A Capped Octahedral MHC$_6$ Compound of a Platinum Group Metal

Beatriz Eguillor,[a] Miguel A. Esteruelas,[a]* Virginia Lezáun,[a] Montserrat Oliván,[a] Enrique Oñate,[a] Jui-Yi Tsai,[b] and Chuanjun Xia[b]

[a] Dr. B. Eguillor, Prof. Dr. M. A. Esteruelas, V. Lezáun, Dr. M. Oliván, Dr. E. Oñate

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de Zaragoza – CSIC, 50009 Zaragoza, Spain

E-mail: maester@unizar.es

[b] Dr. J.-Y. Tsai, Dr. C. Xia

Universal Display Corporation, 375 Phillips Boulevard, Ewing, New Jersey 08618, United States

Supporting information for this article is given via a link at the end of the document.

Abstract: A MHC$_6$ complex of a platinum group metal with a capped octahedral arrangement of donor atoms around the metal center has been characterized. This osmium compound OsH$\{\kappa^2$-C,C-(PhBIm-C$_6$H$_4$)$\}_3$, which reacts with HBF$_4$ to afford the 14 e$^-$ species [Os$\{\kappa^2$-C,C-(PhBIm-C$_6$H$_4$)$\}$(Ph$_2$BIm)$_2$]BF$_4$ stabilized by two agostic interactions, has been obtained by reaction of OsH$_6$(PiPr$_3$)$_2$ with N,N'-diphenylbenzimidazolium chloride ([Ph$_2$BImH]Cl) in the presence of NEt$_3$. Its formation takes place through the C,C,C-pincer compound OsH$_2\{\kappa^3$-C,C,C-(C$_6$H$_4$-BIm-C$_6$H$_4$)$\}$(PiPr$_3$)$_2$, the dihydrogen derivative OsCl$\{\kappa^2$-C,C-(PhBIm-C$_6$H$_4$)$\}$(η^2-H$_2$)(PiPr$_3$)$_2$, and the five-coordinate osmium(II) species OsCl$\{\kappa^2$-C,C-(PhBIm-C$_6$H$_4$)$\}$(PiPr$_3$)$_2$.

Transition metal complexes containing only carbon and hydrogen donor atoms at the metal coordination sphere form the family of *blue-blood* organometallic compounds, which have played a determinant role in the conceptual development of the current chemistry. They are stabilized by a metal center in low oxidation state and have usually four-, five-, or six-coordination numbers.[1]

The oxidation state of the metal center determines the coordination number and the geometry of the complexes. High oxidation states are mainly stabilized with oxidizing ligands such as oxygen and halides, in particular fluoride and chloride. Hydride, with a minimal steric influence, is also ideal to achieve high coordination numbers.[2] With the notable exception of the methyl group [3] and combinations cyclopentadienyl-hydride,[4] donor carbon ligands have rarely stabilized *blue-blood* organometallic compounds in high oxidation states and coordination numbers higher than six.

Seven-coordinate *blue-blood* organometallic compounds are known for 5 and 6 group metals, have a MC_7 core, and have been stabilized by using linear isocyanide ligands. Ellis and co-workers have reported homoleptic heptakis(isocyanide)–vanadium(I), –niobium(I), and –tantalum(I) derivatives. Although for the coordination number seven the most common polyhedron is the pentagonal bipyramid,[5] the VC_7 core has the form of a distorted monocapped trigonal prism.[6] However, the TaC_7 core is best described as a capped octahedron slightly distorted towards a capped trigonal prism.[7] The heptakis(isocyanide)–chromium(II), –molybdenum(II), and –tungsten(II) counterparts have been described by the groups of Lippard,[8] Walton,[9] and San Filippo.[10] For these compounds, a capped octahedral arrangement or a capped trigonal prism of C_{2v} symmetry have been also observed depending upon the metal center and the substituent of the isocyanide.

We here report the first seven-coordinate *blue-blood* organometallic compound of a platinum group metal. In contrast to those of 5 and 6 group metals, it has a MHC_6 core and is stabilized by three orthometalated NHC ligands.

Saturated transition metal polyhydride complexes have the ability of losing molecular hydrogen to afford unsaturated species, which coordinate and subsequently activate σ-bonds. In agreement with this, the hexahydride complex $OsH_6(PiPr_3)_2$ (**1**) has proven to promote the chelate-assisted C-H cleavage in a wide range of organic molecules,[11] as well as the direct activation of the C-H bond situated between the nitrogen atoms of imidazolium and benzimidazolium salts.[12] In accordance with this ability, complex **1** is able to induce the orthometalation of a phenyl substituent of *N,N'*-diphenylbenzimidazolium chloride ([Ph_2BImH]Cl) in addition to the coordination of the benzimidazolylidene moiety. As a consequence of this, the treatment of its decalin solutions with 3.0 equiv of the salt and 3.0 equiv of NEt_3, under reflux, for 20 h leads to the seven-coordinate MHC_6 compound $OsH\{\kappa^2\text{-}C,C\text{-}(PhBIm\text{-}C_6H_4)\}_3$ (**2** in Scheme 1), which was isolated as a white solid in 63% yield.
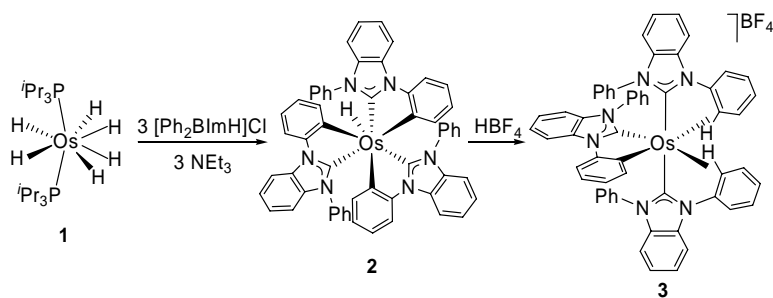
Scheme 1. Preparation and protonation of complex **2**.

Figure 1 shows a view of the structure of **2**. The coordination polyhedron around the osmium atom can be described as a capped octahedron of C_3 symmetry with the Os-H bond contained in the C_3 symmetry axis and the hydride ligand located at the center of the trigonal face defined by the carbene carbon atoms. The analysis of the orbitals of the molecule reveals that this hydride position allows the interaction between the s orbital of the hydride and the formally vacant p orbitals of the carbene carbon atoms (Figure 2). The presence of the hydride in the complex is consistent with a signal at -9.90 ppm in the ^{1}H NMR spectrum.
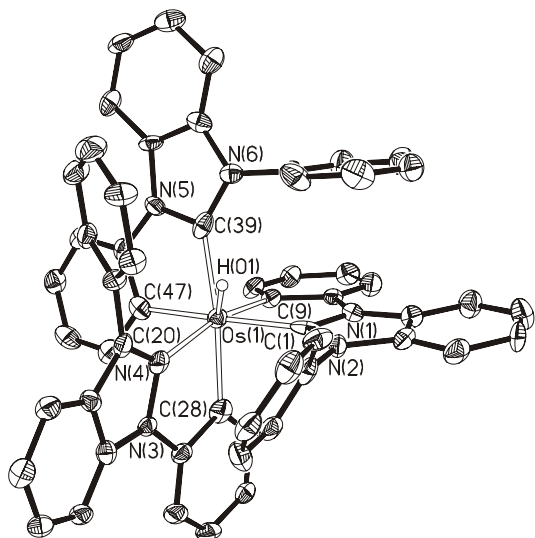

Figure 1. ORTEP diagram of complex **2** (50% probability ellipsoids). Hydrogen atoms (except the hydride) are omitted for clarity. Selected bond lengths and angles are given in Table S1.
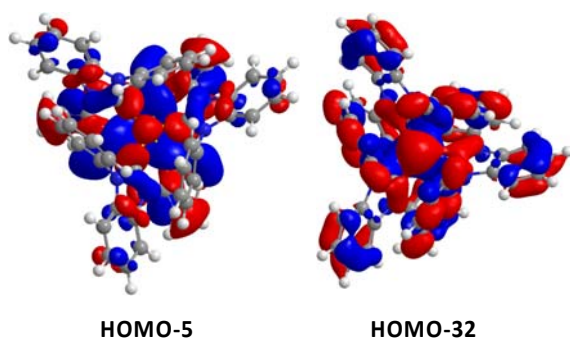
HOMO-5   **HOMO-32**

Figure 2. HOMO-5 and HOMO-32 of complex **2** calculated at the B3LYP/(6-31g**+ SDD) level (isosurface value 0.02).

Complex **2** has Brønsted base character. Thus, in dichloromethane, it reacts with HBF$_4$·OEt$_2$ to afford the salt [Os{κ^2-*C*,*C*-(PhBIm-C$_6$H$_4$)}(Ph$_2$BIm)$_2$]BF$_4$ (**3** in Scheme 1), as a result of the protonation of one of the orthometalated phenyl groups and the reductive elimination of the hydride and other orthometalated phenyl. The salt was isolated as an orange solid in 85% yield and characterized by X-ray diffraction analysis. The structure (Figure 3) reveals an octahedral arrangement of ligands around the metal center, including agostic interactions between the osmium atom and the formed bonds, which are *trans* disposed to the remaining orthometalated chelate group. The agostic interactions are strongly supported by the Os-C(22) (2.473(6) Å), Os-H(22) (1.92(6) Å) and C(22)-H(22) (1.12(6) Å) distances and the Os-C(41) (2.452(6) Å), Os-H(41) (1.83(6) Å) and C(41)-H(41) (1.13(6) Å) bond lengths, which compare well with those reported for other Os-H-C agostic interactions.[13] Furthermore, the respective r_{bp} values of 0.7(1) and 0.6(1) Å agree well with those calculated for other δ agostic interactions.[14] In accordance with these values, the agostic interactions persist in [D$_2$]dichloromethane at temperatures lower than 223 K. Thus, the ^{1}H NMR spectra at these temperatures contain two phenyl resonances at 1.86 and 1.49 ppm, whereas the INEPT ^{13}C spectrum at 213 K shows C-H coupling constants of 114 and 112 Hz for phenyl resonances at 98.4 and 92.9 ppm, respectively, which are about 50 Hz lower than the other $^1J_{\mathrm{C-H}}$ coupling constants. This extreme case[15] of two agostic interactions is forced by the exceptionally high Lewis acidity of the generated 14-valence electrons, non π-stabilized, osmium(II) cation.
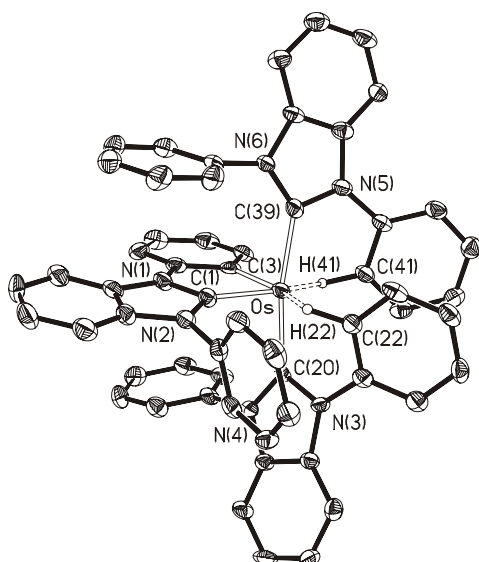
Figure 3. ORTEP diagram of the cation of complex **3** (50% probability ellipsoids). Hydrogen atoms (except those involved in the agostic interactions) are omitted for clarity. Selected bond lengths and angles are given in Table S2.

Chloride plays a fundamental role in the formation of **2**, in agreement with previous observations indicating that the anion markedly influences the stoichiometry of the resulting complex and the coordination fashion of the NHC ligand in reactions of imidazolium and benzimidazolium salts with polyhydrides of platinum group metals.[16] When [Ph$_2$BImH]BF$_4$ was used instead of the chloride salt, the dihydride-osmium(IV) complex OsH$_2${κ^3-C,C,C-(C$_6$H$_4$-BIm-C$_6$H$_4$)}(PiPr$_3$)$_2$ (**4** in Scheme 2) was formed,[17] as a result of the *ortho*-CH bond activation of both phenyl substituents. This compound is also notable, mainly for two reasons: i) it is the first species containing a dianionic C,C,C-pincer ligand in the osmium chemistry [18] and ii) the orthometalation of both phenyl substituents has no precedent for *N,N'*-diphenylbenzimidazolium and only once has been reported for *N,N'*-(diaryl)imidazolium counterparts.[19] Furthermore, it demonstrates the versatility of the NHC ligand, which can stabilize highly unsaturated species by means of agostic interactions and can act as neutral monodentate,[20] monoanionic chelate [21] and dianionic pincer through reversible C-H bond activations of the phenyl groups.
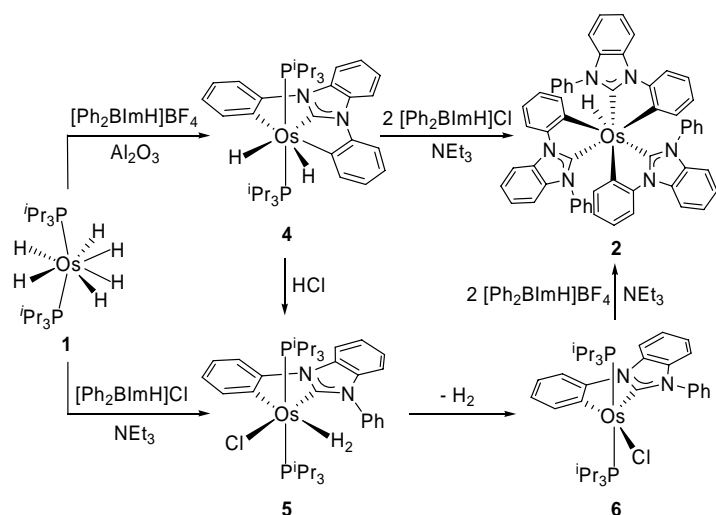
Scheme 2. Synthesis of complexes **4**, **5** and **6**, and formation of complex **2** from complexes **4** and **6**.

Complex **4**, which was isolated as colorless crystals in 49% yield, was also characterized by X-ray diffraction analysis. The structure (Figure 4) proves the formation of the pincer ligand with the activated phenyl groups situated pseudo *trans* (C(9)-Os-C(15) = 144.92(15)°). In contrast to **2**, the coordination geometry around the metal center can be rationalized as a distorted pentagonal bipyramid with axial phosphines and the hydrides, separated by 1.63(4) Å, lying in the equatorial plane along with the pincer. At room temperature, the ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra, in [D$_6$]benzene, are consistent with its X-ray structure, showing equivalent hydrides, metalated phenyl groups, and phosphines. Thus, the ^{1}H NMR spectrum contains only one triplet (J_{H-P} = 19.0 Hz) at -5.96 ppm for the hydride ligands, the ^{13}C{^{1}H} NMR spectrum shows only one triplet (J_{C-P} = 6.3 Hz) at 149.8 ppm for the metalated carbon atom of the activated phenyl groups, and the ^{31}P{^{1}H} NMR spectrum contains a singlet at 10.5 ppm for the phosphines.
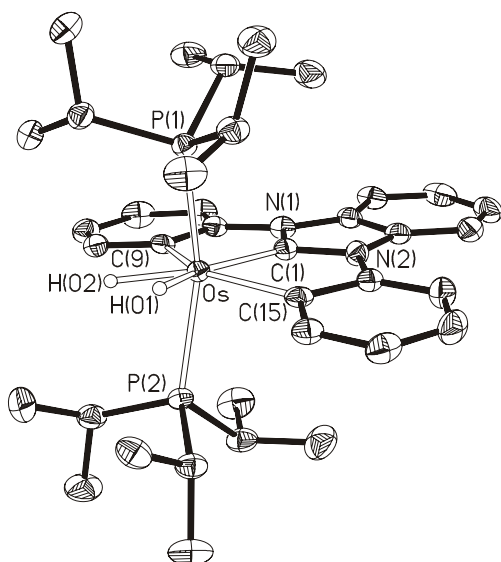
Figure 4. ORTEP diagram of complex **4** (50% probability ellipsoids). Hydrogen atoms (except the hydrides) are omitted for clarity. Selected bond lengths and angles are given in Table S3.

Complex **4** is an intermediate in the formation of **2**. In accordance with this, treatment of decalin solutions of **4** with 2.0 equiv of [Ph_2BImH]Cl and 2.0 equiv of NEt_3, under reflux, also led to **2**. The question is: what is the role of the chloride anion? In the search for information in this direction and some new intermediate, we treated complex **1** with 1.0 equiv of [Ph_2BImH]Cl and 2.0 equiv of NEt_3 in toluene, under reflux. Under these conditions, a mixture of the chloride-osmium(II)-dihydrogen derivative OsCl{κ^2-C,C-($PhBIm$-C_6H_4)}(η^2-H_2)($PiPr_3$)$_2$ (**5**) and the five-coordinate species, resulting from the dihydrogen dissociation, OsCl{κ^2-C,C-($PhBIm$-C_6H_4)}($PiPr_3$)$_2$ (**6**) was obtained. Because the difference in stoichiometry between **4** and **5** is an HCl molecule, we added HCl dissolved in toluene to a toluene solution of **4** and, as expected, complex **5** was formed, which losses H_2 to afford **6**. Both **5** and **6** are intermediates in the formation of **2**. Treatment of the mixture, in decalin, with 2.0 equiv of [Ph_2BImH]BF_4 and 2.0 equiv of NEt_3, under reflux, also yields **2** (Scheme 2). These reactions suggest that the role of the chloride anion is to stabilize the five-coordinate osmium(II) intermediate **6**: the π-donor ability of the chloride anion partially cancels the unsaturated character of the metal center.

Complexes **5** and **6** co-crystallized in a toluene-methanol mixture to afford crystals suitable for X-ray diffraction analysis. Figures 5 and 6 show the structures of both compounds. The geometry around the osmium atom of **5** can be rationalized as a

distorted octahedron with *trans*-phosphines. In the perpendicular plane the chloride ligand is disposed *trans* to the carbene carbon atom, as expected for the π-acceptor character of the benzimidazolylidene unit.[12c] The geometry around the osmium atom of **6** can be described as a distorted trigonal bipyramid with apical phosphines and inequivalent angles of 76.5(3)º (C-Os-C), 120.62(18)º (Cl-Os-C_{aryl}) and 162.87(19)º (Cl-Os-C_{BIm}) within the Y-shaped equatorial plane.
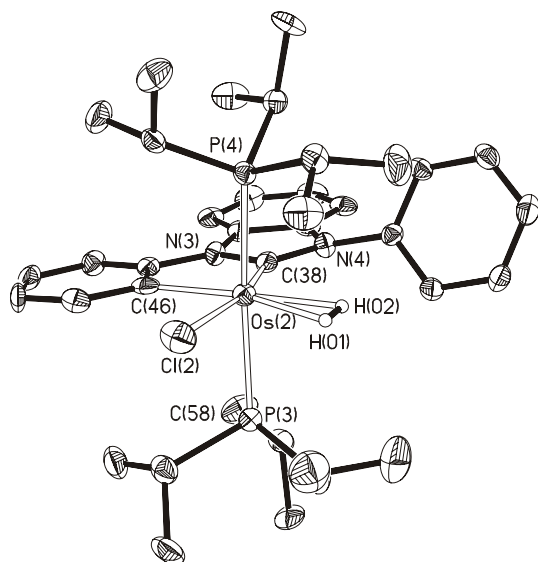

Figure 5. ORTEP diagram of complex **5** (50% probability ellipsoids). Hydrogen atoms (except those of the dihydrogen molecule) are omitted for clarity. Selected bond lengths and angles are given in Table S4.
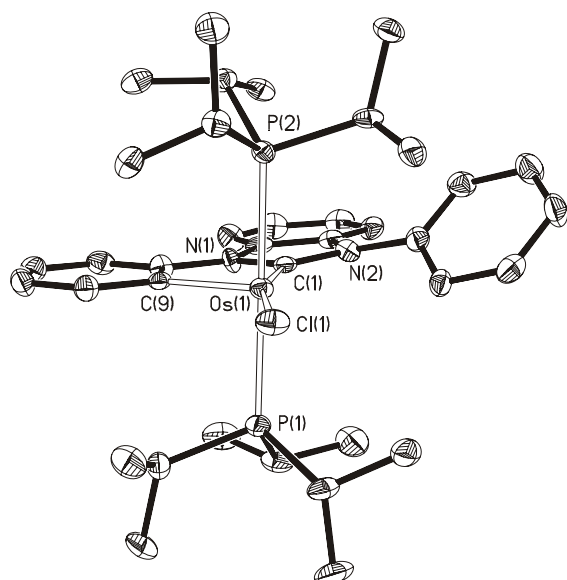

Figure 6. ORTEP diagrams of complex **6** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in Table S5.

The presence of the dihydrogen ligand in **5** is strongly supported by its ^{1}H NMR spectrum in [D$_2$]dichloromethane, which contains the characteristic dihydrogen resonance at -4.27 ppm with a 400 MHz T_1(min) value of 15±1 ms at 213 K. This value corresponds to a H-H distance of 0.84 Å (fast spinning) or 1.06 Å (slow spinning).[22] In accordance with the latter, a H-D coupling constant of 20.2 Hz was obtained from the species containing a partially deuterated η^2-HD ligand.[23]

In conclusion, the first seven-coordinate *blue-blood* organometallic compound of a platinum group metal has been discovered. This novel complex, which has a OsHC$_6$ core with three orthometalated NHC ligands and reacts with HBF$_4$ to afford a highly unsaturated 14-valence electrons fragment stabilized by two agostic interactions, has been prepared in a one-pot synthesis procedure by reaction of the hexahydride OsH$_6$(PiPr$_3$)$_2$ with *N,N'*-diphenylbenzimidazolium chloride. The anion of the salt plays a main role during the process, stabilizing a key intermediate osmium(II) intermediate, and the NHC ligand acts as both dianionic C,C,C-pincer and monoanionic C,C-chelate.

References

[1] *Comprehensive Organometallic Chemistry III* (Eds.-in-chief: R. H Crabtree, D. M. Mingos), Elsevier, **2007**.

[2] G. G. Hlatky, R. H. Crabtree, *Coord. Chem. Rev.* **1985**, *65*, 1-48.

[3] a) V. Pfennig, N. Robertson, K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1350-1352; b) B. Roessler, K. Seppelt, *Angew. Chem. Int. Ed.* Engl. **2000**, *39*, 1259-1261.

[4] a) W. A. Herrmann, H. G. Theiler, P. Kiprof, J. Tremmel, R. Blom, *J. Organomet. Chem.* **1990**, *395*, 69-84; b) C. A. Bayse, M. Couty, M. B. Hall, *J. Am. Chem. Soc.* **1996**, *118*, 8916-8919; c) T. Shima, H. Suzuki, *Organometallics* **2005**, *24*, 3939-3945; d) C. L. Gross, G. S. Girolami, *Organometallics* **2007**, *26*, 160-166.

[5] a) D. Casanova, P. Alemany, J. M. Bofill, S. Alvarez, *Chem. Eur. J.* **2003**, *9*, 1281-1295; b) F. Villafañe, *Coord. Chem. Rev.* **2014**, *281*, 86-99.

[6] M. E. Minyaev, J. E. Ellis, *Acta Cryst.* **2015**, *E71*, 431-434.

[7] M. V. Barybin, W. W. Brennessel, B. E. Kucera, M. E. Minyaev, V. L. Sussman, V. C. Young, Jr., J. E. Ellis, *J. Am. Chem. Soc.* **2007**, *129*, 1141-1150.

[8] a) D. L. Lewis, S. J. Lippard, *J. Am. Chem. Soc.* **1975**, *97*, 2697-2702; b) D. J. Szalda, J. C. Dewan, S. J. Lippard, *Inorg. Chem.* **1981**, *20*, 3851-3857; c) J. C. Dewan, S. J. Lippard, *Inorg. Chem.* **1982**, *21*, 1682-1684; d) J. C. Dewan, W. S. Mialki, R. A. Walton, S. J. Lippard, *J. Am. Chem. Soc.* **1982**, *104*, 133-136.

[9] P. Brandt, F. A. Cotton, J. C. Sekutowski, T. E. Wood, R. A. Walton, *J. Am. Chem. Soc.* **1979**, *101*, 6588-6593.

[10] W. A. LaRue, A. T. Liu, J. San Filippo, Jr., *Inorg. Chem.* **1980**, *19*, 315-320.

[11] a) M. A. Esteruelas, A. B. Masamunt, M. Oliván, E. Oñate, M. Valencia, *J. Am. Chem. Soc.* **2008**, *130*, 11612-11613; b) O. Crespo, B. Eguillor, M. A. Esteruelas, I. Fernández, J. García-Raboso, M. Gómez-Gallego, M. Martín-Ortiz, M. Oliván, M. A. Sierra, *Chem. Commun.* **2012**, *48*, 5328-5330.

[12] a) B. Eguillor, M. A. Esteruelas, M. Oliván, M. Puerta, *Organometallics* **2008**, *27*, 445-450; b) B. Eguillor, M. A. Esteruelas, J. García-Raboso, M. Oliván, E. Oñate, I. M. Pastor, I. Peñafiel, M. Yus, *Organometallics* **2011**, *30*, 1658-1667; c) T. Bolaño, M. A. Esteruelas, I. Fernández, E. Oñate, A. Palacios, J.-Y. Tsai, C. Xia, *Organometallics* **2015**, *34*, 778-789; d) T. Bolaño, M. A. Esteruelas, M. P. Gay, E. Oñate, I. M. Pastor, M. Yus, *Organometallics* **2015**, *34*, 3902-3908.

[13] a) M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro, E. Sola, *J. Am. Chem. Soc.* **1996**, *118*, 89-99; b) T. B. Wen, Z. Y. Zhou; C.-P. Lau, G. Jia, *Organometallics* **2000**, *19*, 3466-3468; c) R. Castro-Rodrigo, M. A. Esteruelas, A. M. López, E. Oñate, *Organometallics* **2008**, *27*, 3547-3555; d) B. Eguillor, M. A. Esteruelas, I. Fernández, M. Gómez-Gallego, A. Lledós, M. Martín-Ortiz, M. Oliván, E. Oñate, M. A. Sierra, *Organometallics* **2015**, *34*, 1898-1910.

[14] R. H. Crabtree, E. M. Holt, M. Lavin, S. M. Morehouse, *Inorg. Chem.* **1985**, *24*, 1986-1992.

[15] Transition metal complexes with two agostic interactions are very rare. For some relevant examples, see: a) D. Huang, J. C. Huffman, J. C. Bollinger, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1997**, *119*, 7398-7399; b) A. C. Cooper, E. Clot, J. C. Huffman, W. E. Streib, F. Maseras, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1999**, *121*, 97-106; c) W. Baratta, E. Herdtweck, P, Rigo, *Angew. Chem. Int. Ed.* **1999**, *38*, 1629-1631; d) W. Baratta, C. Mealli, E. Herdtweck, A. Ienco, S. A. Mason, P. Rigo, *J. Am. Chem. Soc.* **2004**, *126*, 5549-5562; e) N. M. Scott, V. Pons, E. D. Stevens, D. M.

Heinekey, S. P. Nolan, *Angew. Chem. Int. Ed.* **2005**, *44*, 2512-2515; f) T. M. Douglas, A. B. Chaplin, A. S. Weller, *Organometallics* **2008**, *27*, 2918-2921; g) L. J. Sewell, A. B. Chaplin, J. A. B. Abdalla, A. S. Weller, *Dalton Trans.* **2010**, *39*, 7437-7439.

[16] a) S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *J. Am. Chem. Soc.* **2002**, *124*, 10473-10481; b) L. N. Appelhans, D. Zuccaccia, A. Kovacevic, A. R. Chianese; J. R. Miecznikowski, A. Macchioni, E. Clot, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 16299-16311; c) M. Baya, B. Eguillor, M. A. Esteruelas, M. Oliván, E. Oñate, *Organometallics* **2007**, *26*, 6556-6563; d) R. G. Alabau, B. Eguillor, J. Esler, M. A. Esteruelas, M. Oliván, E. Oñate, J.-Y. Tsai, C. Xia, *Organometallics* **2014**, *33*, 5582-5596.

[17] Although the reaction takes place in the presence of NEt_3, in this case, Al_2O_3 is a more appropriate base.

[18] For dianionic-pincer ligands previously reported in the osmium chemistry, see: a) P. Gupta, R. J. Butcher, S. Bhattacharya, *Inorg. Chem.* **2003**, *42*, 5405-5411; b) R. Acharyya, S.-M. Peng, G.-H. Lee, S. Bhattacharya, *Inorg. Chem.* **2003**, *42*, 7378-7380 (C,N,X (X = C, O)); c) L. Casarrubios, M. A. Esteruelas, C. Larramona, J. G. Muntaner, E. Oñate, M. A. Sierra, *Inorg. Chem.* **2015**, *54*, 10998-11006 (N,C,C); d) Z.-Y. Li, W.-Y. Yu, C.-M. Che, C.-K. Poon, R.-J. Wang, T. C. W. Mak, *J. Chem. Soc., Dalton Trans.* **1992**, 1657-1661; e) J. Xiang, W. L. Man, S.-M. Yiu, S.-M. Peng, T.-C. Lau, *Chem. Eur. J.* **2011**, *17*, 13044-13051 (O,N,O).

[19] N. Stylianides, A. A. Danopoulos, D. Pugh, F. Hancock, A. Zanotti-Gerosa, *Organometallics* **2007**, *26*, 5627-5635.

[20] For previously reported complexes containing this ligand as neutral monodentate, see: J. M. Berlin, K. Campbell, T. Ritter, T. W. Funk, A. Chlenov, R. H. Grubbs, *Org. Lett.* **2007**, *9*, 1339-1342.

[21] For previously reported complexes containing this ligand as monoanionic chelate, see: a) A. Tronnier, A. Pöthig, S. Metz, G. Wagenblast, I. Münster, T. Strassner, *Inorg. Chem.* **2014**, *53*, 6346-6356; b) A. Tronnier, U. Heinemeyer, S. Metz, G. Wagenblast, I. Muenster, T. Strassner, *J. Mat. Chem. C* **2015**, *3*, 1680-1693.

[22] M. T. Bautista, E. P. Cappellani, S. D. Drouin, R. H. Morris, C. T. Schweitzer, A. Sella, J. Zubkowski, *J. Am. Chem. Soc.* **1991**, *113*, 4876-4887.

[23] a) P. A. Maltby, M. Schlaf, M. Steinbeck, A. J. Lough, R. H. Morris, W. T. Klooster, T. F. Koetzle, R. C. Srivastava, *J. Am. Chem. Soc.* **1996**, *118*, 5396-5407; b) T. A. Luther, D. M. Heinekey, *Inorg. Chem.* **1998**, *37*, 127-132.

Scheme and Figure legends

Scheme 1. Preparation and protonation of complex **2**.

Figure 1. ORTEP diagram of complex **2** (50% probability ellipsoids). Hydrogen atoms (except the hydride) are omitted for clarity. Selected bond lengths and angles are given in Table S1.

Figure 2. HOMO-5 and HOMO-32 of complex **2** calculated at the B3LYP/(6-31g**+ SDD) level (isosurface value 0.02).

Figure 3. ORTEP diagram of the cation of complex **3** (50% probability ellipsoids). Hydrogen atoms (except those involved in the agostic interactions) are omitted for clarity. Selected bond lengths and angles are given in Table S2.

Scheme 2. Synthesis of complexes **4**, **5** and **6**, and formation of complex **2** from complexes **4** and **6**.

Figure 4. ORTEP diagram of complex **4** (50% probability ellipsoids). Hydrogen atoms (except the hydrides) are omitted for clarity. Selected bond lengths and angles are given in Table S3.

Figure 5. ORTEP diagram of complex **5** (50% probability ellipsoids). Hydrogen atoms (except those of the dihydrogen molecule) are omitted for clarity. Selected bond lengths and angles are given in Table S4.

Figure 6. ORTEP diagrams of complex **6** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in Table S5.

Entry for the Table of Contents

A seven-coordinate $OsHC_6$ organometallic compound has been discovered, which reacts with HBF_4 to afford a highly unsaturated 14-valence electrons fragment stabilized by two agostic interactions.
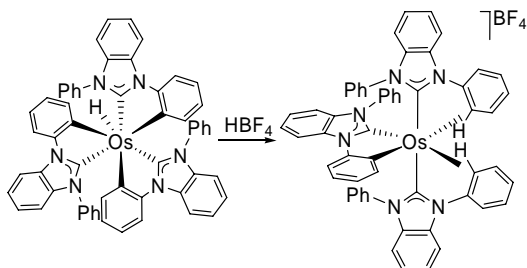
Keywords: osmium • agostic interaction • capped octahedron • NHC • hydride