

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230708071>

Multiple C-H Bond Activation of Phenyl-Substituted Pyrimidines and Triazines Promoted by an Osmium Polyhydride: Formation of Osmapolycycles with Three, Five, and Eight Fused Rings

ARTICLE in ORGANOMETALLICS · FEBRUARY 2010

Impact Factor: 4.13 · DOI: 10.1021/om901030q

CITATIONS

20

READS

26

9 AUTHORS, INCLUDING:



Miguel A Esteruelas

University of Zaragoza

367 PUBLICATIONS 12,147 CITATIONS

SEE PROFILE



Israel Fernández

Complutense University of Madrid

187 PUBLICATIONS 3,016 CITATIONS

SEE PROFILE



Antonio Herrera

Complutense University of Madrid

69 PUBLICATIONS 481 CITATIONS

SEE PROFILE



Miguel A Sierra

Complutense University of Madrid

247 PUBLICATIONS 3,675 CITATIONS

SEE PROFILE

Multiple C–H Bond Activation of Phenyl-Substituted Pyrimidines and Triazines Promoted by an Osmium Polyhydride: Formation of Osmapolycycles with Three, Five, and Eight Fused Rings

Miguel A. Esteruelas,^{*,†} Israel Fernández,[‡] Antonio Herrera,[‡] Mamen Martín-Ortiz,[‡] Roberto Martínez-Álvarez,[‡] Montserrat Oliván,[†] Enrique Oñate,[†] Miguel A. Sierra,^{*,‡} and Marta Valencia[†]

[†]*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain and* [‡]*Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain*

Received November 30, 2009

The reactions of the hexahydride complex $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ (**1**) with 4,5-dimethyl-2,6-bis(4-methylphenyl)pyrimidine (**H₂L1**), 2,4,6-tris-(4-methylphenyl)-1,3,5-triazine (**H₄L2**), and 2,4,6-triphenylpyrimidine (**H₄L3**) have been studied. Complex **1** reacts with **H₂L1** to give a mixture of the metallapolycyclic derivatives $\text{OsH}_3(\text{HL1})(\text{P}^i\text{Pr}_3)_2$ (**2**) and $\text{OsH}_2(\text{L1})(\text{P}^i\text{Pr}_3)_2$ (**3**). Compound **2** arises from the coordination of the N3-pyrimidine nitrogen atom to osmium and the *ortho*-CH bond activation of the C2-bonded phenyl group. The formation of **3** involves the coordination of the N1-pyrimidine nitrogen atom to osmium and the *ortho*-CH bond activation of both phenyl groups. The reaction of **1** with **H₄L2** leads to a mixture of $\text{OsH}_2(\text{H}_2\text{L2})(\text{P}^i\text{Pr}_3)_2$ (**4**) and $(\text{P}^i\text{Pr}_3)_2\text{H}_2\text{Os}(\text{L2})\text{OsH}_2(\text{P}^i\text{Pr}_3)_2$ (**5**), containing five and eight fused rings, respectively. Complex **4** results from the coordination of the N1-triazine nitrogen atom to osmium and the *ortho*-CH bond activation of the phenyl groups at positions 2 and 6 of the triazine ring. Complex **5** results from the coordination of the N1 and N3 of triazine to two different metal centers along with a double *ortho*-CH bond activation in each proximal phenyl group. Complex **1** reacts with **H₄L3** to afford $\text{OsH}_2(\text{H}_2\text{L3})(\text{P}^i\text{Pr}_3)_2$ (**6**) and $(\text{P}^i\text{Pr}_3)_2\text{H}_2\text{Os}(\text{L3})\text{OsH}_2(\text{P}^i\text{Pr}_3)_2$ (**7**), which are related to **4** and **5**, respectively. Complexes **2**, **3**, **4**, and **5** have been characterized by X-ray diffraction analysis. The structures prove the planarity of their cores and suggest electron delocalization through the polycyclic system. Quantum chemical calculations (DFT level) on model compounds clearly indicate that the Os–C and Os–N bonds of the newly formed metallapolycycles exhibit a remarkable double-bond character that is higher for the Os–C bond, in very good agreement with the experimental findings.

Introduction

The synthesis of metallacycles has been a hot topic in organometallic chemistry for nearly half a century.¹ Reasons behind this unabated and continuous interest in these classes of compounds arise not only because of their involvement in several C–C and C–X (X = heteroatom) forming reactions but for their structural properties. This last aspect has resulted in the preparation of metallabenzenes² and related metallacarbycles.³ Substantial progress is being made in the synthesis and the study of heteroatom-containing species, including metallathiabenzenes,⁴ metallapyridines,⁵ metallapyryliums,⁶ metallathiophenes,⁷ metallapyrroles,⁸ and metallafurans.⁹

Higher π -electron metallacyclic compounds are also known. The isolation of the first metallanaphthalene by

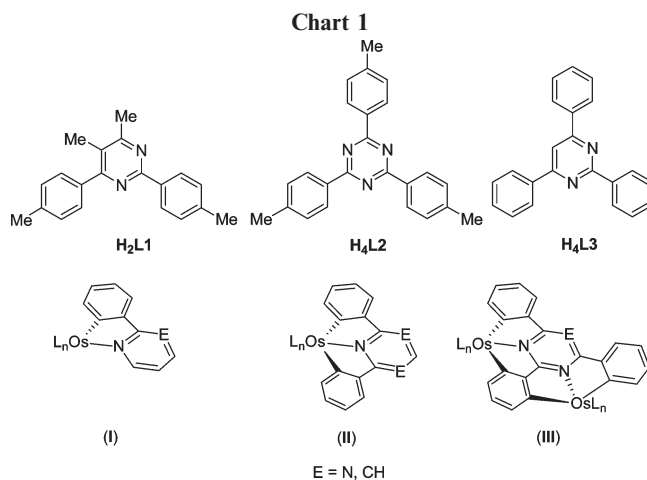
Paneque and co-workers¹⁰ extended the aromatic metallacycles to fused bicyclic compounds.¹¹ Metallaisoindoles,¹² metallabenzofurans,¹³ metallabenzothiaabenzenes,¹⁴ metallaindolizines,¹⁵ metallabenzothiazoles, and metallabenzoxazoles¹⁶ are new interesting classes of this type of compounds with heteroatoms. The formation at -78°C of ruthenaphenanthrene oxides has been reported,¹⁷ and the intermediacy of rhenaphenanthrene species in the reactions of 2,2'-dilithiobiphenyl with $\text{ReBr}(\text{CO})_4(\text{PPh}_3)$ has been suggested.¹⁸ Recently, 1,7-diosma-2,4-triaza-*s*-indacene and 1,7-diosmapyrrolo[3,4-*f*]isoindole derivatives have also been prepared and characterized by X-ray diffraction analysis.¹⁹ Nevertheless, lack of a flexible method to prepare fused polycyclic metallacycles having more than three fused rings prevents the study of the structural properties of these compounds.

The activation of C–H bonds is usually promoted by low-valent complexes.²⁰ The participation of high-valent compounds, in particular hydride derivatives, in these reactions is rare. In spite of this fact, previous work has shown that the osmium(VI) complex $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ efficiently activates C–H bonds of different organic substrates.^{9b,19,21} This reactivity

*Corresponding author. E-mail: maester@unizar.es (M.A.E.); sierraor@quim.ucm.es (M.A.S.).

(1) (a) Blecke, J. R. *Chem. Rev.* **2001**, 101, 1205. (b) Wright, L. J. *Dalton Trans.* **2006**, 1821. (c) Landorf, C. W.; Haley, M. M. *Angew. Chem., Int. Ed.* **2006**, 45, 3914. (d) Blecke, J. R. *Acc. Chem. Res.* **2007**, 40, 1035.

makes $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ a good choice to build metallapolycycles by reactions with appropriate phenyl-substituted pyrimidines and triazines: 4,5-dimethyl-2,6-bis(4-methylphenyl)pyrimidine (**H₂L1**), 2,4,6-tris(4-methylphenyl)-1,3,5-triazine (**H₄L2**), and 2,4,6-triphenylpyrimidine (**H₄L3**). These reactions involve the one-pot activation of one or two (for **H₂L1**) and two or four (for **H₄L2** and **H₄L3**) C–H bonds to yield compounds of type **I**, **II**, and **III**, with three, five, and eight fused cycles, respectively (Chart 1).



(2) (a) Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811. (b) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Clayton, Jr.; Robinson, K. D. *J. Am. Chem. Soc.* **1994**, *116*, 4093. (c) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Chiang, M. Y.; Robinson, K. D.; Beatty, A. M. *Organometallics* **1997**, *16*, 606. (d) Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M. *J. Am. Chem. Soc.* **1999**, *121*, 2597. (e) Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 750. (f) Jacob, V.; Weakley, T. J. R.; Haley, M. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3470. (g) Gilbertson, R. D.; Lau, T. L. S.; Lanza, S.; Wu, H.-P.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2003**, *22*, 3279. (h) Xia, H.; He, G.; Zhang, H.; Wen, T. B.; Sung, H. H. Y.; Williams, I. D.; Jia, G. *J. Am. Chem. Soc.* **2004**, *126*, 6862. (i) Hung, W. Y.; Zhu, J.; Wen, T. B.; Yu, K. P.; Sung, H. H. Y.; Williams, I. D.; Lin, Z.; Jia, G. *J. Am. Chem. Soc.* **2006**, *128*, 13742. (j) Ilg, K.; Paneque, M.; Poveda, M. L.; Rendón, N.; Santos, L. L.; Carmona, E.; Mereiter, K. *Organometallics* **2006**, *25*, 2230. (k) Zhang, H.; Xia, H.; He, G.; Wen, T. B.; Gong, L.; Jia, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2920. (l) Clark, G. R.; Lu, G.-L.; Roper, W. R.; Wright, L. J. *Organometallics* **2007**, *26*, 2167. (m) Zhu, J.; Jia, G.; Lin, Z. *Organometallics* **2007**, *26*, 1986. (n) Paneque, M.; Poveda, M. L.; Rendón, N.; Alvarez, E.; Carmona, E. *Eur. J. Inorg. Chem.* **2007**, 2711. (o) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Santos, L. L.; Alvarez, E.; Salazar, V.; Mereiter, K.; Oñate, E. *Organometallics* **2007**, *26*, 3403. (p) Zhang, H.; Feng, L.; Gong, L.; Wu, L.; He, G.; Wen, T. B.; Yang, F.; Xia, H. *Organometallics* **2007**, *26*, 2705. (q) Clark, G. R.; Johns, P. M.; Roper, W. R.; Wright, L. J. *Organometallics* **2008**, *27*, 451. (r) Gong, L.; Lin, Y.; He, G.; Zhang, H.; Wang, H.; Wen, T. B.; Xia, H. *Organometallics* **2008**, *27*, 309. (s) Gong, L.; Chen, Z.; Lin, Y.; He, X.; Wen, T. B.; Xu, X.; Xia, H. *Chem.—Eur. J.* **2009**, *15*, 6258.

(3) (a) Ng, S. M.; Huang, X.; Wen, T. B.; Jia, G.; Lin, Z. *Organometallics* **2003**, *22*, 3898. (b) Wen, T. B.; Ng, S. M.; Hung, W. Y.; Zhou, Z. Y.; Lo, M. F.; Shek, L.-Y.; Williams, I. D.; Lin, Z.; Jia, G. *J. Am. Chem. Soc.* **2003**, *125*, 884. (c) Jia, G. *Acc. Chem. Res.* **2004**, *37*, 479. (d) Barrio, P.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2004**, *126*, 1946. (e) He, G.; Zhu, J.; Hung, W. Y.; Wen, T. B.; Sung, H. H.-Y.; Williams, I. D.; Lin, Z.; Jia, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 9065. (f) Jia, G. *Coord. Chem. Rev.* **2007**, *251*, 2167.

(4) (a) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199. (b) Chin, R. M.; Jones, W. D. *Angew. Chem., Int. Ed.* **1992**, *31*, 357. (c) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Moneti, S.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 4370. (d) Bleeke, J. R.; Hinkle, P. V. *J. Am. Chem. Soc.* **1999**, *121*, 595. (e) Bleeke, J. R.; Hinkle, P. V.; Rath, N. P. *Organometallics* **2001**, *20*, 1939.

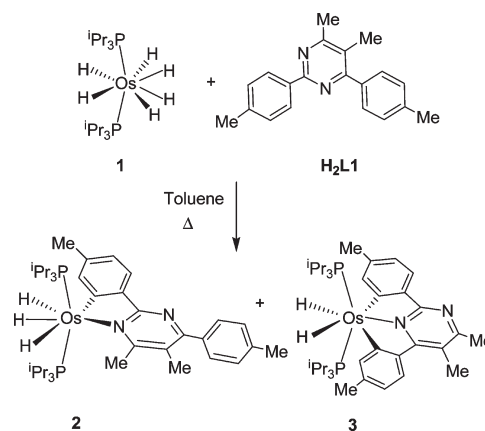
(5) (a) Thorn, D. L.; Hoffman, R. *Nouv. J. Chim.* **1979**, *3*, 39. (b) Iron, M. A.; Lucassem, A. C. B.; Cohen, H.; van der Boom, M. E.; Martin, J. M. L. *J. Am. Chem. Soc.* **2004**, *126*, 11699. (c) De Proft, F.; Geerlings, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 242. (d) Fernández, I.; Freking, G. *Chem.—Eur. J.* **2007**, *13*, 5873. (e) Feng, S. G.; White, P. S.; Templeton, J. L. *Organometallics* **1993**, *12*, 1765. (f) Weeller, K. J.; Filippov, I.; Briggs, P. M.; Wigley, D. E. *Organometallics* **1998**, *17*, 322. (g) Liu, B.; Wang, H.; Xie, H.; Zeng, B.; Chen, J.; Tao, J.; Wen, T. B.; Cao, Z.; Xia, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5430.

(6) (a) Bleeke, J. R.; Blanchard, J. M. B. *J. Am. Chem. Soc.* **1997**, *119*, 5443. (b) Bleeke, J. R.; Blanchard, J. M. B.; Donnay, E. *Organometallics* **2001**, *20*, 324.

(7) (a) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1993**, *12*, 985. (b) Lu, G.-L.; Roper, W. R.; Wright, L. J.; Clark, G. R. *J. Organomet. Chem.* **2005**, *690*, 972.

(8) (a) Albarado, Y.; Daff, P. J.; Pérez, P. J.; Poveda, M. L.; Sánchez-Delgado, R. A.; Carmona, E. *Organometallics* **1996**, *15*, 2192. (b) Legzdins, P.; Lumb, S. A. *Organometallics* **1997**, *16*, 1825. (c) Alias, F. M.; Poveda, M. L.; Sellin, M.; Carmona, E. *Organometallics* **1998**, *17*, 4124. (d) Legzdins, P.; Lumb, S. A.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 854. (e) Baya, M.; Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2005**, *24*, 1225. (f) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 3965. (g) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Mereiter, K. *Organometallics* **2007**, *26*, 3120. (h) Bleeke, J. R.; Putprasert, P.; Thananathanachon, T.; Rath, N. P. *Organometallics* **2008**, *27*, 5744.

Scheme 1



This paper reports the preparation, characterization, and the study of the π -orbitals of these novel fused metallapolycyclic systems.

Results and Discussion

Synthesis and Characterization of the New Osmapolycycles. Treatment under reflux of toluene solutions of the hexahydride complex $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ (**1**) with 1.0 equiv

(9) (a) Bleeke, J. R.; New, P. R.; Blanchard, J. M. B.; Haile, T.; Beatty, A. M. *Organometallics* **1996**, *14*, 5127. (b) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2635. (c) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2004**, *23*, 6015. (d) Li, X.; Chen, P.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2005**, *24*, 4810. (e) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 1428. (f) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 5989. (g) Bierstedt, A.; Clark, G. R.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2006**, *691*, 3846. (h) Esteruelas, M. A.; López, A. M.; Oliván, M. *Coord. Chem. Rev.* **2007**, *251*, 795. (i) Gong, L.; Lin, Y.; Wen, T. B.; Zhang, H.; Zeng, B.; Xia, H. *Organometallics* **2008**, *27*, 2584. (j) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 4680. (k) Lin, Y.; Gong, L.; Xu, H.; He, X.; Wen, T. B.; Xia, H. *Organometallics* **2009**, *28*, 1524.

(10) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Salazar, V.; Oñate, E.; Mereiter, K. *J. Am. Chem. Soc.* **2003**, *125*, 9898. (11) Liu, B.; Xie, H.; Wang, H.; Wu, L.; Zhao, Q.; Chen, J.; Wen, T. B.; Cao, Z.; Xia, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5461.

(12) (a) Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **2000**, *19*, 275. (b) Esteruelas, M. A.; Lledós, A.; Oliván, M.; Oñate, E.; Tajada, M. A.; Ujaque, G. *Organometallics* **2003**, *22*, 3753. (c) Buil, M. L.; Esteruelas, M. A.; Goni, E.; Oliván, M.; Oñate, E. *Organometallics* **2006**, *25*, 3076.

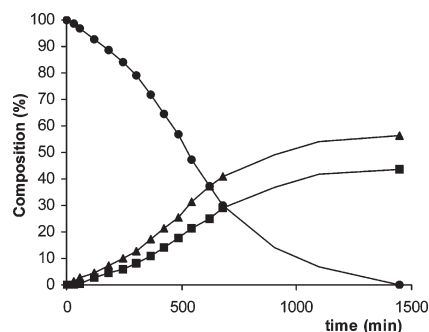


Figure 1. Time versus composition of the reaction mixture of **1** with 4,5-dimethyl-2,6-bis(4-methylphenyl)pyrimidine. Complexes **1** (●), **2** (■), and **3** (▲). The progress of the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

of 4,5-dimethyl-2,6-bis(4-methylphenyl)pyrimidine (**H₂L1**) produces after 32 h the quantitative transformation of the starting compound into a mixture of the metallapolycyclic derivatives $\text{OsH}_3(\text{HL1})(\text{P}^i\text{Pr}_3)_2$ (**2**) and $\text{OsH}_2(\text{L1})(\text{P}^i\text{Pr}_3)_2$ (**3**) (Scheme 1).

These compounds result from the competition between a single and double aromatic *ortho*-CH bond activation, directed by the pyrimidine nitrogen atoms. Compound **2** arises from the thermal activation of **1** to give an $\text{OsH}_4(\text{P}^i\text{Pr}_3)_2$ species, which coordinates the N3-pyrimidine nitrogen atom and subsequently activates the *ortho*-C–H bond of the C2-bonded phenyl group, with the concomitant loss of molecular hydrogen. Formation of complex **3** follows an analogous pattern, but now Os coordinates the N1-pyrimidine nitrogen atom and the *ortho*-C–H bonds of both phenyl groups are activated. Figure 1 shows that the formation of complex **3** (double CH bond activation) is slightly favored with respect to the formation of complex **2** (single CH bond activation).

Complexes **2** and **3** were isolated as pure red and orange crystals in 25% and 36% yield, respectively, and characterized by elemental analysis, IR, ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, and X-ray diffraction analysis. Figures 2 and 3 show views of the molecular geometry of **2** and **3**, respectively.

Complex **2** is a 6-osmapyrimido[2,1-*a*]isoindole derivative. The metallatricycle core is planar (maximum deviation 0.117(3) Å for N(2)), and the bond lengths lie between that expected for single and double bonds. The Os–C(8) distance 2.111(3) Å is similar to the Os–C bond lengths reported for osmafurans,^{9b,c,e,f,h–k} osmapyrroles,^{8e,f} and related compounds,^{12,19} while the Os–N(1) distance of 2.219(3) Å compares well with the Os–N bond lengths found in lower π -electron osmacyclic nitrogen-containing compounds.^{8e,12}

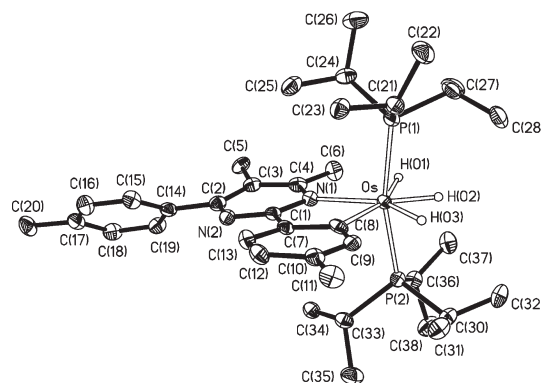


Figure 2. Molecular diagram of complex **2**. Selected bond lengths (Å) and angles (deg): Os–C(8) 2.111(3), Os–N(1) 2.219(3), N(1)–C(4) 1.354(4), C(3)–C(4) 1.399(5), C(2)–C(3) 1.397(5), C(2)–N(2) 1.337(4), N(2)–C(1) 1.335(4), C(1)–N(1) 1.365(4), C(1)–C(7) 1.446(4), C(7)–C(8) 1.416(5), C(8)–C(9) 1.409(4), C(9)–C(10) 1.375(5), C(10)–C(12) 1.404(5), C(12)–C(13) 1.371(5), C(13)–C(7) 1.401(5), H(01)–H(02) 1.46(4), H(02)–H(03) 1.72(4); P(1)–Os–P(2) 165.72(3), C(8)–Os–N(1) 77.08(11).

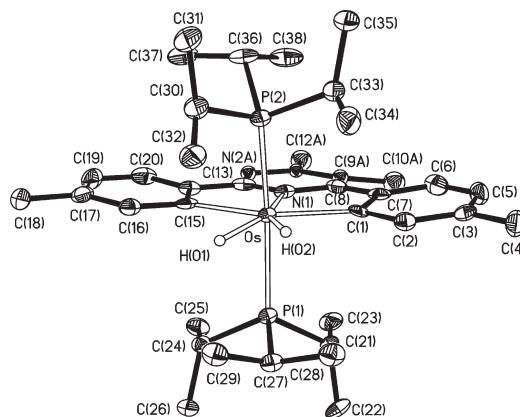


Figure 3. Molecular diagram of complex **3**. Selected bond lengths (Å) and angles (deg): Os–N(1) 2.101(4), Os–C(1) 2.106(5), Os–C(15) 2.110(5), N(1)–C(13) 1.353(7), N(1)–C(8) 1.361(7), C(1)–C(2) 1.410(7), C(1)–C(7) 1.422(7), C(2)–C(3) 1.381(7), C(3)–C(5) 1.387(8), C(5)–C(6) 1.373(8), C(6)–C(7) 1.399(7), C(7)–C(8) 1.458(8), C(8)–C(9A) 1.454(12), C(9A)–C(11A) 1.370(13), N(2A)–C(13) 1.291(10), N(2A)–C(11A) 1.332(11), C(13)–C(14) 1.452(8), C(14)–C(20) 1.397(8), C(14)–C(15) 1.415(7), C(15)–C(16) 1.414(7), C(16)–C(17) 1.392(7), C(17)–C(19) 1.385(8), C(19)–C(20) 1.377(8); P(1)–Os–P(2) 161.95(5), N(1)–Os–C(1) 75.43(19), N(1)–Os–C(15) 75.51(19), C(1)–Os–C(15) 150.9(2).

The N–C bond lengths are between 1.335(4) and 1.365(4) Å, whereas the C–C distances lie between 1.375(5) and 1.446(4) Å.

The coordination geometry around the osmium atom of **2** can be described as a distorted pentagonal bipyramid with axial phosphines (P(1)–Os–P(2) = 165.72(3)°) and the hydride ligands lying in the equatorial plane. In agreement with this phosphine disposition, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in toluene-*d*₈ contains a singlet at 21.4 ppm, which is temperature-invariant between 363 and 203 K. In contrast to the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the ^1H NMR spectrum is temperature-dependent. At temperatures higher than 363 K, it shows a single hydride resonance at –10.1 ppm, which is consistent

(13) Clark, G. R.; Johns, P. M.; Roper, W. R.; Wright, L. J. *Organometallics* **2006**, 25, 1771.

(14) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Moneti, S.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1994**, 116, 4370.

(15) (a) Esteruelas, M. A.; Fernández, I.; Fuertes, S.; López, A. M.; Oñate, E.; Sierra, M. A. *Organometallics* **2009**, 28, 4876. (b) Castro-Rodrigo, R.; Esteruelas, M. A.; Fuertes, S.; López, A. M.; Mozo, S.; Oñate, E. *Organometallics* **2009**, 28, 5941.

(16) Wang, T.; Li, S.; Zhang, H.; Lin, R.; Han, F.; Lin, Y.; Wen, T. B.; Xia, H. *Angew. Chem., Int. Ed.* **2009**, 48, 6453.

(17) Yang, J.; Jones, W. M.; Dixon, J. K.; Allison, N. T. *J. Am. Chem. Soc.* **1995**, 117, 9776.

(18) Mike, C. A.; Feredé, R.; Allison, N. T. *Organometallics* **1988**, 7, 1457.

(19) Esteruelas, M. A.; Masamunt, A. B.; Oliván, M.; Oñate, E.; Valencia, M. *J. Am. Chem. Soc.* **2008**, 130, 11612.

with the operation of two thermally activated site exchange processes, in agreement with the behavior of analogous osmium trihydride derivatives. It has been proposed that these exchanges go through dihydrogen states.²² Two decoalescences are observed, the first one around 343 K, and the second around 208 K. Thus, at 203 K, three resonances at -7.51 , -9.77 , and -12.51 ppm are observed. A monodimensional NOESY experiment at 223 K indicated that the latter corresponds to the hydride ligand disposed *cisoid* to the metalated phenyl group (H(03) in Figure 2). The 400 MHz $T_{1(\min)}$ values were found at 273 K, when the H(01) and H(02) hydride ligands display only one resonance at -8.62 ppm. They (102 ± 3 ms for H(01) and H(02) and 129 ± 3 ms for H(03)) are consistent with the H(01)–H(02) and H(02)–H(03) separations of 1.46(4) and 1.72(4) Å, respectively, as determined by X-ray diffraction analysis. In agreement with a shorter H(01)–H(02) separation, the activation enthalpy for the position exchange between these hydrides is smaller than that for the position exchange between H(02) and H(03), namely, 9 versus 11 kcal·mol⁻¹. The most noticeable resonance in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in benzene-*d*₆ at room temperature is a triplet at 185.6 ppm having a C–P coupling constant of 7.3 Hz, which corresponds to the metalated carbon atom C(8) of the tricycle. This chemical shift compares well with those reported for related polycyclic compounds containing metalated aromatic six-membered rings,^{9j,12,15b,19,21a,b,d} while it is shifted toward lower field with regard to the chemical shifts reported for aryl derivatives (δ 125–160).^{12c,21c,23}

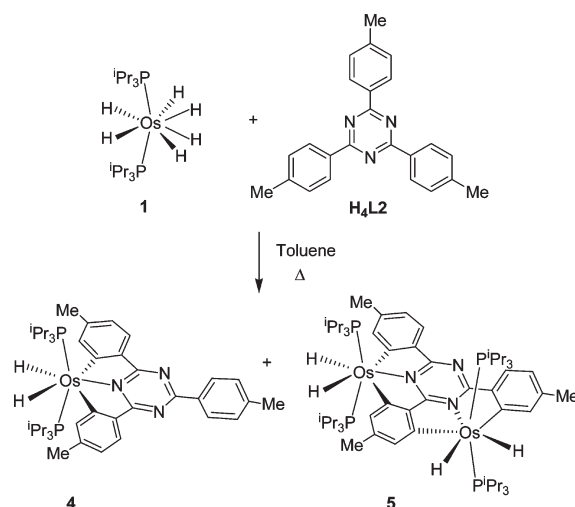
Complex **3** is a planar osmapolycycle (maximum deviation 0.211(5) Å for C(5)) having five fused units (two five-membered rings and three six-membered rings). The significant electron delocalization through the polycyclic system translates into bond lengths between those expected for single and double bonds. Accordingly, the Os–N(1) (2.101(4) Å) distance is about 0.1 Å shorter than the Os–N

bond length in **2**, whereas the Os–C(1) (2.106(5) Å) and Os–C(15) (2.110(5) Å) distances are statistically identical with the Os–C bond lengths in the latter. Within each cycle, the C–C distances are statistically identical with values depending upon the cycle type: between 1.373(8) and 1.422(7) Å for the six-membered C₆ rings, between 1.415(7) and 1.458(8) Å for the five-membered rings, and between 1.370(13) and 1.454(12) Å for the six-membered C₄N₂ ring. The N(1)–C(13) (1.353(7) Å), N(1)–C(8) (1.361(7) Å), and N(2A)–C(11A) (1.332(11) Å) bond lengths are statistically identical and slightly longer than the N(2A)–C(13) (1.291(10) Å) distance.

The coordination geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the phosphine ligands in axial positions (P(1)–Os–P(2) = 161.95(5) Å) and the hydrides lying in the equatorial plane. The H(01)–H(02) separation is 1.54(6) Å. In agreement with this ligand disposition, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in benzene-*d*₆ shows a singlet at 0.0 ppm, whereas the ^1H NMR spectrum contains two hydride resonances at -7.78 and -8.16 ppm, which appear as double triplets with H–P and H–H coupling constants of 15.2 and 12.0 Hz, respectively. In agreement with **2**, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the OsC resonances of the polycycle are observed at 183.4 and 173.9 ppm, as triplets with C–P coupling constants of 6.9 and 7.4 Hz, respectively.

Treatment of toluene solutions of **1** with 1.0 equiv of 2,4,6-tris(4-methylphenyl)-1,3,5-triazine (**H₄L2**) under reflux leads after 36 h to the quantitative transformation of the hexahydride starting compound into a 6:1 mixture of complexes OsH₂(H₂L2)(P^{*i*}Pr₃)₂ (**4**) and (P^{*i*}Pr₃)₂H₂Os(L2)OsH₂(P^{*i*}Pr₃)₂ (**5**), according to Scheme 2. The increase of the **1**:**H₄L2** molar ratio produces an increase of the formed amount of **5**. However all attempts to obtain a single reaction product were unsuccessful.

Scheme 2



Complex **4**, which is related to **3**, results from the coordination of the N1-triazine nitrogen atom to the metal center followed by the activation of an *ortho*-CH bond of the phenyl groups at the 2 and 6 positions of the triazine ring. Complex **5** is the result of the coordination of the N1 and N3 nitrogen atoms of triazine to two osmium centers followed by a double *ortho*-CH bond activation in each proximal phenyl group, which results in the double C–H activation of the

(20) (a) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91. (d) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (e) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (f) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437. (g) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (h) Crabtree, R. H. *J. Organomet. Chem.* **2004**, *689*, 4083. (i) Carmona, E.; Paneque, M.; Santos, L. L.; Salazar, V. *Coord. Chem. Rev.* **2005**, *249*, 1729. (j) Esteruelas, M. A.; López, A. M. *Organometallics* **2005**, *24*, 3584. (k) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471. (l) Jones, W. D. *Inorg. Chem.* **2005**, *44*, 4475. (m) Godula, K.; Sames, D. *Science* **2006**, *312*, 67.

(21) (a) Barea, G.; Esteruelas, M. A.; Lledós, A.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **1998**, *17*, 4065. (b) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Tomás, J. *Organometallics* **2001**, *20*, 442. (c) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1340. (d) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 3627. (e) Baya, M.; Eguillor, B.; Esteruelas, M. A.; Lledós, A.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 5140. (f) Baya, M.; Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 6556. (g) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Puerta, M. *Organometallics* **2008**, *27*, 445. (h) Esteruelas, M. A.; Forcen, E.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 6188. (i) Eguillor, B.; Esteruelas, M. A.; García-Raboso, J.; Oliván, M.; Oñate, E. *Organometallics* **2009**, *28*, 3700.

(22) See for example: (a) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Ruiz, N.; Sola, E.; Tolosa, J. I. *Inorg. Chem.* **1996**, *35*, 7811. (b) Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *J. Am. Chem. Soc.* **1997**, *119*, 9691. (c) Castillo, A.; Barea, G.; Esteruelas, M. A.; Lahoz, F. J.; Lledós, A.; Maseras, F.; Modrego, J.; Oñate, E.; Oro, L. A.; Ruiz, N.; Sola, E. *Inorg. Chem.* **1999**, *38*, 1814. (d) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 4498. (e) Baya, M.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Inorg. Chem.* **2009**, *48*, 2677.

(23) Liu, S. H.; Lo, S. T.; Wen, T. B.; Williams, I. D.; Zhou, Z. Y.; Lau, C. P.; Jia, G. *Inorg. Chim. Acta* **2002**, *334*, 122. (b) Pool, D. H.; Shapley, P. A. *Organometallics* **2004**, *23*, 2326.

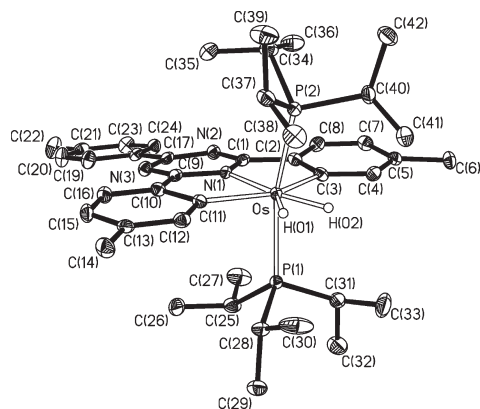


Figure 4. Molecular diagram of complex **4**. Selected bond lengths (Å) and angles (deg): Os–N(1) 2.085(3), Os–C(3) 2.118(3), Os–C(11) 2.128(3), N(1)–C(1) 1.354(4), N(1)–C(9) 1.356(4), N(2)–C(17) 1.342(4), N(2)–C(1) 1.346(4), N(3)–C(9) 1.338(4), N(3)–C(17) 1.339(4), C(1)–C(2) 1.447(4), C(2)–C(8) 1.398(5), C(2)–C(3) 1.418(4), C(3)–C(4) 1.423(4), C(4)–C(5) 1.392(5), C(5)–C(7) 1.406(5), C(7)–C(8) 1.371(5), C(9)–C(10) 1.439(4), C(10)–C(16) 1.396(4), C(10)–C(11) 1.425(4), C(11)–C(12) 1.416(4), C(12)–C(13) 1.385(4), C(13)–C(15) 1.405(5), C(15)–C(16) 1.367(5); P(1)–Os–P(2) 163.52(3), N(1)–Os–C(3) 75.04(11), N(1)–Os–C(11) 75.44(11), C(3)–Os–C(11) 150.47(13).

phenyl group at the C2 position of the C_3N_3 ring by the two Os centers. Overall, the reaction is a quadruple C–H activation by two Os centers in a single organic substrate.

Complex **4** was obtained as pure red crystals in 26% yield and, as complexes **2** and **3**, characterized by elemental analysis, IR, 1H , $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and X-ray diffraction analysis. Figure 4 shows a view of its molecular geometry. Like in complex **3**, the osmapolycycle containing five fused units is planar (maximum deviation 0.263(4) Å for C(17)). The Os–N(1) bond length of 2.085(3) Å as well as the Os–C(3) and Os–C(11) distances of 2.118(3) and 2.128(3) Å, respectively, are statistically identical with the related parameters of **3**. The C–N and C–C bond lengths also agree well with those of complex **3**. The C–N distances lie in the range 1.338(4)–1.356(4) Å, whereas the C–C bond lengths are between 1.367(5) and 1.447(5) Å.

The coordination geometry around the metal center can also be rationalized as a distorted pentagonal bipyramid with axial phosphines (P(1)–Os–P(2)) = 163.52(3)° and the hydrides lying in the equatorial plane. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 0.0 ppm, whereas the hydride ligands in the 1H NMR spectrum display at –7.30 ppm a triplet with a H–P coupling constant of 15.6 Hz, which agrees with this ligand disposition. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance corresponding to the equivalent metalated carbon atoms appears at 179.4 ppm as a triplet with a C–P coupling constant of 6.8 Hz.

A few red crystals of **5** suitable for an X-ray diffraction study were obtained by slow diffusion of methanol into a toluene solution of a 4:1 mixture of **4** and **5**. Figure 5 shows a view of its molecular geometry.

The structure proves the formation of a diosmapolycycle having eight fused rings (four five-membered rings and four six-membered rings), which is also almost planar (maximum deviation 0.536(6) Å for C(6)). The structural parameters of this polycycle are similar to those observed in the polycycles of **2**–**4**. The Os(1)–N(1) and Os(2)–N(2) distances of

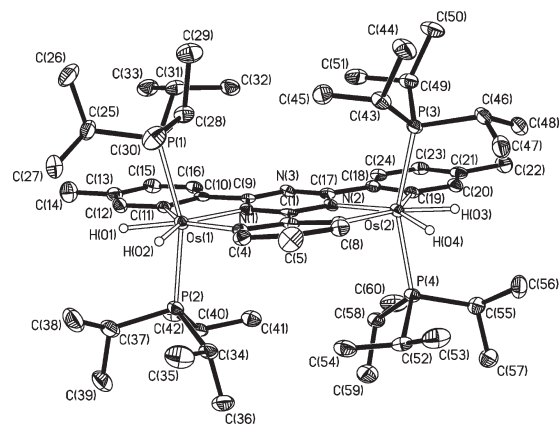


Figure 5. Molecular diagram of complex **5**. Selected bond lengths (Å) and angles (deg): Os(1)–N(1) 2.095(3), Os(2)–N(2) 2.089(4), Os(1)–C(11) 2.139(4), Os(2)–C(19) 2.161(4), Os(1)–C(3) 2.184(4), Os(2)–C(8) 2.176(4), N(1)–C(1) 1.329(5), N(1)–C(9) 1.361(5), N(2)–C(1) 1.343(5), N(2)–C(17) 1.360(5), N(3)–C(17) 1.337(5), N(3)–C(9) 1.353(5), C(1)–C(2) 1.390(5), C(2)–C(8) 1.419(6), C(2)–C(3) 1.433(6), C(3)–C(4) 1.404(6), C(4)–C(5) 1.400(6), C(5)–C(7) 1.404(6), C(7)–C(8) 1.416(5), C(9)–C(10) 1.448(6), C(10)–C(16) 1.398(6), C(10)–C(11) 1.437(5), C(11)–C(12) 1.398(6), C(12)–C(13) 1.396(6), C(13)–C(15) 1.392(6), C(15)–C(16) 1.371(6), C(17)–C(18) 1.454(6), C(18)–C(24) 1.399(5), C(18)–C(19) 1.418(6), C(19)–C(20) 1.406(6), C(20)–C(21) 1.390(5), C(21)–C(23) 1.392(6), C(23)–C(24) 1.375(6); P(1)–Os(1)–P(2) 160.38(4), P(3)–Os(2)–P(4) 157.43(4), N(1)–Os(1)–C(11) 73.57(14), N(1)–Os(1)–C(3) 75.57(14), C(11)–Os(1)–C(3) 149.10(16), N(2)–Os(2)–C(19) 72.65(14), N(2)–Os(2)–C(8) 75.53(14), C(19)–Os(2)–C(8) 148.00(16).

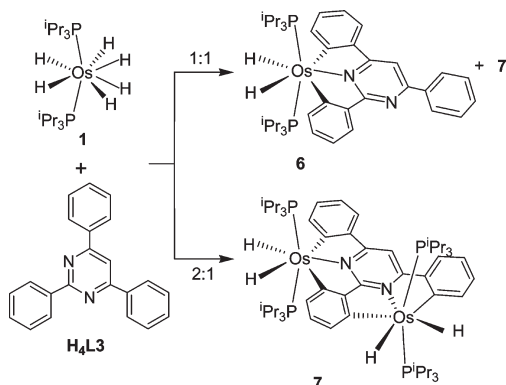
2.095(3) and 2.089(4) Å, respectively, are statistically identical with the Os–N bond lengths in the other polycycles, while the Os–C distances of 2.139(4) (Os(1)–C(11)), 2.161(4) (Os(2)–C(19)), 2.176(4) (Os(2)–C(8)), and 2.184(4) (Os(2)–C(3)) Å are between 0.04 and 0.08 Å longer. The N–C and C–C bond lengths also compare well with those of **2**–**4**. The N–C distances lie in the range 1.329(5)–1.361(5) Å, whereas the C–C bond lengths are between 1.371(6) and 1.453(6) Å.

The coordination geometries around the osmium atoms are similar to those of the metal centers of **3** and **4**, i.e., distorted pentagonal bipyramids with axial phosphines (P(1)–Os(1)–P(2)) = 160.38(4)° and P(3)–Os(2)–P(4)) = 157.43(4)° with the hydride ligands lying in the equatorial plane. The $^{31}P\{^1H\}$, 1H , and $^{13}C\{^1H\}$ NMR spectra are consistent with this ligand distribution. Thus, the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 2.5 ppm, whereas the hydride ligands display at –7.13 and –8.71 ppm double triplets with a H–H coupling constant of 8.0 Hz and H–P coupling constants of 16.0 and 18.4 Hz, respectively. The metalated carbon atoms of the polycycle give rise to two triplets at 176.3 and 172.6 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The C–P coupling constants of 8.9 and 6.4 Hz, respectively, are consistent with those observed in **3** and **4**.

2,4,6-Triphenylpyrimidine (**H₄L3**) has a higher tendency to form the diosmapolycycle having eight fused units than 2,4,6-tris(4-methylphenyl)-1,3,5-triazine (**H₄L2**). Treatment under reflux of a toluene solution of **1** with 1.0 equiv of the pyrimidine for 7 h affords a mixture of the osmapolycycle **6**, having five fused cycles, and the diosmapolycycle **7**, having

eight fused cycles, in a 4:1 molar ratio. However, under the same conditions, the treatment of **1** with 0.5 equiv of the pyrimidine for 21 h quantitatively forms **7**, which is isolated as a dark red solid in 73% yield (Scheme 3).

Scheme 3



Complex **6** was separated from the mixture as an orange solid in 13% yield and characterized by elemental analysis, IR, and ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. In agreement with **3** and **4**, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 0.3 ppm. In the ^1H NMR spectrum the hydride ligands display an ABX_2 spin system ($\text{X} = ^{31}\text{P}$) centered at -7.53 ppm and defined by $\Delta\nu = 25$ Hz, $J_{\text{A-B}} = 12.2$ Hz, and $J_{\text{A-X}} = J_{\text{B-X}} = 15.4$ Hz. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the inequivalent metalated carbon atoms of the polycycle give rise to two triplets at 181.4 and 174.9 ppm with C–P coupling constants of 6.8 and 7.1 Hz, respectively.

The $^{31}\text{P}\{^1\text{H}\}$, ^1H , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of complex **7** agree well with those of octacycle **5**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a singlet at 2.4 ppm. In the ^1H NMR spectrum, the hydride resonances appear at -7.40 and -8.87 ppm as double triplets with a H–H coupling constant of 11.0 Hz and H–P coupling constants of 21.8 and 23.8 Hz, respectively. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the resonances due to the metalated carbon atoms of the polycycle are observed at 178.6 and 169.7 ppm as triplets with C–P coupling constants of 7.2 and 6.7 Hz, respectively.

2. Bonding Situations of the New Osmapolycyclic Complexes.

Chart 2 presents the BP86/def2-SVP-optimized geometries of the complexes **2M**, **3M**, and **5M**, which are used as models of **2**; **3**, **4**, and **6**; and **5** and **7**, respectively. The geometrical parameters calculated for **2M** show a reasonably good agreement with those obtained for **2** by X-ray diffraction analysis. The structural parameters of **3M** agree with those of **3** and **4**, whereas the structural parameters of **5M** are consistent with those of **5**. The major deviations between experimental and computational data are found in the donor–acceptor bonds, which may become shorter in the solid state.²⁴ Therefore, the selected BP86/def2-SVP method is accurate enough to accomplish the aim of our study.

In order to analyze the bonding situations in complexes **2–7** in more detail, the nature of the bonding interactions of

the osmium atoms was investigated with the AIM (atoms in molecules)²⁵ and with the NBO (natural bond orbital)²⁶ methods on the model compound **2M**. Figure 6 shows the contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ in the plane of the newly formed five-membered ring. Both, the Os–N and Os–C bonds in **2M** clearly exhibit an area of charge concentration ($\nabla^2\rho(r) < 0$, solid lines) at the nitrogen and carbon ends. Moreover, they have the shape of a droplet-like appendix directed toward the osmium atom, which is typical for a closed-shell donor–acceptor bond.²⁷ As expected, the newly formed ring involving the transition metal in complex **2M** is characterized by the AIM method as a five-membered cyclic species possessing one Os–C and one Os–N bond path and one OsNC_3 ring critical point.

As stated above, the experimental data (X-ray diffraction and NMR chemical shifts) suggest a remarkable π -character for the Os–C and Os–N bonds. Interestingly, the computed ellipticities (ϵ_c) by the AIM method, which are a measure of the double-bond character of a bond,²⁸ indicate that both bonds exhibit a clear π -bonding, being higher in the Os–C bond than in the Os–N bond (ϵ_c Os–C = 0.87 and ϵ_c Os–N = 0.48). A similar conclusion can be derived from the second-order perturbation theory of the NBO method which shows a higher electronic delocalization from the d_π atomic orbital of the osmium to the $\pi^*(\text{C–C})$ molecular orbital (associated second-order energy of $7.4 \text{ kcal}\cdot\text{mol}^{-1}$) than to the corresponding $\pi^*(\text{N–C})$ molecular orbital (associated second-order energy of $5.6 \text{ kcal}\cdot\text{mol}^{-1}$).

The examination of the Kohn–Sham molecular orbitals agrees with this description. As readily seen in Figure 7, which shows the most relevant π -orbitals of the C_s -symmetric compound **2M**, the main π -bonding interaction between the phenyl-pyrimidine fragment and the metal moiety occurs in the $13a''$ (bonding combination) and $16a''$ (“antibonding” combination) molecular orbitals. The d contributions are 17% (d_{xz}) and 41% (d_{yz}), respectively. Strikingly, in these molecular orbitals the d atomic orbitals interact with the π -system of the metalated ring of the phenyl-pyrimidine ligand. However, the other double-occupied d atomic orbital, which is oriented to the π -system of the nitrogen-containing aromatic ring, practically does not interact with the ligand and remains as the nonbonding orbital $15a''$.

Similarly, the π -molecular orbitals of the other model complexes **2M'**, **3M**, and **5M** show nearly identical features as those of complex **2M** (Figure 8). We can therefore conclude that the newly synthesized osmium-containing polycycles present quite similar bonding situations, namely, a high degree of π -character of the respective Os–C and Os–N bonds, with the former bond possessing a higher double-bond character as seen from the experimental data.

Conclusion

This study has revealed that the hexahydride complex $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ activates *ortho*-CH bonds of phenyl substituents of 4,5-dimethyl-2,6-bis(4-methylphenyl)pyrimidine,

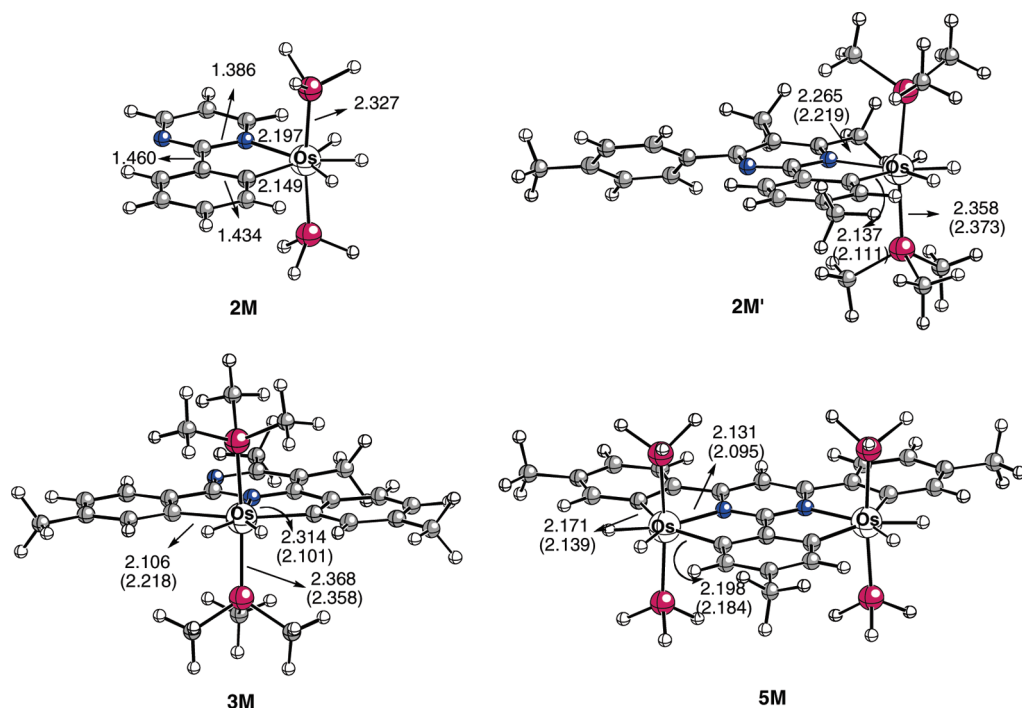
(24) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741.

(25) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: Oxford, 1990.

(26) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (d) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(27) Braunschweig, H.; Fernández, I.; Frenking, G.; Radacki, K.; Seeler, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 5215, and references therein.

(28) (a) The bond ellipticity at the bond critical point is defined by the ratio of the curvatures (eigenvalues of the Hessian of ρ) along the two axes perpendicular to the bond. For details see ref 25. (b) Vyboishchikov, S. F.; Frenking, G. *Chem.—Eur. J.* **1998**, *4*, 1428.

Chart 2. Model Compounds Studied Computationally^a

^a All structures correspond to fully optimized BP86/def2-SVP geometries. Bond lengths are given in angstroms (experimental data from X-ray in parentheses). Unless otherwise stated, white, gray, blue, and pink colors denote hydrogen, carbon, nitrogen, and phosphorus atoms, respectively.

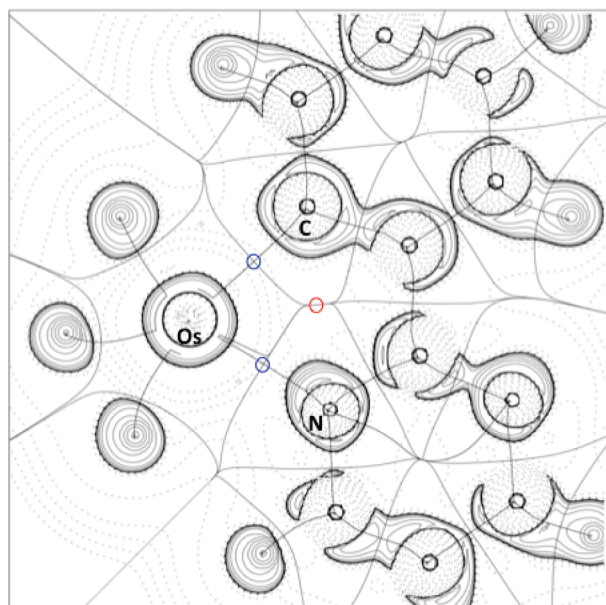


Figure 6. Contour line diagrams $\nabla^2\rho(r)$ of the complex **2M** in the OsNC_3 ring plane. Solid lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$), while dashed lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The solid lines connecting the atomic nuclei are the bond paths. The solid lines separating the atomic basins indicate the zero-flux surfaces crossing the molecular plane.

2,4,6-tris(4-methylphenyl)-1,3,5-triazine, and 2,4,6-triphenylpyrimidine to give, in addition to a 6-osmapyrimido-[2,1-a]isindole derivative, novel polycyclic compounds of five and eight fused cycles, which have no counterpart in conventional organic chemistry. The X-ray structures of four of them prove the planarity of their cores and suggest

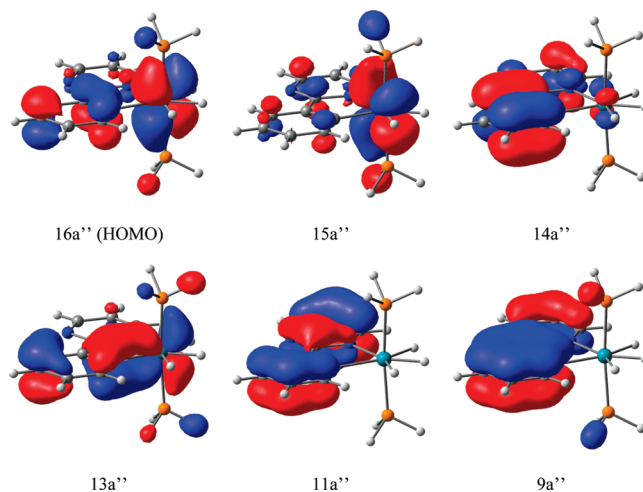


Figure 7. Plot of the valence π -orbitals of complex **2M** (BP86/def2-SVP level). The value of the outermost contour line is 0.035.

electronic delocalization through the polycyclic systems. Quantum chemical calculations on model compounds suggest that the Os–C and Os–N bonds of the newly formed metallapolycycles exhibit some double-bond character that is higher for the Os–C bond.

Experimental Section

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents (except methanol, which was dried and distilled under argon) were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Gemini 2000, Bruker ARX 300 MHz, Bruker Avance 300 MHz, Bruker Avance 400 MHz,

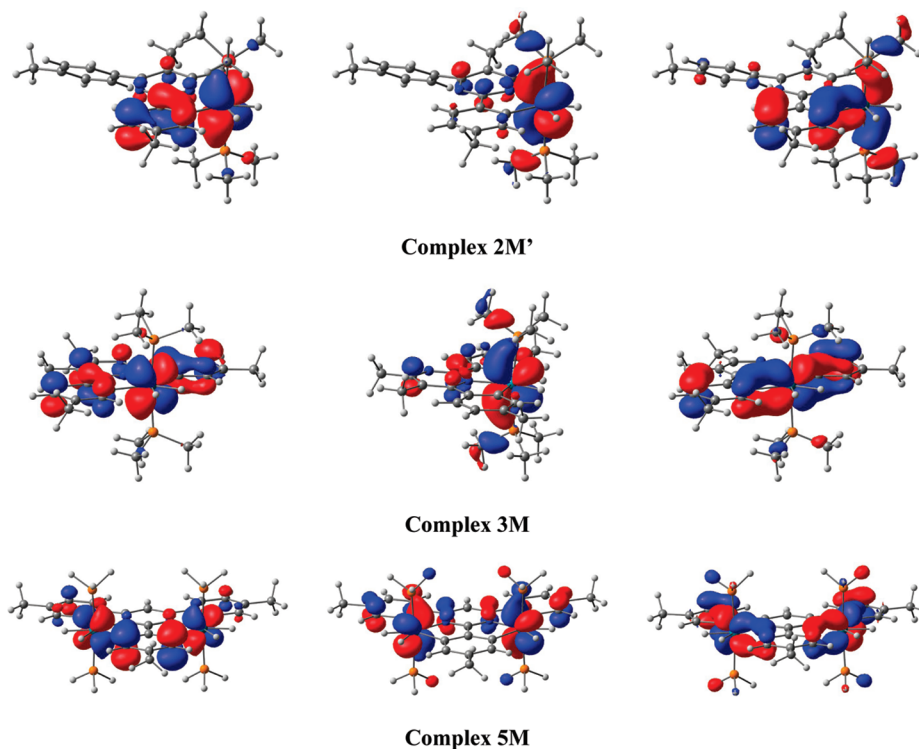


Figure 8. Plot of the π -orbitals of complexes **2M'**, **3M**, and **5M** (BP86/def2-SVP level). The value of the outermost contour line is 0.035.

or Bruker Avance 500 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H , $^{13}\text{C}\{^1\text{H}\}$) or to external 85% H_3PO_4 ($^{31}\text{P}\{^1\text{H}\}$). Coupling constants J and N are given in hertz. Infrared spectra were recorded on a Perkin-Elmer Spectrum One or Spectrum 100 spectrometer as Nujol mulls or neat solids. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. 4,5-Dimethyl-2,6-bis(4-methylphenyl)pyrimidine²⁹ and 2,4,6-triphenylpyrimidine³⁰ were prepared according to the general method for the one-step synthesis of pyrimidines,³⁰ 2,4,6-tris(4-methylphenyl)-1,3,5-triazine³¹ was prepared according to the method for the synthesis of *s*-triazines,³² and $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ (**1**) was prepared as previously reported.³³

Kinetic Analyses. The activation parameters for the hydride exchanges in complex **2** were obtained as follows: (a) For the exchange between the two hydrides located at lower fields (i.e., the exchange of lower energy barrier) $^1\text{H}\{^{31}\text{P}\}$ spectral simulation was employed: Experimental exchange broadened line shapes were iteratively fit using the gNMR³⁴ program, with the line width in the absence of exchange fixed at the lowest measured values. The activation parameters, ΔH^\ddagger and ΔS^\ddagger , were obtained from a linear least-squares fit of $\ln(k/T)$ versus

$1/T$ (Eyring equation). Errors were computed by published methods.³⁵ The error in temperature was assumed to be 1 K; error in k was estimated as 10%. (b) For the exchange that takes place at high temperatures it was not possible to simulate the $^1\text{H}\{^{31}\text{P}\}$ NMR spectra, and then we used the method of Shanan-Atidi and Bar-Eli³⁶ for analysis of exchange between unequal populations. The activation energy of exchange was calculated using eq 1, where k_B = Boltzmann's constant, h = Planck's constant, T_c = temperature of coalescence (K), δ_ν = chemical shift difference in the static spectrum (Hz), and ΔP = difference in mole fractions of the exchanging nuclei. For this problem the ratio is 2:1, so that $\Delta P = 1/3$ (i.e., $2/3 - 1/3$). X is evaluated as 2.0823 from Table 6.1 of Sandström's text.³⁷

$$\Delta G^\ddagger = RT \ln \left[\frac{k_B}{h\pi} \left(\frac{T_c}{\delta_\nu} \right) \left(\frac{X}{1 + \Delta P} \right) \right] \quad (1)$$

Reaction of $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ with 4,5-Dimethyl-2,6-bis(4-methylphenyl)pyrimidine (H₂L1**): Synthesis of Complexes **2** and **3**.** 4,5-Dimethyl-2,6-bis(4-methylphenyl)pyrimidine (66 mg, 0.23 mmol) was added to a solution of $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ (**1**) (117 mg, 0.23 mmol) in toluene (10 mL) and heated under reflux for 32 h, changing the color from pale yellow to dark red. The progress of the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, which showed quantitative conversion to a 40:60 mixture of complexes **2** and **3**. After this time the mixture was cooled to room temperature and the solvent was evaporated. Extraction of the resulting residue with pentane allows the isolation of both complexes in pure form: Complex **3** is extracted with pentane (15 mL), while complex **2** remains in the residue. After drying both portions, addition of methanol afforded red (**2**) and orange (**3**) solids, which were washed with further portions of methanol and dried in vacuo. Yield of complex **2**: 45 mg (25%); complex **3**: 65 mg (36%).

(36) Shanan-Atidi; Bar-Eli *J. Phys. Chem.* **1970**, *74*, 961.

(37) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

(29) Martínez-Alvarez, R.; Herrera Fernández, A.; Chioua, M.; Ramiro, P.; Villalba Vilchez, N.; Guzmán Torres, F. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 2480.

(30) García Martínez, A.; Herrera Fernández, A.; Moreno Jiménez, F.; García Fraile, A.; Subramanian, L. R.; Hanack, M. *J. Org. Chem.* **1992**, *57*, 1627.

(31) Forsberg, J. H.; Spaziano, V. T.; Klump, S. P.; Sanders, K. M. *J. Heterocycl. Chem.* **1988**, *25*, 767.

(32) Herrera, A.; Martínez-Alvarez, R.; Ramiro, P.; Chioua, M.; Chioua, R. *Synthesis* **2004**, 503.

(33) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288.

(34) Budzelaar, P. H. M. *gNMR*, version 4.1; Ivory Soft: Englewood, CO, 1999 (Published by Cherwell Scientific Publishing Limited, Oxford, U.K.).

(35) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

Complex 2. Anal. Calcd for $C_{38}H_{64}N_2OsP_2$: C, 56.97; H, 8.05; N, 3.05. Found: C, 56.43; H, 8.23; N, 2.70. IR (neat compound, cm^{-1}): $\nu(Os-H)$; 2127 (w), 2090 (w); $\nu(C=N)$ $\nu(C=C)$ 1584 (m), 1546 (m). 1H NMR (400 MHz, C_6D_6 , 293 K): δ 8.84 (d, $J_{H-H} = 7.2$, 1H, *CH*-arom), 8.40 (s, 1H, *CH*-arom), 7.64 (d, $J_{H-H} = 8.0$, 2H, *CH*-arom), 7.06 (d, $J_{H-H} = 8.0$, 2H, *CH*-arom), 6.99 (d, $J_{H-H} = 7.2$, 1H, *CH*-arom), 3.21 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 1.96 (m, 6H, $PCH(CH_3)_2$), 1.02 (dvt, $J_{H-H} = 6.8$, $N = 12.4$, 18H, $PCHCH_3$), 0.94 (dvt, $J_{H-H} = 6.8$, $N = 12.0$, 18H, $PCHCH_3$), -8.62 (br, 2H, Os-H), -12.91 (br, 1H, Os-H). 1H NMR (400 MHz, C_7D_8 , 203 K, high-field region): δ -7.51 (br, 1H, Os-H), -9.77 (br, 1H, Os-H), -12.51 (br, 1H, Os-H). $^{13}C\{^1H\}$ NMR (100.63 MHz, C_6D_6 , 293 K): δ 185.6 (t, $J_{P-C} = 7.3$, Os-C), 174.1, 167.7, 162.5, 142.6, 138.8, 138.7, 136.8, 119.9 (all s, *C*-arom), 146.2, 130.1, 129.7, 129.0, 120.7 (all s, *CH*-arom), 32.6, 22.2, 21.2, 17.8 (all s, CH_3), 27.6 (vt, $N = 23.4$, $PCH(CH_3)_2$), 20.2 (s, $PCH(CH_3)_2$), 20.0 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6 , 293 K): δ 21.4 (s). $T_{1(\min)}$ (ms, OsH, 400 MHz, C_7D_8 , 273 K): 102 ± 3 (-8.62 ppm); 129 ± 3 (-12.91 ppm).

Complex 3. Anal. Calcd for $C_{38}H_{62}N_2OsP_2$: C, 57.12; H, 7.82; N, 3.51. Found: C, 56.61; H, 7.62; N, 3.46. IR (neat compound, cm^{-1}): $\nu(Os-H)$ 2150 (w); $\nu(C=N)$ $\nu(C=C)$ 1583 (m), 1548 (m). 1H NMR (400 MHz, C_6D_6 , 293 K): δ 8.69 (d, $J_{H-H} = 7.8$, 1H, *CH*-arom), 8.40, 8.19 (all s, 1H, *CH*-arom), 8.12 (d, $J_{H-H} = 8.4$, 1H, *CH*-arom), 6.98 (d, $J_{H-H} = 8.4$, 1H, *CH*-arom), 6.95 (d, $J_{H-H} = 7.8$, 1H, *CH*-arom), 2.67, 2.40, 2.39, 2.34 (all s, 3H, CH_3), 2.02 (m, 6H, $PCH(CH_3)_2$), 0.85 (dvt, $J_{H-H} = 6$, $N = 12.2$, 18H, $PCHCH_3$), 0.83 (dvt, $J_{H-H} = 6.4$, $N = 12.4$, 18H, $PCHCH_3$), -7.78 (dt, $J_{H-H} = 12.0$, $J_{H-P} = 15.2$, 1H, Os-H), -8.16 (dt, $J_{H-H} = 12.0$, $J_{H-P} = 15.2$, 1H, Os-H). $^{13}C\{^1H\}$ NMR (75.445 MHz, C_6D_6 , 293 K): δ 183.4 (t, $J_{P-C} = 6.9$, Os-C), 173.9 (t, $J_{P-C} = 7.4$, Os-C), 171.6, 170.2, 164.4, 145.6, 143.8, 139.4, 138.2, 116.6 (all s, *C*-arom), 148.1, 146.6, 130.4, 127.6, 121.8, 120.6 (all s, *CH*-arom), 23.4, 22.0, 21.6, 17.0 (all s, CH_3), 26.8 (vt, $N = 24.4$, $PCH(CH_3)_2$), 19.3 (s, $PCH(CH_3)_2$), 19.3 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6 , 293 K): δ 0.0 (s).

Reaction of $OsH_6(P^iPr_3)_2$ with 2,4,6-Tris(4-methylphenyl)-1,3,5-triazine (H_4L_2): Synthesis of Complexes 4 and 5. 2,4,6-Tris(4-methylphenyl)-1,3,5-triazine (136 mg, 0.38 mmol) was added to a solution of **1** (200 mg, 0.38 mmol) in toluene (10 mL) and heated under reflux. After 48 h, the resulting dark red solution was cooled to room temperature and the solvent was evaporated in vacuo. The obtained residue was extracted with diethyl ether (25 mL), getting a dark red solution that was taken to dryness. 1H and $^{31}P\{^1H\}$ NMR spectra of this residue in C_6D_6 show the presence of two complexes (**4** and **5**) in a ratio 8:1. Complex **4** could be isolated as a pure red solid by addition of methanol.

Complex 4. Yield: 86 mg (26%). Anal. Calcd for $C_{42}H_{63}N_3OsP_2$: C, 58.51; H, 7.36; N, 4.87. Found: C, 58.23; H, 7.58; N, 4.61. IR (neat compound, cm^{-1}): $\nu(Os-H)$; 1892 (w); $\nu(C=C)$, $\nu(C=N)$; 1584 (m), 1537 (m). 1H NMR (400 MHz, C_6D_6 , 293 K): δ 9.19 (d, $J_{H-H} = 8.0$, 2H, *CH*-arom), 9.19 (d, $J_{H-H} = 7.6$, 2H, *CH*-arom), 8.31 (s, 2H, *CH*-arom), 7.21 (d, $J_{H-H} = 8.0$, 2H, *CH*-arom), 7.07 (d, $J_{H-H} = 7.6$, 2H, *CH*-arom), 2.39 (s, 6H, CH_3), 2.14 (s, 3H, CH_3), 1.90 (m, 6H, $PCH(CH_3)_2$), 0.75 (dvt, $J_{H-H} = 6.6$, $N = 12.6$, 36H, $PCHCH_3$), -7.30 (t, $J_{H-P} = 15.6$, 2H, Os-H). $^{13}C\{^1H\}$ NMR (100.63 MHz, C_6D_6 , 293 K): δ 179.4 (t, $J_{P-C} = 6.8$, Os-C), 177.9, 169.9, 142.6, 141.5, 141.1, 134.4 (all s, *C*-arom), 147.4, 129.9, 129.3, 229.2, 122.2 (all s, *CH*-arom), 26.9 (vt, $N = 24.8$, $PCH(CH_3)_2$), 22.2, 21.4 (all s, CH_3), 19.1 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6 , 293 K): δ 0.0 (s).

Complex 5. 1H NMR (400 MHz, C_6D_6 , 293 K): δ 8.88 (d, $J_{H-H} = 8.0$, 2H, *CH*-arom), 8.37, 7.65 (all s, 2H, *CH*-arom), 7.06 (d, $J_{H-H} = 8.0$, 2H, *CH*-arom), 2.51 (s, 3H, CH_3), 2.41 (s, 6H, CH_3), 2.03 (m, 12H, $PCH(CH_3)_2$), 0.91 (dvt, $J_{H-H} = 6.4$, $N = 12.8$, 36H, $PCHCH_3$), 0.84 (dvt, $J_{H-H} = 6.2$, $N = 12.2$, 36H, $PCHCH_3$), -7.13 (dt, $J_{H-H} = 8.0$, $J_{H-P} = 16.0$, 2H, Os-H),

-8.71 (dt, $J_{H-H} = 8.0$, $J_{H-P} = 18.4$, 2H, Os-H). $^{13}C\{^1H\}$ NMR (100.63 MHz, C_6D_6 , 293 K): δ 176.3 (t, $J_{P-C} = 8.9$, Os-C), 172.6 (t, $J_{P-C} = 6.4$, Os-C), 174.3, 171.9, 152.3, 141.1, 139.9, 139.7 (all s, *C*-arom), 148.7, 141.3, 129.1, 122.0 (all s, *CH*-arom), 27.2 (vt, $N = 24.5$, $PCH(CH_3)_2$), 22.5, 22.1 (all s, CH_3), 20.2 (s, $PCH(CH_3)_2$), 19.8 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6 , 293 K): δ 2.5 (s).

Reaction of $OsH_6(P^iPr_3)_2$ with 1 equiv of 2,4,6-Triphenylpyrimidine (H_4L_3): Synthesis of Complex 6. 2,4,6-Triphenylpyrimidine (45 mg, 0.15 mmol) was added to a solution of **1** (90 mg, 0.16 mmol) in toluene (5 mL) and heated under reflux. The solution changed from pale yellow to dark red. After 7 h, the mixture was cooled to room temperature and the solvent was evaporated in vacuo. Addition of pentane (2 mL) caused the precipitation of an orange solid, which was washed with pentane (2×4 mL) and then methanol (4 mL) and dried in vacuo. Yield: 20 mg (13%). 1H and $^{31}P\{^1H\}$ NMR spectra show that the reaction is quantitative, but the obtained yield is very low due to the high solubility of the complex in pentane. Anal. Calcd for $C_{43}H_{64}N_2OsP_2$: C, 59.97; H, 7.49; N, 3.25. Found: C, 60.25; H, 8.49; N, 3.40. IR (neat compound, cm^{-1}): $\nu(Os-H)$; 2147 (w); $\nu(C=N)$, $\nu(C=C)$; 1582 (m), 1571 (m). 1H NMR (400 MHz, C_6D_6 , 293 K): δ 8.90 (d, $J_{H-H} = 6.0$, 1H, *CH*-arom), 8.46 (d, $J_{H-H} = 8.8$, 1H, *CH*-arom), 8.38 (d, $J_{H-H} = 7.2$, 2H, *CH*-arom), 7.92 (s, 1H, *CH*-arom), 7.90 (d, $J_{H-H} = 6.0$, 1H, *CH*-arom), 7.30-6.90 (m, 7H, *CH*-arom), 1.95 (m, 6H, $PCH(CH_3)_2$), 0.77 (dvt, $J_{H-H} = 5.8$, $N = 11.0$, 18H, $PCHCH_3$), 0.76 (dvt, $J_{H-H} = 6.0$, $N = 10.8$, 18H, $PCHCH_3$), -7.53 (ABX₂ spin system, $\Delta\nu = 25$, $J_{H-H} = 12.2$, $J_{H-P} = 15.4$, 2H, Os-H). $^{13}C\{^1H\}$ NMR (100.63 MHz, C_6D_6 , 293 K): δ 181.4 (t, $J_{P-C} = 6.8$, Os-C), 174.9 (t, $J_{P-C} = 7.1$, Os-C), 174.3, 172.5, 161.9, 145.7, 137.7, 128.1 (all s, *C*-arom), 146.8, 146.0, 131.0, 130.6, 130.5, 128.7, 128.3, 128.1, 127.9, 126.3, 120.6, 120.1, 102.3 (all s, *CH*-arom), 27.0 (vt, $N = 24.6$, $PCH(CH_3)_2$), 19.2 (s, $PCH(CH_3)_2$), 19.1 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6 , 293 K): δ 0.3 (s).

Reaction of $OsH_6(P^iPr_3)_2$ with 0.5 equiv of 2,4,6-Triphenylpyrimidine (H_4L_3): Synthesis of Complex 7. **1** (100 mg, 0.19 mmol) was added to a solution of 2,4,6-triphenylpyrimidine (30 mg, 0.10 mmol) in toluene (5 mL) and heated under reflux. The solution changed from pale yellow to dark red. After 21 h, the mixture was cooled to room temperature and the solvent was evaporated in vacuo. Addition of pentane (2 mL) caused the precipitation of a red solid, which was washed with pentane (2×4 mL) and then methanol (4 mL) and dried in vacuo. Yield: 95 mg (73%). Anal. Calcd for $C_{61}H_{106}N_2Os_2P_4$: C, 52.82; H, 7.51; N, 2.09. Found: C, 53.66; H, 7.76; N, 1.96. IR (neat compound, cm^{-1}): $\nu(Os-H)$; 2221 (w), 2147 (w), 2107 (w); $\nu(C=C)$, $\nu(C=N)$; 1569 (m), 1549 (s). 1H NMR (400 MHz, C_6D_6 , 293 K): δ 8.47 (d, $J_{H-H} = 7.6$, 2H, *CH*-arom), 7.92 (d, $J_{H-H} = 7.4$, 2H, *CH*-arom), 7.77 (d, $J_{H-H} = 7.2$, 2H, *CH*-arom), 8.19 (s, 1H, *CH*-arom), 7.62 (t, $J_{H-H} = 4.8$, 2H, *CH*-arom), 7.02 (t, $J_{H-H} = 7.6$, 2H, *CH*-arom), 6.78 (t, $J_{H-H} = 7.2$, 1H, *CH*-arom), 2.08 (m, 12H, $PCH(CH_3)_2$), 0.918 (dvt, $J_{H-H} = 6.6$, $N = 13.0$, 36 H, $PCHCH_3$), 0.85 (dvt, $J_{H-H} = 6.4$, $N = 12.4$, 36 H, $PCHCH_3$), -7.40 (dt, $J_{H-H} = 11.0$, $J_{H-P} = 21.8$, 2H, Os-H), -8.87 (dt, $J_{H-H} = 11.0$, $J_{H-P} = 23.8$, 2H, Os-H). $^{13}C\{^1H\}$ NMR (100.63 MHz, C_6D_6 , 293 K): δ 178.6 (t, $J_{P-C} = 7.2$, Os-C), 169.7 (t, $J_{P-C} = 6.7$, Os-C), 168.3, 156.3, 145.9, 128.4 (all s, *C*-arom), 147.8, 139.7, 130.5, 129.4, 127.2, 120.1, 93.5 (all s, *CH*-arom), 27.1 (vt, $N = 24.0$, $PCH(CH_3)_2$), 20.3 (s, $PCH(CH_3)_2$), 19.7 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6 , 293 K): δ 2.4 (s).

Structural Analysis of Complexes 2, 3, 4, and 5. Crystals suitable for the X-ray diffraction study were obtained by cooling a solution in pentane at 4 °C (**2** and **3**) or by slow diffusion of methanol into solutions of the complexes in toluene (**4** and **5**). X-ray data were collected on a Bruker Smart APEX CCD (**2**, **3**, **4**) and an Oxford Diffraction Xcalibur TS (**5**) using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data were collected over the complete

Table 1. Crystal Data Collection and Refinement for 2, 3, 4, and 5

	2	3	4	5
Crystal Data				
formula	C ₃₈ H ₆₄ N ₂ OsP ₂	C ₃₈ H ₆₂ N ₂ OsP ₂	C ₄₂ H ₆₃ N ₃ OsP ₂	C ₆₀ H ₁₀₅ N ₃ Os ₂ P ₄ ·C ₄ H ₁₀
molecular wt	801.05	799.04	862.09	1446.87
color and habit	dark orange, prism	orange, prism	orange, prism	purple, plate
size, mm	0.12, 0.06, 0.06	0.08, 0.05, 0.03	0.14, 0.06, 0.04	0.21, 0.12, 0.02
symmetry, space group	monoclinic, <i>P</i> 2(1)/ <i>c</i>	triclinic, <i>P</i> $\bar{1}$	triclinic, <i>P</i> $\bar{1}$	triclinic, <i>P</i> $\bar{1}$
<i>a</i> , Å	19.939(6)	10.724(3)	11.5757(15)	10.6776(2)
<i>b</i> , Å	16.984(5)	11.504(3)	11.7795(15)	15.1579(4)
<i>c</i> , Å	11.087(3)	15.107(4)	15.744(2)	21.7645(3)
α , deg	90	88.454(4)	111.362(2)	108.752(2)
β , deg	93.605(5)	77.692(4)	91.549(2)	97.1420(10)
γ , deg	90	82.541(5)	97.397(2)	92.741(2)
<i>V</i> , Å ³	3747.3(18)	1805.4(8)	1976.3(4)	3295.24(12)
<i>Z</i>	4	2	2	2
<i>D</i> _{calc} , g cm ^{−3}	1.420	1.470	1.449	1.458
Data Collection and Refinement				
diffractometer	Bruker Smart APEX	Bruker Smart APEX	Bruker Smart APEX	Oxford Diffraction Xcalibur TS
λ (Mo K α), Å			0.71073	
monochromator			graphite oriented	
scan type			ω scans	
μ , mm ^{−1}	3.516	3.648	3.340	3.990
2 θ , range deg	3, 58	4, 58	4, 58	4, 58
temp, K	100(2)	100(2)	100(2)	150(2)
no. of data collect	46 190	16 401	24 987	62 671
no. of unique data	9298 (<i>R</i> _{int} = 0.0538)	8532 (<i>R</i> _{int} = 0.0567)	9484 (<i>R</i> _{int} = 0.0409)	14 417 (<i>R</i> _{int} = 0.0560)
no. of params/restraints	415/3	414/33	456/0	712/2
<i>R</i> ₁ ^a [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0323	0.0439	0.0321	0.0308
<i>wR</i> ₂ ^b [all data]	0.0561	0.0891	0.0667	0.0585
GoF	0.896	0.963	1.034	0.866

$$^a R_1(F) = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2(F^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2 \}^{1/2}.$$

sphere and were corrected for absorption by using a multiscan method applied with the CrisAlys RED package³⁸ for complex **5** and with the SADABS program³⁹ for complexes **2**, **3**, and **4**. The structures of all compounds were solved by the Patterson method. Refinement, by full-matrix least-squares on *F*² with SHELXL97,⁴⁰ was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms (except hydride ligands) were calculated and refined using a restricted riding model. Hydride ligands were observed in the difference Fourier maps and refined with restrained Os–H bond length (1.59(1) Å, CSD). The pyrimidine ring of complex **3** was found to be disordered, simulating *C*₂ symmetry about the osmium–nitrogen axis. The disordered atoms were defined with two moieties (50, 50), complementary occupancy factors,

isotropic atoms, and restrained geometry. In all complexes, the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense. Crystal data and details of the data collection and refinement are given in Table 1.

Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 03 suite of programs.⁴¹ The geometries of the molecules were optimized at the gradient-corrected DFT level of theory using Becke's exchange functional in conjunction with Perdew's correlation functional (BP86)⁴² in combination with the double- ξ valence plus polarization def2-SVP basis set.⁴³ Calculation of the vibrational frequencies⁴⁴ at the optimized geometries showed that the compounds are minima on the potential energy surface.

Donor–acceptor interactions have been computed using the natural bond orbital (NBO) method. The energies associated with these two-electron interactions have been computed according to the following equation:

$$\Delta E_{\phi\phi^*}^{(2)} = -n_{\phi} \frac{\langle \phi^* | \hat{F} | \phi \rangle^2}{\varepsilon_{\phi^*} - \varepsilon_{\phi}}$$

where \hat{F} is the DFT equivalent of the Fock operator and ϕ and ϕ^* are two filled and unfilled natural bond orbitals having ε_{ϕ} and ε_{ϕ^*} energies, respectively; n_{ϕ} stands for the occupation number of the filled orbital.

Acknowledgment. Financial support from the MICINN of Spain (project numbers CTQ2008-00810,

(38) *CrysAlis; RED. A program for Xcalibur CCD System X-ray diffraction data reduction*; Oxford Diffraction Ltd.: Oxford, UK, 2005.

(39) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33–38. *SADABS: Area-detector absorption correction*; Bruker-AXS: Madison, WI, 1996.

(40) *SHELXTL Package v. 6.10*; Bruker-AXS: Madison, WI, 2000. Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

(41) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, rev. D01*; Gaussian, Inc.: Wallingford, CT, 2004.

(42) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(43) Weigend, F.; Alhrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(44) McIver, J. W.; Komornicki, A. K. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

CTQ2007-67730-C02-01/BQU, and Consolider Ingenio 2010 CSD2007-00006), the Diputación General de Aragón (E35), and the CAM CCG07-UCM/PPQ-2596 is acknowledged. I.F. is a Ramón y Cajal Fellow. M. M.-O. thanks the MICINN for a FPI predoctoral grant.

Supporting Information Available: X-ray analysis and crystal structure determination, including bond lengths and angles of compounds **3**, **2**, **4**, and **5**. Cartesian coordinates with the total energies of the computed compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.