (s, CH), 122.3 (s, C_q), 112.5 (s, CH), 111.4 (s, CH), 110.0 (s, CH), 35.7 (s, NCH_3).

Preparation of OsH{κ^2-C,C-(MeBIm*-C_6H_4)}$_3$ (13): A solution of complexes **11a** and **11b** (150.0 mg, 0.161 mmol), [PhMeBim*H]I (58.5 mg, 0.161 mmol) and NEt_3 (317.1 µL, 0.91 mmol) in DMF (5 ml) was stirred for three hours at 95 ºC. A pale solid precipitated and the solution was filtered off. The resulting white solid was washed with MeOH (3x3 mL). Yield 135.0 mg (94 %). Anal. Calcd. for $C_{48}H_{46}N_6Os$; C 64.26 %; H 5.17 %; N 9.37 %. Found: C 64.00 %; H 4.93 %; N 9.35 %. HRMS (electrospray, *m/z*): calcd. for $C_{48}H_{46}N_6Os$ [M]$^+$: 898.3397; found: 898.3364. IR (ATR, cm^{-1}): (Os-H) 2123 (s).

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.0-7.9 (m, 6H, 6 CH), 7.1-7.0 (m, 3H, CH), 6.98 (s, 3H, CH), 6.6-6.4 (m, 3H, CH), 6.3-6.1 (m, 3H, CH), 3.23 (s, 9H, NCH_3), 2.46 and 2.36 (both s, 9 H each, both -CH_3), -9.89 (s, 1H, Os-H). $^{13}C\{^1H\}$ + HMBC + HSQC NMR (75.47 MHz, CD_2Cl_2, 298 K): δ 194.1 (s, N*C*N), 155.6 and 149.8 (both s, 2 C_q), 137.2 (s, CH), 135.9 (s, C_q), 131.4 (s, C_q) 131.2 (s, C_q), 131.0 (s, C_q), 123.4 (s, CH), 122.3 (s, CH), 112.4 (s, CH), 112.3 (s, C_q), 110.6 (s, CH), 35.6 (s, NCH_3), 20.6 and 20.4 (both s, 2 CH_3).

Structural Analysis of Complexes 4, 8, 10c and 12. X-ray data were collected for the complexes on a Bruker Smart APEX CCD (**8**, **10c**) or APEX CCD DUO (**10c** and **12**) diffractometers equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ= 0.71073 Å) operating at 50 kV and 40 mA (**4**) or 30 mA (**8**, **10c**, and **12**). Data were collected over the complete sphere. Each frame exposure time was 10 s (**8**, **10c**, and **12**), or 20 s (**4**) 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 Patterson or direct methods and refined by full-matrix least squares on F^2 with SHELXL97,[24] including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms (except hydrides) were observed in the least Fourier Maps or calculated, and refined freely or using a restricted riding model. In **12**, hydrogen bonded to metal atoms was observed in the last cycles of refinement but refined too close to metals, so a restricted refinement model was used for all of them (d(Os-H= 1.59(1) Å). The dichloromethane solvent molecules in **4** and a phenyl group in **10c** were observed disordered and refined with different moieties with complementary occupancy factors and isotropic displacement paramerters.

Crystal data for **4**: $C_{24}H_{25}ClN_2Os$, 0.225(CH_2Cl_2), M_W 586.22, yellow, irregular block (0.20 x 0.14 x 0.09), triclinic, space group P-1, *a*: 12.9012(14) Å, *b*: 15.4777(17) Å, *c*: 22.973(3) Å, *α*: 76.540(2)°, *β*: 83.6930(10)°, *γ*: 76.701(2)°, *V* = 4334.0(8) Å^3, *Z* = 8, *Z'* = 4, D_{calc}: 1.797 g cm^{-3}, F(000): 2284, T = 100(2) K, μ 6.076 mm^{-1}. 48199 measured reflections (2θ: 3-58º, ω scans 0.3º), 22007 unique (R_{int} = 0.0273); min./max. transm. Factors 0.677/0.862. Final agreement factors were R^1 = 0.0298 (18912 observed reflections, I > 2σ(I)) and wR^2 = 0.0725; data/restraints/parameters 22007/82/1078; GoF = 1.023. Largest peak and hole 3.013 (close to osmium atom) and -1.385 e/ Å^3.

Crystal data for **8**: $C_{22}H_{23}N_6Os$, CF_3O_3S, CH_2Cl_2, M_W 795.66, colourless, irregular block (0.24 x 0.21 x 0.14), triclinic, space group P-1, *a*: 8.7097(4) Å, *b*: 13.2661(7) Å, *c*: 13.7956(7) Å, *α*: 69.4460(10)°, *β*: 80.3970(10)°, *γ*: 78.8170(10)°, *V* = 1455.70(13) Å^3, *Z* = 2, *Z'* = 1, D_{calc}: 1.815 g cm^{-3}, F(000): 776, T = 100(2) K, μ 4.692 mm^{-1}. 15454 measured reflections (2θ: 3-58º, ω scans 0.3º), 6653 unique (R_{int} = 0.0201); min./max. transm. Factors 0.676/0.862. Final agreement factors were R^1 = 0.0232 (6279 observed reflections, I > 2σ(I)) and wR^2 = 0.0583; data/restraints/parameters 6653/0/375; GoF = 1.006. Largest peak and hole 1.199 (close to osmium atoms) and -0.983 e/ Å^3.

Crystal data for **10c**: $C_{34}H_{32}N_7Os$, CF_3O_3S, M_W 877.94, colourless, irregular block (0.11 x 0.04 x 0.04), triclinic, space group P-1, *a*: 12.3099(14) Å, *b*: 14.2086(16) Å, *c*: 21.270(2) Å, *α*: 73.721(2)°, *β*: 83.081(2)°, *γ*: 76.522(2)°, *V* = 3466.7(7) Å^3, *Z* = 4, *Z'* = 2, D_{calc}: 1.682 g cm^{-3}, F(000): 1736, T = 153(2) K, μ 3.801 mm^{-1}. 31879 measured reflections (2θ: 3-57º, ω scans 0.3º), 12823 unique (R_{int} = 0.0750); min./max. transm. Factors 0.625/0.862. Final agreement factors were R^1 = 0.0605 (7994 observed reflections, I > 2σ(I)) and wR^2 = 0.1299; data/restraints/parameters 12823/8/882; GoF = 1.028. Largest peak and hole 2.122 (close to osmium atoms) and -1.716 e/ Å^3.

Crystal data for **12**: $C_{42}H_{34}N_6Os$, C_2H_3N, M_W 854.01, green, irregular block (0.19 x 0.14 x 0.08), monoclinic, space group P2$_1$/c, *a*: 11.0513(12) Å, *b*: 19.438(2) Å, *c*: 16.4337(18) Å, *β*: 97.889(2)°, *V* = 3496.9(7) Å^3, *Z* = 4, *Z'* = 1, D_{calc}: 1.622 g cm^{-3}, F(000): 1704, T = 100(2) K, μ 3.691 mm^{-1}. 38075 measured reflections (2θ: 3-58º, ω scans 0.3º), 8978 unique (R_{int} = 0.0458); min./max. transm. Factors 0.675/0.862. Final agreement factors were R^1 = 0.0283 (7172 observed reflections, I > 2σ(I)) and wR^2 = 0.0642; data/restraints/parameters 8978/1/476; GoF = 1.023. Largest peak and hole 1.200 and -1.103 e/ Å^3.

Computational details, full reaction profile and cartesian coordinates of calculated complexes: The optimization of **10c** was performed at the DFT level using the B3LYP functional[25] supplemented with the Grimme's dispersion correction D3[26] as implemented in Gaussian09.[27] Os atom was described by means of an effective core potential SDD for the inner electron[28] and its associated double-ζ basis set for the outer ones, complemented with a set of f-polarization functions.[29] The 6-31G** basis set was used for the H, C, N and P atoms.[30]

The Quantum Theory of Atoms in Molecules analyses of **10c** were performed with the AIMAII software package.[31]

ASSOCIATED CONTENT

Supporting Information

^{1}H NMR, $^{13}C\{1H\}$ APT and ^1H-^1H NOESY NMR spectra utilized for the characterization of all the complexes and centroids calculation of complex **10c** (PDF).

Crystallographic data for compounds **4**, **8**, **10c**, and **12** (CIF).

Cartesian coordinates of calculated compound (XYZ).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Preparation of Capped Octahedral $OsHC_6$-Complexes by Sequential Carbon-Directed C-H Bond Activation Reactions