Δ^2- and Δ^3-Azaosmetine Complexes as Intermediates in the Stoichiometric Imination of Phenylacetylene with Oximes

Ricardo Castarlenas, Miguel A. Esteruelas,* and Enrique Oñate

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

Received January 2, 2001

Complexes $[Os\{(E)\text{-}CH{=}CHPh\}Cl(=N{=}CR_2)(P^iPr_3)_2][CF_3SO_3]$ [CR_2 = CMe_2 (**1**), $\overline{C(CH_2)_4CH_2}$ (**2**)] react with carbon monoxide to give the Δ^2-1,2-azaosmetine derivatives $[\overline{OsCl(=CHCH(Ph)N=CR_2}\}(CO)(P^iPr_3)_2][CF_3SO_3]$ [CR_2 = CMe_2 (**3**), $\overline{C(CH_2)_4CH_2}$ (**4**)], as a result of the coordination of carbon monoxide to the osmium atoms of **1** and **2** and the carbon−nitrogen coupling between the styryl and azavinylidene ligands. The structure of **3** in the solid state has been determined by an X-ray diffraction study. Complexes **3** and **4** can be deprotonated with MeLi to give the Δ^3-1,2-azaosmetine compounds $\overline{Os\{CH{=}C(Ph)N{=}CR_2}\}Cl(CO)(P^iPr_3)_2$ [CR_2 = CMe_2 (**5**), $\overline{C(CH_2)_4CH_2}$ (**6**)], which react with molecular hydrogen to afford the 2-aza-1,3-butadienes $CH_2{=}C(Ph)N{=}CR_2$ [CR_2 = CMe_2 (**7**), $\overline{C(CH_2)_4CH_2}$ (**8**)] and $OsH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$. The carbonylation of the cations of **3** and **4** leads to $[Os\{(Z)\text{-}CH{=}C(Ph)NH{=}CR_2\}Cl(CO)_2(P^iPr_3)_2]^+$ [CR_2 = CMe_2 (**9**), $\overline{C(CH_2)_4CH_2}$ (**10**)]. The $[BF_4]^-$ salts of **9** and **10** have been obtained by carbonylation of **5** and **6** and subsequent protonation of the resulting η^1-azabutadiene intermediates $Os\{(Z)\text{-}CH{=}C(Ph)N{=}CR_2\}Cl(CO)_2(P^iPr_3)_2$ [CR_2 = CMe_2 (**11**), $\overline{C(CH_2)_4CH_2}$ (**12**)]. The structure of the $[BF_4]^-$ salt of **10** in the solid state has also been determined by an X-ray diffraction study.

Introduction

The hydroamination of alkenes and alkynes in the presence of transition-metal complexes is an attractive route to prepare numerous classes of organo−nitrogen molecules.[1] Two basic approaches have been employed. They involve either alkene/alkyne or amine activation routes.[2] Alkene/alkyne activation is generally accomplished with late-transition-metal complexes, which render coordinated olefins/alkynes more susceptible to attack by exogeneous amine-nucleophiles.[3] The alternative amine activation route uses N−H oxidative addition to electron-rich late-transition-metal centers.[4] Recently, it has been shown that alkyne-cycloaddition reactions on early-transition-metal−nitrogen multiple bonds, to afford azametallacyclobutenes, are also important mechanistic steps in the amination of alkynes.[5]

Among the group of organo−nitrogen molecules widely used as intermediates in organic synthesis, 2-aza-1,3-dienes play a prominent role, as has been shown by Barluenga and co-workers.[6] This type of heterodienes are able to react with typical electron-deficient dienophiles in Diels−Alder reactions. Their utility in organic synthesis is indicated not only in cycloaddition reactions but also in other types of processes such as cyclocondensation reactions, halogenations, etc.[6b,7] At first glance, a direct and general synthetic strategy to obtain 2-aza-1,3-dienes should be the addition of N-protio

(1) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675.
(2) (a) Taube, R. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrman, W. A., Eds.; VCH: Weinheim, 1996; Vol. 1, 507. (b) Burling, S.; Field, L. D.; Messerle, B. A. *Organometallics* **2000**, *19*, 87.
(3) See for example: (a) Beller, M.; Eichberger, M.; Trauthwein, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2225. (b) Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 9546.
(4) See for example: (a) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738. (b) Uchimaru, Y. *Chem. Commun.* **1999**, 1133.
(5) (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (b) Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7994. (c) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708. (d) de With, J.; Horton, A. D.; Orpen, A. G. *Organometallics* **1993**, *12*, 1493. (e) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2753. (f) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705. (g) Lee, S. Y.; Bergman, R. G. *Tetrahedron* **1995**, *51*, 4255. (h) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974. (i) Hanna, T. A.; Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 3292. (j) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *J. Org. Chem.* **1996**, *61*, 4532. (k) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1757. (l) Arredondo, V. M.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 4871. (m) Polse, J. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 13405. (n) Harlan, C. J.; Tunge, J. A.; Bridgewater, B. M.; Norton, J. R. *Organometallics* **2000**, *19*, 2365. (o) Zuckerman, R. L.; Krska, S. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 751.
(6) See for example: (a) Barluenga, J.; Joglar, J.; González, F. J.; Fustero, S. *Synlett* **1990**, 129. (b) Barluenga, J.; Aznar, F.; Fustero, S.; Tomás, M. *Pure Appl. Chem.* **1990**, *62*, 1957.
(7) (a) Georg, G. I.; He, P.; Kant, J.; Mudd, J. *Tetrahedron Lett.* **1990**, *31*, 451. (b) Georg, G. I.; He, P.; Kant, J.; Wu, Z.-J. *J. Org. Chem.* **1993**, *58*, 5771.

10.1021/om010005k CCC: $20.00
Publication on Web 05/04/2001

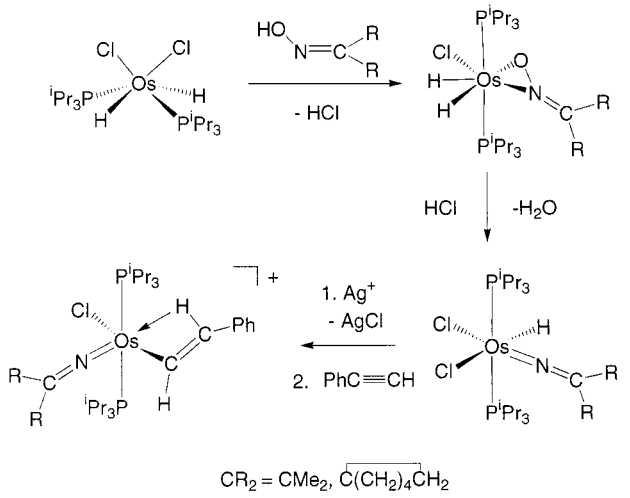
imines to nonactivated alkynes, in the presence of a transition-metal complex. However, although organic chemists have developed various synthetic aproaches,[8] this route has not been investigated.

The use of N-protio imines as amination reagents has a serious limitation, the known low stability of the N-protio ketimines.[9] With the aim of finding an alternative, two years ago we initiated a research program centered in the use of oximes. It was known from work in our group that the use of transition-metal complexes with several hydrogen atoms bonded to the metallic center, first, allows the access of several organic molecules into the metal; second, this access can be sequential and selective; and third, a wide range of organometallic functional groups can be obtained. All this facilitates different types of coupling reactions and the generation of organic fragments with a rich organic chemistry, which permits the growth of the ligands.[10]

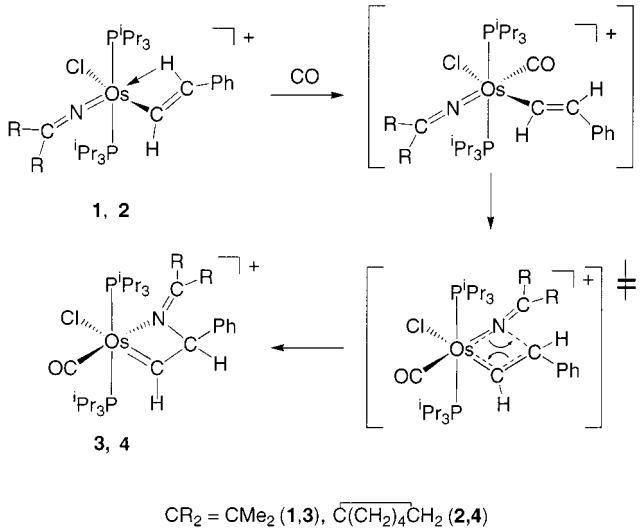
These precedents prompted us to study the reactions of the dihydride−dichloro complex $OsH_2Cl_2(P^iPr_3)_2$ with acetone oxime, cyclohexanone oxime, and phenylacetylene. In an initial stage, the oximes were introduced into the metallic center[11] and the oxygen atom was eliminated by reaction of the resulting oximate compounds with HCl[12] (Scheme 1). The alkyne was introduced into the osmium atom by treatment of $OsHCl_2(=N=CR_2)(P^iPr_3)_2$ [CR_2 = CMe_2, $\overline{C(CH_2)_4CH_2}$] with $Ag[CF_3SO_3]$ at room temperature and the subsequent addition of phenylacetylene at −25 °C. Then, we attempted the coupling of the alkenyl and azavinylidene ligands of $[Os\{(E)\text{-}CH{=}CHPh\}Cl(=N=CR_2)(P^iPr_3)_2]^+$ by means of the additions of NaCl, H_2O, and CH_3CN. However, the formation of the imine−vinylidene derivatives $OsCl_2(=C=CHPh)(NH=CR_2)(P^iPr_3)_2$ and $[OsCl(=C=CHPh)(NH=CR_2)L(P^iPr_3)_2]^+$ (L = H_2O, CH_3CN) was observed, as a result of the novel hydrogen transfer from the styryl ligands to the azavinylidene groups.[13] We have now observed that, in contrast to NaCl, H_2O, and CH_3CN, carbon monoxide promotes the coupling of the styryl and azavinylidene ligands.

In this paper, we report the remaining steps to obtain 2-aza-1,3-dienes, as well as the characterization of the organometallic intermediates, including Δ^2-1,2- and Δ^3-1,2-azaosmetine derivatives.

Scheme 1



Scheme 2



Results and Discussion

1. Coupling between the Alkenyl and Azavinylidene Ligands of $[Os\{(E)\text{-}CH{=}CHPh\}Cl(=N=CR_2)(P^iPr_3)_2][CF_3SO_3]$ [CR_2 = CMe_2, $\overline{C(CH_2)_4CH_2}$]. Under atmospheric pressure of carbon monoxide, complexes $[Os\{(E)\text{-}CH{=}CHPh\}Cl(=N=CR_2)(P^iPr_3)_2][CF_3SO_3]$ [CR_2 = CMe_2 (**1**), $\overline{C(CH_2)_4CH_2}$ (**2**)], in 1:1 mixtures of dichloromethane/diethyl ether as solvent, afford after 1 h the Δ^2-1,2-azaosmetine derivatives $[\overline{OsCl\{=CHCH(Ph)N=CR_2\}(CO)(P^iPr_3)_2}][CF_3SO_3]$ [CR_2 = CMe_2 (**3**), $\overline{C(CH_2)_4CH_2}$ (**4**)], which were isolated as yellow solids in about 80% yield.

The formation of these compounds can be rationalized as intramolecular [2+2] cycloaddition reactions between

(8) (a) Barluenga, J.; Joglar, J.; Fustero, S.; Gotor, V.; Krüger, C.; Romão, M. J. *Chem. Ber.* **1985**, *118*, 3652. (b) Chen, S.-F.; Mariano, P. S. *Tetrahedron Lett.* **1985**, *26*, 47. (c) Barluenga, J.; Ferrero, M.; Palacios, F. *Tetrahedron Lett.* **1990**, *31*, 3497. (d) Ghosez, L.; Bayard, Ph.; Nshimyumukiza, P.; Gouverneur, V.; Sainte, F.; Beaudegnies, R.; Rivera, M.; Frisque-Hesbain, A.-M.; Wynants, C. *Tetrahedron* **1995**, *51*, 11021. (e) Palacios, F.; Alonso, C.; Rubiales, G. *J. Org. Chem.* **1997**, *62*, 1146. (f) Palacios, F.; Gil, M. J.; Martínez de Marigorta, E.; Rodríguez, M. *Tetrahedron Lett.* **1999**, *40*, 2411.

(9) (a) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; McGraw-Hill Book Co.: New York, 1968; Chapter 16, p 656. (b) Robertson, G. M. In *Comprehensive Organic Functional Group Transformations*; Katritzley, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, England, 1995; Vol. 3, pp 403−432.

(10) See for example: (a) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663. (b) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 1669. (c) Esteruelas, M. A.; Liu, F.; Oñate, E.; Sola, E.; Zeier, B. *Organometallics* **1997**, *16*, 2919. (d) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **1997**, *16*, 3169. (e) Bohanna, C.; Callejas, B.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N.; Valero, C. *Organometallics* **1998**, *17*, 373. (f) Bohanna, C.; Buil, M. L.; Esteruelas, M. A. Oñate, E.; Valero, C. *Organometallics* **1999**, *18*, 5176. (g) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Oliván, M.; Oñate, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2000**, *19*, 4327, and references therein. (h) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2000**, *19*, 5098.

(11) Castarlenas, R.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Jean, Y.; Lledós, A.; Martín, M.; Tomàs, J. *Organometallics* **1999**, *18*, 4296.

(12) Castarlenas, R.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Jean, Y.; Lledós, A.; Martín, M.; Oñate, E,; Tomàs, J. *Organometallics* **2000**, *19*, 3100.

(13) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2000**, *19*, 5454.

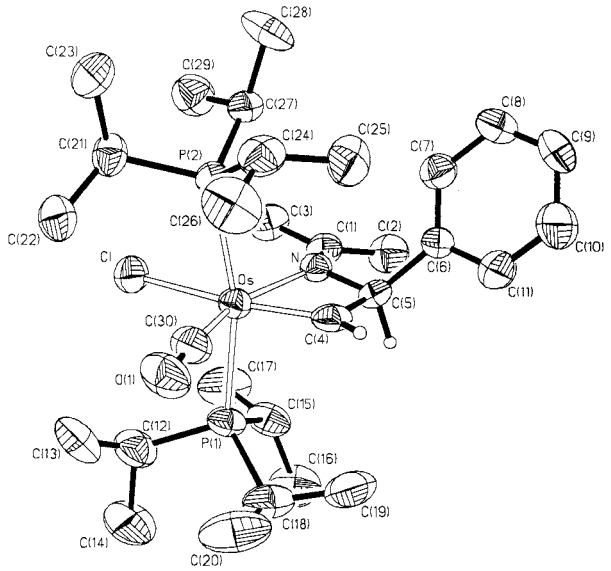


Figure 1. Molecular diagram for $[OsCl\{=CHCH(Ph)N=CMe_2\}(CO)(PiPr_3)_2]^+$ (**3**). Thermal ellipsoids are shown at 50% probability.

the osmium−azavinylidene bonds and the carbon−carbon double bond of the styryl ligands (Scheme 2). In agreement with the lability of the agostic interactions and with the formation of the previously reported complexes $Os\{(E)\text{-}CH{=}CHPh\}Cl_2(=N{=}CR_2)(P^iPr_3)_2$ and $[Os\{(E)\text{-}CH{=}CHPh\}Cl(=N{=}CR_2)L(P^iPr_3)_2][CF_3SO_3]$ ($L = H_2O$, CH_3CN),[13] the first step of these transformations should be the coordination of carbon monoxide trans to the azavinylidene ligands. Thus, the strong π-acceptor power of the carbonyl could excite the π-donor nature of the azavinylidene groups, increasing the double bond character of the osmium−azavinylidene bonds and, in this way, activating the intramolecular cyclization between the Os−N and C−C double bonds. The very low π-acceptor capacity of the chlorine, water, and acetonitrile ligands could explain why the above-mentioned six-coordinate alkenyl−azavinylidene complexes evolve into imine−vinylidene derivatives instead of Δ^2-1,2-azaosmetine compounds. In addition, it should be noted that the formation of **3** and **4** indicates that the cycloaddition reactions between metal−nitrogen and carbon−carbon double bonds can occur not only with early transition metals but also with late transition metals, when the latter coordinate π-acidic ligands.

Complexes **3** and **4** were characterized by MS, elemental analysis, IR, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Complex **3** was further characterized by an X-ray crystallographic study. A view of the molecular geometry of the cation of the salt is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with the two phosphorus atoms of the phosphine ligands occupying opposite positions [P(1)−Os−P(2)] = 167.17(8)°]. The perpendicular plane is formed by the chlorine and carbonyl ligands mutually cis disposed [Cl−Os−C(30) = 102.7(3)°], the heterometallacycle with the nitrogen atom trans disposed to the carbonyl group [N−Os−C(30) = 160.4(4)°], and the C(4) atom trans disposed to the chlorine [Cl−Os−C(4) = 162.3(3)°].

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[OsCl\{=HCH(Ph)N=CMe_2\}(CO)(P^iPr_3)_2][CF_3SO_3]$ (3)

Os−Cl	2.500(2)	Os−P(2)	2.487(2)
Os−C(4)	1.890(10)	N−C(1)	1.301(11)
Os−C(30)	1.854(10)	N−C(5)	1.497(10)
Os−N	2.260(7)	C(4)−C(5)	1.520(13)
Os−P(1)	2.496(2)	C(5)−C(6)	1.542(12)
P(1)−Os−P(2)	167.17(8)	Cl−Os−C(30)	102.7(3)
P(1)−Os−N	92.9(2)	Cl−Os−C(4)	162.3(3)
P(1)−Os−Cl	84.86(17)	C(30)−Os−C(4)	94.8(4)
P(1)−Os−C(30)	88.1(3)	Os−N−C(1)	145.4(6)
P(1)−Os−C(4)	93.84(18)	Os−N−C(5)	90.8(5)
N−Os−Cl	96.84(18)	N−C(5)−C(4)	97.6(7)
N−Os−C(30)	160.4(4)	Os−C(4)−C(5)	105.7(6)
N−Os−C(4)	65.6(3)	C(2)−C(1)−C(3)	115.8(8)

The four atoms Os, C(4), C(5), and N forming the heterometallacycle and the iminic atoms C(1), C(2), and C(3) are almost planar. The deviations from the plane are −0.150 Å (Os), 0.03 Å [C(4)], 0.09 Å [C(5)], 0.10 Å [N], −0.16 Å [C(1)], −0.16 Å [C(2)], and 0.08 Å [C(3)]. In agreement with the distances and angles found in osmium−carbene compounds,[14] the Os−C(4) bond length and the Os−C(4)−C(5) angle are 1.890(10) Å and 105.7(6)°, respectively. The C(4)−C(5) distance [1.520(13) Å] agrees well with the average of the $C(sp_2)-C(sp_3)$ single bond distances [1.48(3) Å],[15] whereas the N−C(5) bond length [1.497(10) Å] supports the C−N single bond formulation and is about 0.2 Å longer than the N−C(1) distance [1.301(11) Å]. The latter is similar to the C−N double bond distances observed in imine transition metal complexes,[16] azavinylidene compounds,[17] organic azaallenium cations,[18] and 2-azaallenyl complexes.[19] The Os−N bond length [2.260(7) Å], which is about 0.2 Å longer than those found in the imine complexes

(14) (a) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939. (b) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1988**, *358*, 411. (c) Clark G. R.; Hodgson, D. J.; Ng, M. M. P.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Chem Soc., Chem. Commun.* **1988**, 1552. (d) Werner, H.; Weber, B.; Nürnberg, O.; Wolf, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1025. (e) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935. (f) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184.

(15) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(16) See for example: (a) Faller, J. W.; Ma, Y.; Smart, C. J.; DiVerdi, M. J. *J. Organomet. Chem.* **1991**, *420*, 237. (b) Knight, D. A.; Dewey, M. A.; Stark, G. A.; Bennett, B. K.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4523. (c) Yeh, W.-Y.; Ting, C.-S.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 1417. (d) Gunnoe, T. B.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 6916.

(17) See for example: (a) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148. (b) Daniel, T.; Knaup, W.; Dziallas, M.; Werner, H. *Chem. Ber.* **1993**, *126*, 1981. (c) Werner, H.; Daniel, T.; Braun, T.; Nürnberg, O. *J. Organomet. Chem.* **1994**, *480*, 145. (d) Powell, K. R.; Pérez, P. J.; Luan, L.; Feng, S. G.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **1994**, *13*, 1851. (e) Esteruelas, M. A.; Lahoz, F. J.; Oliván, M.; Oñate, E.; Oro L. A. *J. Organometallics* **1994**, *13*, 3315.

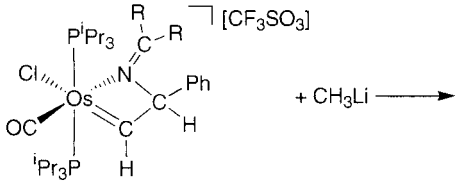
(18) (a) Jochims, J. C.; Abu-El-Halawa, R.; Jibril, I.; Huttner, G. *Chem. Ber.* **1984**, *117*, 1900. (b) Al-Talib, M.; Jochims, J. C. *Chem. Ber.* **1984**, *117*, 3222. (c) Al-Talib, M.; Jibril, I.; Würthwein, E.-U.; Jochims, J. C.; Huttner, G. *Chem. Ber.* **1984**, *117*, 3365. (d) Kupfer, R.; Würthwein, E.-U.; Nagel, M.; Allmann, R. *Chem. Ber.* **1985**, *118*, 643. (e) Al-Talib, M.; Jibril, I.; Huttner, G.; Jochims, J. C. *Chem. Ber.* **1985**, *118*, 1876. (f) Al-Talib, M.; Jochims, J. C.; Zsolnai, L.; Huttner, G. *Chem. Ber.* **1985**, *118*, 1887. (g) Würthwein, E.-U.; Kupfer, R.; Allmann, R.; Nagel, M. *Chem. Ber.* **1985**, *118*, 3632. (h) Krestel, M.; Kupfer, R.; Würthwein, E.-U. *Chem. Ber.* **1987**, *120*, 1271.

(19) (a) Seitz, F.; Fischer, H.; Riede, J. *J. Organomet. Chem.* **1985**, *287*, 87. (b) Aumann, R.; Althaus, S.; Krüger, S.; Betz, P. *Chem. Ber.* **1989**, *122*, 357. (c) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423.

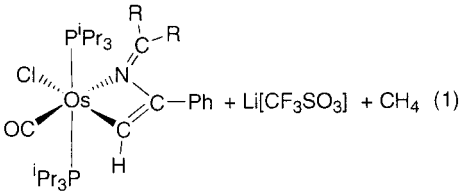
$OsCl_2(=C=CHPh)(NH=CMe_2)(P^iPr_3)_2$ [2.072(7) Å] and $[OsCl(=C=CHPh)(NH=CMe_2)(H_2O)(P^iPr_3)_2][CF_3SO_3]$ [2.067(5) Å],[13] reveals the tension within the four-membered ring. The angles within the heterometallacycle are between 65.6(3)° [N−Os−C(4)] and 105.7(6)° [Os−C(4)−C(5)].

In agreement with the presence of a carbonyl ligand in **3** and **4**, the IR spectra of these compounds show a ν(CO) band at 1958 cm^{-1} in both complexes. In addition, the spectra contain a ν(C=N) absorption at 1648 (**3**) and 1625 (**4**) cm^{-1}, along with the characteristic streching bands of the free $[CF_3SO_3]^-$ anion[20] at about 1264, 1226, 1144, and 1036 cm^{-1}. In the ^1H NMR spectra of both compounds, the most noticeable resonances are two singlets at 15.84 and 5.49 (**3**) and 16.57 and 5.77 (**4**) ppm, corresponding to the H_α and H_β hydrogen atoms of the azaosmetine unit. In the $^{13}C\{^1H\}$ NMR spectra, the resonances due to the C(sp^2) atoms of the heterometallacycle appear at about 273 ppm, as triplets with C−P coupling constants of about 7 Hz, whereas the resonances due to C(sp^3) atoms of the heterometallacycle are observed as singlets at about 100 ppm. The $^{31}P\{^1H\}$ NMR spectra show AB spin systems at 26.0 and 18.8 (**3**) and 32.9 and 23.7 (**4**) ppm, with P−P coupling constants of about 195 Hz.

2. Release of 2-Aza-1,3-butadienes from the Osmium Atom. The Δ^2-1,2-azaosmetine complexes **3** and **4** can be converted into the Δ^3-1,2-azaosmetine derivatives $Os\{CH=C(Ph)N=CR_2\}Cl(CO)(P^iPr_3)_2$ [CR_2 = CMe_2 (**5**), $C(CH_2)_4CH_2$ (**6**)] by deprotonation of the C(sp^3) atoms of the azaosmetine units, with equimolecular amounts of MeLi in tetrahydrofuran as solvent (eq 1).



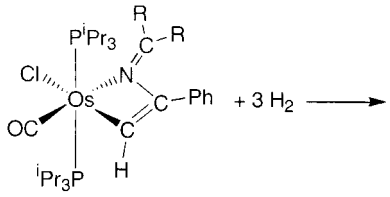
CR_2 = CMe_2 (**3**), $C(CH_2)_4CH_2$ (**4**)



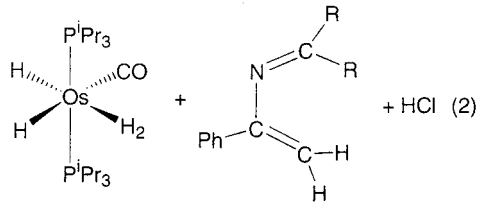
CR_2 = CMe_2 (**5**), $C(CH_2)_4CH_2$ (**6**)

Complexes **5** and **6** were isolated as yellow solids in about 80% yield. In the IR spectra in KBr of these compounds, the most noticeable feature is the absence of any band corresponding to the $[CF_3SO_3]^-$ anion. The ν(CO) and ν(C=N) absorptions appear at 1887 and 1620 (**5**) and 1889 and 1607 (**6**) cm^{-1}, respectively. In the ^1H NMR spectra the resonances due to the Os−CH protons of the heterometallacycles are observed as singlets at 8.80 (**5**) and 9.06 (**6**) ppm. In the $^{13}C\{^1H\}$ NMR spectra the resonances due to the Os−C carbon atoms appear at 149.8 ppm (**5** and **6**), as triplets with C−P coupling constants of about 8 Hz, whereas the =*C*Ph resonances are observed at about 146 ppm, also as triplets but with C−P coupling constants of about 3 Hz. The $^{31}P\{^1H\}$ NMR spectra contain singlets at about 9 ppm.

The azaosmetine units of **5** and **6** are rings analogous to the azametallacycle−butenes generated by alkyne-cycloaddition reactions on early-transition-metal−nitrogen multiple bonds, and as the latter, they are key structures during the amination of alkynes. Thus, complexes **5** and **6** react with molecular hydrogen to give the 2-aza-1,3-butadienes $CH_2=C(Ph)N=CR_2$ [CR_2 = CMe_2 (**7**), $C(CH_2)_4CH_2$ (**8**)] and the well-known dihydride−dihydrogen complex $OsH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (eq 2).[21]



CR_2 = CMe_2 (**5**), $C(CH_2)_4CH_2$ (**6**)



CR_2 = CMe_2 (**7**), $C(CH_2)_4CH_2$ (**8**)

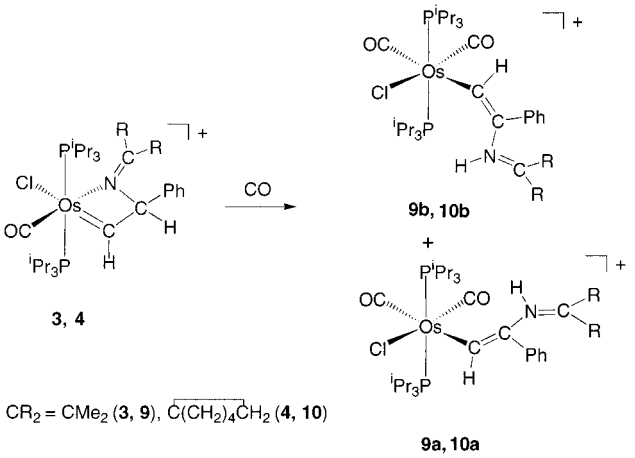
The reactions collected in Schemes 1 and 2 and eqs 1 and 2 constitute the pathway for the stoichiometric amination of phenylacetylene with acetone oxime and cyclohexanone oxime, in the presence of the dihydride−dichloro complex $OsH_2Cl_2(P^iPr_3)_2$. It should be noted that the key step of the process is the formation of the Δ^2-1,2-azaosmetine intermediates **3** and **4**, which appears to occur by [2+2] cycloadditions similar to those proposed by the catalytic hydroamination of alkynes with imido−zirconium complexes.[5c,e,g,i] Because the cycloaddition in the stoichiometric process is intramolecular instead of intermolecular, as in the catalytic reaction, the deprotonation of **3** and **4** is necessary to generate the Δ^3-1,2-azaosmetine intermediates **5** and **6**, which are analogues to the azametallacycles of zirconium formed during the catalytic reactions. The formation of **5** and **6** by deprotonation of **3** and **4**, respectively, is a novel method to form this type of compounds, which, as well as **3** and **4**, were unknown in the chemistry of late transition metals.

3. Δ^2-1,2-Azaosmetine Cations as Intermediates in the Formation of $[Os\{(Z)\text{-}CH=C(Ph)NH=CR_2\}Cl(CO)_2(P^iPr_3)_2]^+$. If the treatment of **1** and **2** with carbon monoxide is prolonged by more than 1 h, in addition to **3** and **4**, the formation of $[Os\{(Z)\text{-}CH=C(Ph)NH=CR_2\}Cl(CO)_2(P^iPr_3)_2]^+$ [CR_2 = CMe_2 (**9**), $C(CH_2)_4CH_2$ (**10**)] is observed. Complexes **9** and **10** are the result of

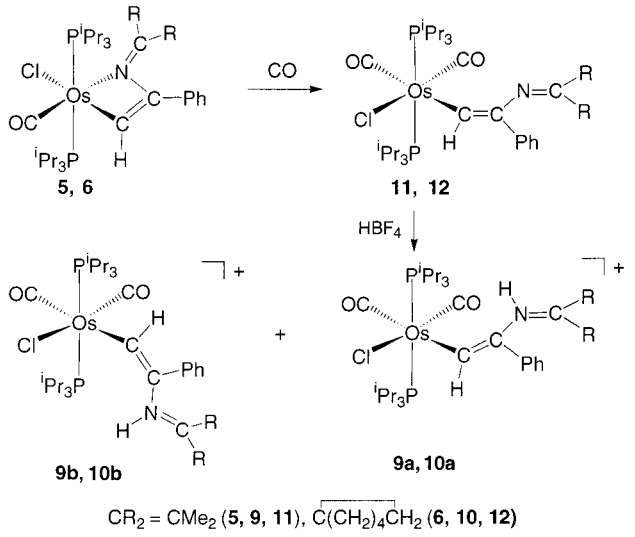
(20) Lawrence, G. A. *Chem. Rev.* **1986**, *86*, 17.

(21) (a) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11. (b) Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 663.

Scheme 3



Scheme 4



the carbonylation of **3** and **4** and the 1,2-hydrogen migration from the *C*HPh carbon atoms to the nitrogen atoms (Scheme 3).

The BF_4 salts of **9** and **10** can be obtained as pure microcrystalline solids, starting from **5** and **6**, according to Scheme 4. Under carbon monoxide atmosphere the heterometallacycles of **5** and **6** are opened, and the coordination of a carbonyl ligand affords the cis-dicarbonyl derivatives Os{(*Z*)-CH=C(Ph)N=CR_2}Cl$(CO)_2$-$(P^iPr_3)_2$ [CR_2 = CMe_2 (**11**), $C(CH_2)_4CH_2$ (**12**)], which react with HBF_4·OEt_2 to give **9** and **10**. The latter are the result of the protonation of the nitrogen atom of the unsaturated η^1-carbon ligands of **11** and **12**.

Complexes **11** and **12** were isolated as yellow solids in about 80% yield. The IR spectra of these compounds in KBr show two ν(CO) bands between 2000 and 1920 cm^{-1}. The mutually cis disposition of the carbonyl ligands is strongly supported by the intensity ratios of the ν(CO) bands, which suggest angles between the carbonyl ligands of about 90°.[22] In the ^1H NMR spectra, the most noticeable resonance is that due to the Os−CH proton, which appears at 7.90 ppm as a triplet with a H−P coupling constant of 2.2 Hz in both compounds. In the $^{13}C\{^1H\}$ NMR spectra, the resonances corresponding to the Os−CH and *C*PhN carbon atoms are observed at 139.5 and 150.3 (**11**) and 140.0 and 149.8 (**12**) ppm, as triplets with C−P coupling constants of about 12 (C_α) and 4 (C_β) Hz. The $^{31}P\{^1H\}$ NMR spectra contain singlets at about 7 ppm.

(22) [*I*(higher ν)]/[*I*(lower ν)] = $\tan^2(\theta/2)$

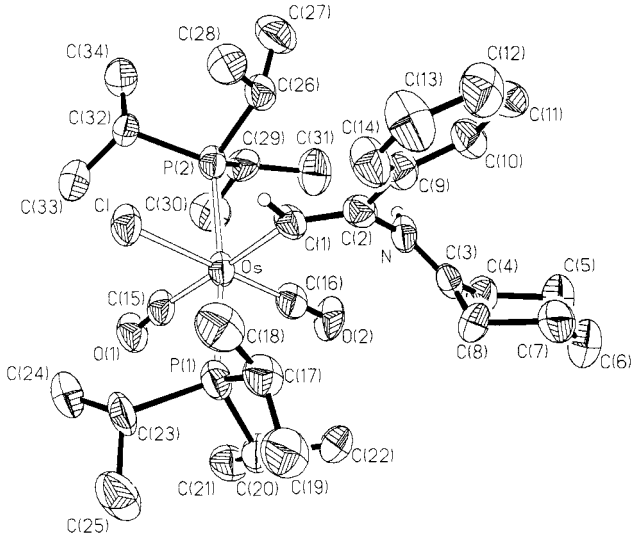


Figure 2. Molecular diagram for [Os{(*Z*)-CH=C(Ph)NH=$C(CH_2)_4CH_2$}Cl$(CO)_2(PiPr_3)_2]^+$ (**10**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex [Os{(*Z*)-CH=C(Ph)NH=$C(CH_2)_4CH_2$}Cl$(CO)_2(P^iPr_3)_2]BF_4$ (10)

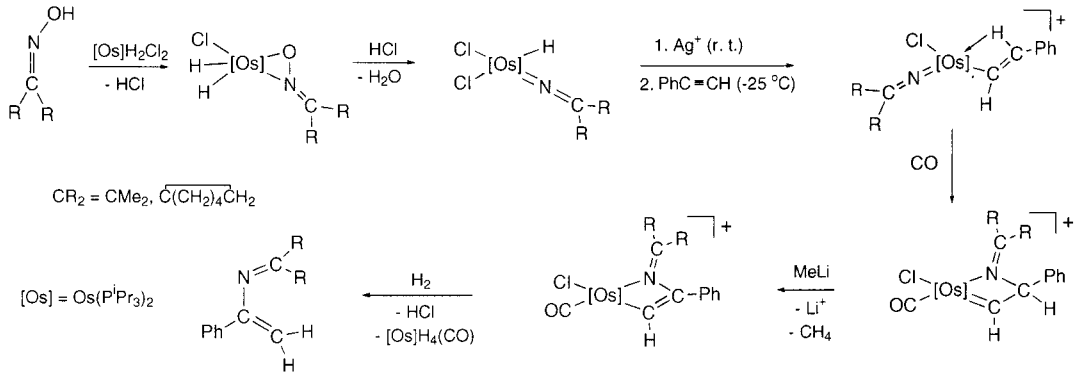
Os−C(1)	2.115(9)	C(15)−O(1)	1.152(10)
Os−Cl	2.450(2)	C(16)−O(2)	1.113(10)
Os−C(15)	1.938(10)	C(1)−C(2)	1.340(12)
Os−C(16)	1.901(11)	C(2)−C(9)	1.494(12)
Os−P(1)	2.458(3)	C(2)−N	1.482(11)
Os−P(2)	2.445(3)	C(3)−N	1.260(12)
		C(3)−C(4)	1.525(14)
P(1)−Os−P(2)	172.16(8)	C(1)−Os−C(16)	93.9(4)
P(1)−Os−C(1)	90.8(3)	C(15)−Os−C(16)	87.4(4)
P(1)−Os−Cl	85.96(10)	Os−C(1)−C(2)	140.4(7)
P(1)−Os−C(15)	89.8(3)	C(1)−C(2)−N	114.4(8)
P(1)−Os−C(16)	93.3(3)	C(9)−C(2)−N	113.0(8)
C(1)−Os−Cl	84.5(3)	C(2)−N−C(3)	126.2(10)
C(1)−Os−C(15)	178.5(4)	N−C(3)−C(4)	117.2(11)

Complexes **9** and **10** were isolated as white solids in 86% (**9**) and 83% (**10**) yield and were characterized by MS, elemental analysis, IR, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Complex **10** was further characterized by an X-ray crystallographic study. Figure 2 shows a view of the molecular geometry of this complex, whereas Table 2 collects selected bond distances and angles.

The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with the two phosphorus atoms of the phosphine ligands occupying opposite positions [P(1)−Os−P(2) = 172.16(8)°]. The perpendicular plane is formed by the carbonyl ligands mutually cis disposed [C(15)−Os−C(16) = 87.4(4)°] and the chlorine and the η^1-carbon ligand also cis disposed [C(1)−Os−Cl = 84.5(3)°].

The unsaturated η^1-carbon ligand shows a *Z* stereochemistry at the C(1)−C(2) double bond. The Os−C(1) bond length [2.115(9) Å] compares well with the Os−C(sp^2) single bond distances found in the complexes

Scheme 5



Os{(*E*)-CH=CHPh}Cl(CO)(P^iPr_3)$_2$ [1.99(1) Å],[23] [Os{CH=C(I)C(O)OCH$_3$}(η^6-C$_6$H$_6$)(P^iPr_3)]$^+$ [2.02(1) Å],[24] Os{CH=CHC(O)OCH$_3$}(C$_2$CO$_2$CH$_3$)(CO)(P^iPr_3)$_2$ [2.103(4) Å],[10a] [Os{C[C(O)OCH$_3$]=CH$_2$}(=C=C=CPh$_2$}(CO)(P^iPr_3)$_2$]$^+$ [2.146(6) Å],[10e] and Os{C(CH$_2$Ph)=CHC$_6$H$_4$}(CO)$_2$(PiPr$_3$)$_2$ [2.180(4) Å].[10d] The C(1)−C(2) distance [1.340(12) Å] is similar to those found in the above-mentioned compounds and agrees well with the average carbon−carbon double bond distances [1.32(1) Å].[15] The C(2)−N [1.482(11) Å] and N−C(3) [1.269(12) Å] distances are statistically identical with the related parameters of **3**.

The separations between the osmium atom and the carbonyl ligands [1.938(10) and 1.901(11) Å], as well as both C−O distances [1.152(10) and 1.113(10) Å], are also statistically identical. This suggests that the trans influence of the chlorine and azoniabutadienyl ligands is similar.

The IR spectra of **9** and **10** in KBr are consistent with the structure shown in Figure 2. In agreement with the presence of a hydrogen atom bonded to the nitrogen atom of the unsaturated η^1-carbon ligands, they show ν(N−H) bands at about 3310 cm^{-1}. Furthermore, in accordance with the mutually cis disposition of the carbonyl ligands, the spectra contain two ν(CO) bands between 2020 and 1940 cm^{-1}. The salt nature of these compounds is supported by very strong bands at about 1050 cm^{-1}, corresponding to the [BF$_4$]$^-$ anion with T_d symmetry.

In solution, complexes **9** and **10** exist as mixtures of the isomers **a** and **b** shown in Schemes 3 and 4. We assume that the major isomers are **9a** and **10a** (66% and 60%, respectively, in acetone-d_6). Isomer **10a** is the one found in the solid state by X-ray diffraction. The existence of these isomers can be explained by hindered rotation around the Os−CH axis. Using a molecular model, it can be easily established that this rotation is highly impeded by the steric demand of the isopropyl groups of the phosphine ligands, while the rotation around the PhC−N axis is free.

In the ^{1}H NMR spectra, each isomer gives rise to a NH resonance between 14 and 11 ppm and an Os−CH resonance between 9 and 8 ppm. In the ^{13}C{^{1}H} NMR spectra, the Os−CH resonances are observed between 158 and 145 ppm, as triplets with C−P coupling constants of about 10 Hz, whereas the =CPh resonances appear between 148 and 139 ppm also as triplets but with C−P coupling constants of about 4 Hz. The ^{31}P{^{1}H} NMR spectra show a singlet for each isomer at about 12 (**9**) and 6 (**10**) ppm.

Concluding Remarks

We have previously shown that the sequential introduction of oximes, such as acetone oxime and cyclohexanone oxime, and phenylacetylene into the osmium atom of OsH$_2$Cl$_2$(P^iPr_3)$_2$ affords the azavinylidene−styryl complexes [Os{(*E*)-CH=CHPh}Cl(=N=CR$_2$)(P^iPr_3)$_2$]$^+$ [CR$_2$ = CMe$_2$, C(CH$_2$)$_4$CH$_2$].[11−13] This study reveals that the coordination of carbon monoxide to the osmium atom of these compounds produces the carbon−nitrogen coupling between the styryl and azavinylidene ligands, to give the corresponding Δ^2-1,2-azaosmetine derivatives [OsCl{=CHCH(Ph)N=CR$_2$}(CO)(P^iPr_3)$_2$]$^+$. This coupling is the key step to form 2-aza-1,3-butadienes by means of the stoichiometric imination of phenylacetylene with the above-mentioned oximes, in the presence of OsH$_2$Cl$_2$(P^iPr_3)$_2$. Thus we also report that the deprotonation of the Δ^2-1,2-azaosmetine complexes with MeLi affords the Δ^3-1,2-azaosmetine compounds Os{CH=C(Ph)N=CR$_2$}Cl(CO)(P^iPr_3)$_2$, which react with molecular hydrogen to give CH$_2$=C(Ph)N=CR$_2$ [CR$_2$ = CMe$_2$, C(CH$_2$)$_4$CH$_2$] and OsH$_2$(η^2-H$_2$)(CO)(P^iPr_3)$_2$.

The Δ^2-1,2-azaosmetine complexes are intermediate species not only to obtain Δ^3-1,2-azaosmetine derivatives but also to form η^1-azoniabutadienyl compounds. Thus, the carbonylation of [OsCl{=CHCH(Ph)N=CR$_2$}(CO)(P^iPr_3)$_2$]$^+$ produces the ring opening of the Δ^2-1,2-azaosmetine units and the 1,2-hydrogen shift from the *C*HPh carbon atom to the nitrogen, to give [Os{(*Z*)-CH=C(Ph)NH=CR$_2$}Cl(CO)$_2$(P^iPr_3)$_2$]$^+$. These compounds are also obtained starting from the Δ^3-1,2-azaosmetine complexes by initial carbonylation and subsequent protonation of the resulting η^1-azabutadienyl derivatives Os{(*Z*)-CH=C(Ph)N=CR$_2$}Cl(CO)$_2$(P^iPr_3)$_2$.

In conclusion, 2-aza-1,3-butadienes can be obtained by stoichiometric imination of phenylacetylene with oximes in the presence of OsH$_2$Cl$_2$(P^iPr_3)$_2$ (Scheme 5).

(23) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2296.
(24) Werner, H.; Weinand, R.; Otto, H. *J. Organomet. Chem.* **1986**, *307*, 49.

The process involves Δ^2- and Δ^3-1,2-azaosmetine intermediates, two novel types of heterometallacyclobutene derivatives, which were unknown in the chemistry of the late transition metals.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials [Os{(*E*)-CH=CHPh}Cl(=N=C$(CH_3)_2$)-($P^iPr_3)_2$][CF_3SO_3] (**1**) [Os{(*E*)-CH=CHPh}Cl{=N=C$(CH_2)_4$-CH_2}($P^iPr_3)^2$][CF_3SO_3] (**2**) were prepared by the published method.[13] ^{1}H NMR spectra were recorded at 300 MHz, and chemical shifts are expressed in ppm downfield from Me_4Si. $^{13}C\{^1H\}$ NMR spectra were recorded at 75.4 MHz, and chemical shifts are expressed in ppm downfield from Me_4Si. $^{31}P\{^1H\}$NMR spectra were recorded at 121.4 MHz, and chemical shifts are expressed in ppm downfield from 85% H_3PO_4. Coupling constants, *J* and *N*, are given in hertz.

Preparation of [OsCl{=CHCH(Ph)N=C$(CH_3)_2$}(CO)-($P^iPr_3)_2$][CF_3SO_3] (3). A green solution of **1** (100 mg, 0.117 mmol) in 5 mL of a mixture of dichloromethane and diethyl ether (1:1) was stirred for 1 h under carbon monoxide atmosphere. The resulting yellow suspension was washed with diethyl ether (2 × 2 mL) and dried in vacuo. Yield: 85 mg (82%). Anal. Calcd for $C_{31}H_{55}NSClF_3O_4OsP_2$: C, 42.19; H, 6.28; N, 1.58; S, 3.62. Found: C, 41.96; H, 6.17; N, 1.65; S 3.35. IR (KBr, cm^{-1}): ν(CO) 1958 (s); ν(C=N) 1648 (m); $\nu_a(SO_3)$ 1264 (s); $\nu_s(CF_3)$ 1226 (s); $\nu_a(CF_3)$ 1144 (s); $\nu_s(SO_3)$ 1036 (s); $\delta_a(SO_3)$ 637 (s). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 15.84 (s, 1H, Os=CH); 7.33 (t, J_{H-H} = 7.5, 2H, $H_{meta-Ph}$); 7.20 (t, J_{H-H} = 7.5, 1H, $H_{para-Ph}$); 7.09 (d, J_{H-H} = 7.5, 2H, $H_{ortho-Ph}$); 5.49 (s, 1H, PhC*H*−N); 2.76 and 2.19 (both s, 6H, {CH_3}$_2$C=N); 2.62 (m, 6H, PCH); 1.4−1.1 (m, 30H, PCHC*H*$_3$); 0.8−0.6 (m, 6H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR plus DEPT (CD_2Cl_2, 20 °C): δ 271.7 (t, J_{C-P} = 7.2, Os=C); 190.7 (s, C=N); 179.6 (t, J_{C-P} = 10.4, CO); 131.7 (s, $C_{ipso-Ph}$); 129.0, 128.2, and 124.8 (all s, C_{Ph}); 120.5 (q, J_{C-F} = 320.0, CF_3); 100.7 (s, Os=CH−*C*HPhN); 27.3 and 25.6 (both s, {*C*H$_3$}$_2$C=N); 24.6−23.4 (m, PCH); 19.3−16.9 (all s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ AB spin system (δ_A = 26.0, δ_B = 18.8, J_{P-P} = 194.0). MS (FAB$^+$): *m*/*z* 734 (M^+).

Preparation of [OsCl{=CHCH(Ph)N=C$(CH_2)_4CH_2$}-(CO)($P^iPr_3)_2$][CF_3SO_3] (4). This complex was prepared as described for **3** starting from 100 mg (0.112 mmol) of **2**. Yield: 84 mg (81%). Anal. Calcd for $C_{34}H_{59}NSClF_3O_4OsP_2$: C, 44.27; H, 6.45; N, 1.52; S, 3.48. Found: C, 44.64; H, 6.64; N, 1.72; S, 3.76. IR (KBr, cm^{-1}): ν(CO) 1958 (s); ν(C=N) 1625 (m); $\nu_a(SO_3)$ 1262 (s); $\nu_s(CF_3)$ 1223 (s); $\nu_a(CF_3)$ 1144 (s); $\nu_s(SO_3)$ 1033 (s); $\delta_a(SO_3)$ 637 (s). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 16.57 (s, 1H, Os=CH); 7.48 (t, J_{H-H} = 7.5, 2H, $H_{meta-Ph}$); 7.38 (d, J_{H-H} = 7.2, 2H, $H_{ortho-Ph}$); 7.35 (t, J_{H-H} = 7.5, 1H, $H_{para-Ph}$); 5.77 (s, 1H, PhC*H*-N); 3.6−3.5 (m, 4H, {CH_2}$_2$C=N); 2.82 (m, 6H, PCH); 1.8−1.2 (m, 36H, PCHC*H*$_3$ and Cy); 0.9−0.7 (m, 6H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR plus APT (CD_2Cl_2, 20 °C): δ 275.5 (t, J_{C-P} = 6.5, Os=C); 194.1 (s, C=N); 179.2 (t, J_{C-P} = 10.5, CO); 132.2 (s, $C_{ipso-Ph}$); 127.3, 126.9, and 124.0 (all s, C_{Ph}); 120.5 (q, J_{C-F} = 320.0, CF_3); 99.0 (s, Os=CH−*C*HPhN); 34.6 and 33.7 (both s, {*C*H$_2$}$_2$C=N); 25.5, 25.4, and 24.0 (all s, Cy); 26.1−22.6 (m, PCH); 18.3−16.7 (all s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ AB spin system (δ_A = 32.9, δ_B = 23.7, J_{P-P} = 196.0). MS (FAB$^+$): *m*/*z* 774 (M^+).

Preparation of Os{CH=C(Ph)N=C$(CH_3)_2$}Cl(CO)($P^iPr_3)_2$ (5). A yellow suspension of **3** (120 mg, 0.136 mmol) in 10 mL of THF was treated with 85 μL of a solution 1.6 M of methyllithium in diethyl ether (0.136 mmol). A solution was obtained immediately, and after 5 min the solvent was evaporated to dryness. Then 10 mL of toluene was added to eliminate by filtration the $LiCF_3SO_3$ formed. After the solution was concentrated to dryness, addition of methanol led to the precipitation of a yellow solid, which was washed with methanol (2 × 2 mL) and dried in vacuo. Yield: 80 mg (80%). Anal. Calcd for $C_{30}H_{54}NClOOsP_2$: C, 49.20; H, 7.43; N, 1.91. Found: C, 48.90; H, 7.47; N, 1.82. IR (KBr, cm^{-1}): ν(CO) 1887 (s); ν(C=N) 1620 (m). ^{1}H NMR (C_6D_6, 20 °C): δ 8.80 (s, 1H, Os−CH); 7.11 (t, J_{H-H} = 7.5, 2H, $H_{meta-Ph}$); 6.95 (t, J_{H-H} = 6.9, 1H, $H_{para-Ph}$); 6.90 (d, J_{H-H} = 7.8, 2H, $H_{ortho-Ph}$); 2.66 (m, 6H, PCH); 2.42 and 1.30 (both s, 6H, {CH_3}$_2$C=N); 1.46 and 1.13 (both dvt, J_{H-H} = 6.9, *N* = 13.5, 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR plus DEPT (C_6D_6, 20 °C): δ 187.2 (t, J_{C-P} = 11.5, CO); 164.3 (s, C=N); 149.8 (t, J_{C-P} = 8.3, Os−*C*H=CPhN); 145.7 (d, J_{C-P} = 2.5, Os−CH=*C*PhN); 141.9 (s, $C_{ipso-Ph}$); 128.2, 125.5, and 125.0 (all s, C_{Ph}); 29.1 and 27.7 (both s, {*C*H$_3$}$_2$C=N); 24.3 (vt, *N* = 23.1, PCH); 20.7 and 19.7 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 9.3 (s). MS (FAB$^+$): *m*/*z* 733 (M^+).

Preparation of Os{CH=C(Ph)N=C$(CH_2)_4CH_2$}Cl(CO)-($P^iPr_3)_2$ (6). This complex was prepared as described for **5** starting from 200 mg (0.217 mmol) of **4** and 136 μL of a 1.6 M solution of methyllithium in diethyl ether (0.217 mmol). Yield: 130 mg (77%). Anal. Calcd for $C_{33}H_{58}NClOOsP_2$: C, 51.31; H, 7.57; N, 1.81. Found: C, 51.24; H, 7.64; N, 1.72. IR (KBr, cm^{-1}): ν(CO) 1889 (s); ν(C=N) 1607 (m). ^{1}H NMR (C_6D_6, 20 °C): δ 9.06 (s, 1H, Os−CH); 7.12 (t, J_{H-H} = 7.8, 2H, $H_{meta-Ph}$); 6.96 (d, J_{H-H} = 7.2, 2H, $H_{ortho-Ph}$); 6.71 (t, J_{H-H} = 7.5, 1H, $H_{para-Ph}$); 3.18 (m, 2H, {CH_2}C=N); 2.82 (m, 6H, PCH); 1.87 (m, 2H, {CH_2}C=N); 1.7−1.4 (m, 6H, Cy); 1.49 and 1.18 (both dvt, J_{H-H} = 6.9, *N* = 13.5, 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR plus DEPT (C_6D_6, 20 °C): δ 187.0 (t, J_{C-P} = 11.0, CO); 170.3 (s, C=N); 149.8 (t, J_{C-P} = 7.8, Os-*C*H=CPhN); 145.9 (t, J_{C-P} = 4.1, Os−CH=*C*PhN); 142.3 (s, $C_{ipso-Ph}$); 128.5, 124.9, and 124.7 (all s, C_{Ph}); 37.4, 36.6, 27.0, and 25.5 (all s, Cy); 24.9 (vt, *N* = 23.0, PCH); 20.7 and 19.8 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 9.1 (s). MS (FAB$^+$): *m*/*z* 773 (M^+) and 738 (M^+ − Cl).

Preparation of H_2C=C(Ph)N=C$(CH_3)_2$ (7). A slow stream of H_2 was bubbled through a yellow solution of **5** (40 mg, 0.054 mmol) in 0.5 mL of benzene-d_6 in a NMR tube for 5 min, and then the NMR tube was sealed under H_2 atmosphere. After 5 h the quantitative formation of $OsH_2(\eta^2$-$H_2)(CO)(P^iPr_3)_2$ and **7** was determined by ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The solution was transferred to a Schlenk-tube and was concentrated to dryness. Compound **7** was extracted with pentane (2 × 2 mL), and the solvent was removed to afford an orange oil. ^{1}H NMR (C_6D_6, 20 °C): δ 7.61 (d, J_{H-H} = 7.8, 2H, $H_{ortho-Ph}$); 7.2−7.1 (m, 3H, H_{Ph}); 4.99 and 4.33 (both s, 2H, =CH_2); 1.87 and 1.52 (both s, 6H, {CH_3}$_2$C=N). $^{13}C\{^1H\}$ NMR plus DEPT (C_6D_6, 20 °C): δ 170.7 (s, C=N); 137.7 (s, $C_{ipso-Ph}$); 127.7 (s, =*C*PhN); 130.0, 129.3, and 125.8 (all s, C_{Ph}); 94.0 (s, =CH_2); 23.8 and 20.2 (both s, {*C*H$_3$}$_2$C=N). MS (EI): 159 (M^+), 103 (M^+ − N=C$(CH_3)_2$.

Preparation of H_2C=CPhN=C$(CH_2)_4CH_2$ (8). This compound was prepared as described for **7** starting from **6** (40 mg, 0.051 mmol). ^{1}H NMR (C_6D_6, 20 °C): δ 7.62 (d, J_{H-H} = 7.8, 2H, $H_{ortho-Ph}$); 7.2−7.1 (m, 3H, H_{Ph}); 4.98 and 4.36 (both s, 2H, =CH_2); 2.5−1.9 (m, 10H, Cy). $^{13}C\{^1H\}$ NMR plus DEPT (C_6D_6, 20 °C): δ 172.8 (s, C=N); 138.2 (s, $C_{ipso-Ph}$); 128.2 (s, =*C*PhN); 129.4, 128.6, and 125.5 (all s, C_{Ph}); 93.7 (s, =CH_2); 39.1, 30.6, 27.8, 27.6, and 25.9 (all s, Cy). MS (EI): 199 (M^+), 103 (M^+ − N=C$(CH_2)_4CH_2$).

Preparation of [Os{(*Z*)-CH=C(Ph)NH=C$(CH_3)_2$}Cl-(CO)$_2$($P^iPr_3)_2$][BF_4] (9). A pale yellow solution of **11** (125 mg, 0.164 mmol) in diethyl ether was treated with tetrafluoroboric acid (22 μL, 0.165 mmol, 54% in diethyl ether). After 15 min a white precipitate was formed, which was washed with diethyl ether (2 × 3 mL) and dried in vacuo. The resulting white microcrystalline solid was found to be (NMR techniques) a mixture of two rotamers (ratio **a**:**b** = 2:1). Yield: 120 mg (86%). Anal. Calcd for $C_{31}H_{55}NBClF_4O_2OsP_2$: C, 43.90; H, 6.54; N,

Table 3. Crystal Data and Data Collection and Refinement for Complexes [OsCl{=CHCH(Ph)N=CMe$_2$}(CO)(P^{i}Pr$_3$)$_2$][CF$_3$SO$_3$] (3) and [Os{(Z)-CH=C(Ph)NH=C(CH$_2$)$_4$CH$_2$}Cl(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (10)

	3	10
formula	$C_{31}H_{55}ClF_3NO_4OsP_2S$	$C_{34}H_{59}BClF_4NO_2OsP\cdot 0.9CH_2Cl_2 0.4THF\ 0.25C_4H_{10}O$
mol wt	882.41	729.78
color and habit	irregular block	irregular block
space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$
a, Å	13.748(2)	10.887(3)
b, Å	16.540(3)	31.389(8)
c, Å	17.438(12)	14.117(4)
β, deg	100.795(6)	97.210(7)
V, Å^3	3895.1(11)	4806(2)
Z	4	4
D_{calc}, g cm^{-3}	1.505	1.391
Data Collection and Refinement		
diffractometer	Bruker-Siemens P4	Bruker-Siemens CCD
λ(Mo Kα), Å	0.71073	
monochromator	graphite oriented	
μ, mm^{-1}	3.525	2.922
scan type	$\omega/2\theta$	ω scans at different φ values
2θ range, deg	$5 \le 2\theta \le 50$	$5 \le 2\theta \le 55$
temp, K	296.0(2)	173.0(2)
no. of data collect	7644 (h: −16, 1; k: −19, 1; l: −20, 20)	31 470 (h: −14, 10; k: −40, 40; l: −11, 18)
no. of unique data	6803 (merging R factor 0.0374)	10 932 (merging R factor 0.1345)
no. of params refined	439	501
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0645	0.0645
wR_2[b] [all data]	0.1321	0.1562
S[c] [all data]	1.021	0.794

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof $= S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections, and p is the number of refined parameters.

1.65. Found: C, 44.19; H, 6.77; N, 1.64. IR (KBr, cm^{-1}): ν(N−H) 3310 (m br); ν(CO) 2018 and 1944 (both s); ν(C=N) 1647 (s); ν(BF$_4$) 1040 (s br). MS (FAB$^+$): m/z 762 (M$^+$). *Rotamer* **a:** ^{1}H NMR (acetone-d_6, 20 °C): δ 13.76 (br, 1H, N−H); 8.24 (s, 1H, Os−CH); 7.5−7.3 (m, 5H, Ph); 2.90 (m, 6H, PCH); 2.71 and 2.02 (both s, 6H, {CH$_3$}$_2$C=N); 1.49 and 1.43 (both dvt, $J_{H-H} = 6.9$, $N = 13.8$, 36H, PCHCH_3). ^{13}C{^{1}H} NMR plus APT (acetone-d_6, 20 °C): δ 184.4 (s, C=N); 182.5 and 177.5 (both t, $J_{C-P} = 7.8$, CO); 147.5 (t, $J_{C-P} = 4.2$, Os−CH=*C*PhN); 145.6 (t, $J_{C-P} = 11.0$, Os−*C*H=CPhN); 140.1 (s, $C_{ipso-Ph}$); 129.7, 128.4, and 126.0 (all s, C_{Ph}); 27.6 and 24.2 (both s, {*C*H$_3$}$_2$C=N); 25.7 (vt, $N = 25.6$, PCH); 19.5 and 19.3 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (acetone-d_6, 20 °C): δ 12.5 (s). *Rotamer* **b:** ^{1}H NMR (acetone-d_6, 20 °C): δ 11.78 (br, 1H, N−H); 8.93 (s, 1H, Os−CH); 7.5−7.3 (m, 5H, Ph); 2.90 (m, 6H, PCH); 2.84 and 2.41 (both s, 6H, {CH$_3$}$_2$C=N); 1.51 and 1.33 (both dvt, $J_{H-H} = 7.2$, $N = 13.8$, 36H, PCHCH_3). ^{13}C{^{1}H} NMR plus APT (acetone-d_6, 20 °C): δ 192.5 (s, C=N); 183.1 and 179.5 (both t, $J_{C-P} = 7.8$, CO); 157.6 (t, $J_{C-P} = 10.2$, Os-*C*H=CPhN); 140.8 (t, $J_{C-P} = 4.5$, Os−CH=*C*PhN); 139.2 (s, $C_{ipso-Ph}$); 129.6, 127.5, and 124.6 (all s, C_{Ph}); 26.7 and 24.0 (both s, {*C*H$_3$}$_2$C=N); 24.9 (vt, $N = 25.6$, PCH); 20.4 and 19.2 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (acetone-d_6, 20 °C): δ 11.8 (s).

Preparation of [OsCl{(*Z*)-CH=C(Ph)−NH=C(CH$_2$)$_4$CH$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (10). This complex was prepared as described for **9** starting from 125 mg (0.155 mmol) of **12** and tetrafluoroboric acid (21 μL, 0.157 mmol, 54% in diethyl ether). The resulting white microcrystalline solid was found to be (NMR techniques) a mixture of two rotamers (ratio **a**:**b** = 3:2). Yield: 115 mg (83%). Anal. Calcd for $C_{34}H_{59}NBClF_4O_2OsP_2$: C, 45.98; H, 6.70; N, 1.58. Found: C, 45.81; H, 6.62; N, 1.55. IR (KBr, cm^{-1}): ν(N−H) 3313 (m br); ν(CO) 2009 and 1928 (both s); ν(C=N) 1639 (s); ν(BF$_4$) 1057 (s br). MS (FAB$^+$): m/z 802 (M$^+$). *Rotamer* **a:** ^{1}H NMR (acetone-d_6, 20 °C): δ 13.31 (br, 1H, N−H); 7.86 (s, 1H, Os−CH); 7.5−7−3 (m, 5H, Ph); 2.63 (m, 6H, PCH); 2.2−1.4 (m, 10H, Cy); 1.25 (m, 36H, PCHCH_3). ^{13}C{^{1}H} NMR (acetone-d_6, 20 °C): δ 189.0 (s, C=N); 182.3 and 177.2 (both t, $J_{C-P} = 7.3$, CO); 146.7 (t, $J_{C-P} = 4.1$, Os−CH=*C*PhN); 145.5 (t, $J_{C-P} = 10.9$, Os−*C*H=CPhN); 140.5 (s, $C_{ipso-Ph}$); 129.5, 128.0, and 125.2 (all s, C_{Ph}); 36.2, 32.9, 26.8, 26.0, and 22.9 (all s, Cy); 25.4 (vt, $N = 25.6$, PCH); 19.3 and 19.1 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (acetone-d_6, 20 °C): δ 6.8 (s). *Rotamer* **b:** ^{1}H NMR (acetone-d_6, 20 °C): δ 11.15 (br, 1H, N−H); 8.61 (s, 1H, Os−CH); 7.5−7−3 (m, 5H, Ph); 2.63 (m, 6H, PCH); 2.2−1.4 (m, 10H, Cy); 1.25 (m, 36H, PCHCH_3). ^{13}C{^{1}H} NMR (acetone-d_6, 20 °C): δ 197.0 (s, C=N); 182.8 and 179.3 (both t, $J_{C-P} = 7.3$, CO); 157.6 (t, $J_{C-P} = 11.0$, Os−*C*H=CPhN); 140.0 (s, $C_{ipso-Ph}$); 139.8 (t, $J_{C-P} = 3.8$, Os−CH=*C*PhN); 129.2, 127.2, and 124.5 (all s, C_{Ph}); 36.6, 33.2, 26.7, 26.0, and 23.5 (all s, Cy); 24.6 (vt, $N = 26.1$, PCH); 20.1 and 19.2 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (acetone-d_6, 20 °C): δ 6.4 (s).

Preparation of OsCl{(*Z*)-CH=C(Ph)N=C(CH$_3$)$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$ (11). Carbon monoxide was bubbled through a yellow solution of **5** (125 mg, 0.171 mmol) in toluene for 15 min. The solvent was concentrated to dryness, and addition of methanol led to the precipitation of a pale yellow solid. The solvent was decanted, and the solid was washed twice with methanol and then dried in vacuo. Yield: 105 mg (81%). Anal. Calcd for $C_{31}H_{54}NClO_2OsP_2$: C, 48.97; H, 7.16; N, 1.89. Found: C, 48.75; H, 7.13; N, 1.82. IR (KBr, cm^{-1}): ν(CO) 1995 and 1926 (both s); ν(C=N) 1648 (s). ^{1}H NMR (C_6D_6, 20 °C): δ 7.90 (t, $J_{H-P} = 2.2$, 1H, Os−CH); 7.51 (d, $J_{H-H} = 8.1$, 2H, $H_{ortho-Ph}$); 7.24 (t, $J_{H-H} = 7.5$, 2H, $H_{meta-Ph}$); 7.02 (t, $J_{H-H} = 7.5$, 1H, $H_{para-Ph}$); 2.75 (m, 6H, PCH); 2.01 and 1.45 (both s, 6H, {CH$_3$}$_2$C=N); 1.40 and 1.06 (both dvt, $J_{H-H} = 7.8$, $N = 14.7$, 36H, PCHCH_3). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 185.2 and 179.6 (both t, $J_{C-P} = 7.5$, CO); 166.1 (s, C=N); 150.3 (t, $J_{C-P} = 4.2$, Os−CH=*C*PhN); 144.4 (t, $J_{C-P} = 1.5$, $C_{ipso-Ph}$); 139.5 (t, $J_{C-P} = 12.0$, Os−*C*H=CPhN); 128.2, 124.9, and 124.7 (all s, C_{Ph}); 27.0 and 23.1 (both s, {*C*H$_3$}$_2$C=N); 23.8 (vt, $N = 25.6$, PCH); 20.7 and 19.0 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 7.2 (s). MS (FAB$^+$): m/z 761 (M$^+$).

Preparation of Os{(*Z*)-CH=C(Ph)N=C(CH$_2$)$_4$CH$_2$}Cl(CO)$_2$(PiPr$_3$)$_2$ (12). This complex was prepared as described for **11** starting from 125 mg (0.162 mmol) of **6**. Yield: 108 mg (83%). Anal. Calcd for $C_{34}H_{58}NClO_2OsP_2$: C, 51.02; H, 7.30; N, 1.75. Found: C, 50.78; H, 7.55; N, 1.82. IR (KBr, cm^{-1}): ν(CO) 1996 and 1925 (both s); ν(C=N) 1650 (s). ^{1}H NMR (C_6D_6, 20 °C): δ 7.90 (t, J_{H-H} = 2.2, 1H, Os−CH); 7.57 (d, J_{H-H} = 8.1, 2H, $H_{ortho-Ph}$); 7.25 (t, J_{H-H} = 7.5, 2H, $H_{meta-Ph}$); 7.03 (t, J_{H-H} = 7.2, 1H, $H_{para-Ph}$); 2.78 (m, 6H, PCH); 2.51 (m, 2H, {CH$_2$}C=N); 2.02 (m, 2H, {CH$_2$}C=N); 1.66 (m, 2H, Cy); 1.42 and 1.10 (both dvt, J_{H-H} = 6.9, N = 14.4, 36H, PCHC*H*$_3$); 1.20 (m, 4H, Cy). ^{13}C{^{1}H} NMR plus DEPT (C_6D_6, 20 °C): δ 185.3 and 179.7 (both t, J_{C-P} = 7.5, CO); 171.3 (s, C=N); 149.8 (t, J_{C-P} = 3.8, Os−CH=*C*PhN); 145.5 (s, $C_{ipso-Ph}$); 140.0 (t, J_{C-P} = 12.1, Os−*C*H=CPhN); 128.4 and 124.8 (both s, C_{Ph}); 38.7, 34.5, 27.5, 26.2, and 26.0 (all s, Cy); 24.0 (vt, N = 25.3, PCH); 20.9 and 19.4 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 7.6 (s). MS (FAB$^+$): *m*/*z* 801 (M$^+$).

Crystal Data for [OsCl{=CHCH(Ph)N=C(CH$_3$)$_2$}(CO)(P^{i}Pr$_3$)$_2$][CF$_3$SO$_3$] (3) and [OsCl{(*Z*)-CH=C(Ph)-NH=C(CH$_2$)$_4$CH$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (10). A summary of the fundamental crystal and refinement data of the compounds **3** and **10** is given in Table 3. Crystals of **3** and **10** were mounted on Bruker P4 (**3**) and Bruker Smart APEX CCD (**10**) diffractometers equipped with a normal focus, 2.4 kW sealed tube X-ray source (molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA. Data were collected over a quadrant (**3**) or hemisphere (**10**) by a combination of three sets. The cell parameters were determined and refined by least-squares fit of 59 carefully centered high-angle reflections (**3**) or all collected reflections (**10**). Each frame exposure time was 10 s (**10**) covering 0.3° in ω (coverage of the unique sets was over 100% complete to at least 25° in θ). Three standard reflections were monitored through data collection for **3**, or the first 100 frames were collected at the end of the data collection to monitor crystal decay for **10**. The absorption correction was made using XEMP (**3**) or SADABS (**10**).[25] The structure was solved by Multan and Fourier methods using SHELXS.[26] Full matrix least-squares refinement was carried out using SHELXL97[26] minimizing $w(F_o^2 - F_c^2)_2$. Weighted R factors (R_w) and goodness of fit S are based on F^2; conventional R factors are based on F.

The triflate anion of **3** was observed severely disordered and was refined with three sites for O and F atoms, two sites for C, and one S atom; restrained geometry and complementary occupancy factors were also used. **10** crystallizes with molecules of disordered solvent, modeled as 0.9 molecule of disordered dichloromethane, 0.4 molecule of THF, and 0.25 molecule of diethyl ether. These molecules were refined with complementary occupancy factors estimated on thermal parameters and restrained geometry.

Acknowledgment. Financial support from the DGES of Spain (Project PB98-1591) is acknowledged. R.C. thanks the "Ministerio de Ciencia y Tecnología" for a grant.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **3** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010005K

(25) *SHELXTL 6.1* and *Smart Apex* v. 5; Bruker Analytical X-ray Systems: Madison, WI, 1997.

(26) Sheldrick, G. M. *SHELXS* and *SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.