Reviews

C−C Coupling and C−H Bond Activation Reactions of Cyclopentadienyl−Osmium Compounds: The Rich and Varied Chemistry of Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ and Its Major Derivatives

Miguel A. Esteruelas* and Ana M. López

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

Received April 11, 2005

The six-coordinate osmium(IV) complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with cyclopentadienyl derivatives of s- or p-block elements to afford cyclopentadienyl−osmium complexes, including Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$. One of the phosphine ligands of this compound is displaced by phenylmethylene, terminal alkynes, and 1,1-diphenyl-2-propyn-1-ol to give Os(η^5-C_5H_5)Cl(=CHPh)(P^iPr_3), Os(η^5-C_5H_5)Cl(=C=CHR)(P^iPr_3), and Os(η^5-C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3), respectively, which give rise to half-sandwich carbyne, η^3-allyl, η^3-benzyl, and substituted olefin derivatives by reactions with electrophiles and nucleophiles. In the presence of chlorine extractors, the rupture of the Os−Cl bond of Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ is favored. The resulting metal fragment activates C(sp^3)−H, C(sp^2)−H, C(sp)−H, and P−H bonds. The C(sp)−H activation of terminal alkynes is the key step to the formation of [Os(η^5-C_5H_5)(=C=CHR)(P^iPr_3)$_2$]$^+$ and [Os(η^5-C_5H_5)(=C=C=CPh_2)(P^iPr_3)$_2$]$^+$. Mixed-ligand allenylidene derivatives of the type [Os(η^5-C_5H_5)(=C=C=CPh_2)L(P^iPr_3)]$^+$ are formed by addition of Lewis bases to the four-electron alkyne complex [Os(η^5-C_5H_5){η^2-HC≡CC(OH)Ph_2}(P^iPr_3)]$^+$. The reactions of the carbonyl derivative [Os(η^5-C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]$^+$ with RXH (X = O, NR) molecules afford Fischer-type alkenylcarbene compounds. The complex Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ also reacts with group 14 element hydride compounds to give OsH(η^5-C_5H_5)Cl(EPh_3)(P^iPr_3) (E = Si, Ge, Sn). Treatment of OsH(η^5-C_5H_5)Cl(EPh_3)(P^iPr_3) (E = Si, Ge) with LiNu reagents (Nu = CH_2CN, $CH_2C(O)CH_3$, alkyl, NR_2, PPh_2) yields four different types of compounds: OsH_2(η^5-$C_5H_4EPh_3$)(Nu)(P^iPr_3), OsH_2(η^5-C_5H_4Nu)(EPh_3)(P^iPr_3), $\overline{OsH_2\{\eta^5\text{-}C_5H_4Si(C_6H_4)Ph_2\}(P^iPr_3)}$, and $\overline{OsH_2\{(\eta^5\text{-}C_5H_5Si(C_6H_4)Ph_2\}(P^iPr_3)}$. The formation of these derivatives has been rationalized on the basis of the tendency of the EPh_3 and Nu ligands of OsH(η^5-C_5H_5)(Nu)(EPh_3)(P^iPr_3) to exchange their positions with the hydrogen atoms of the cyclopentadienyl ring and the stability of these species and OsH_2(η^5-$C_5H_4EPh_3$)(Nu)(P^iPr_3) toward the reductive elimination of H−Nu. One of the phosphines of Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ can be also displaced by molecular hydrogen. The reaction leads to OsH_2(η^5-C_5H_5)Cl(P^iPr_3), which reacts with diphenylacetylene to yield Os(η^5-C_5H_5)Cl(η^2-PhC≡CPh)(P^iPr_3). In methanol, the latter gives rise to the isopropenyldiisopropylphosphine derivative Os(η^5-C_5H_5)Cl{[η^2-CH_2=C(CH_3)]P^iPr_2}, which affords dienylphosphine and iminophosphine compounds by reactions with terminal alkynes and benzonitriles, respectively.

Introduction

The σ-donor and π-acceptor abilities of the cyclopentadienyl ligand stabilize transition-metal complexes in low and high oxidation states. Thus, the cyclopentadienyl group is one of the most important ligands in organometallic chemistry. In 1991, Janiak and Schumann estimated that at that time more than 80% of all known organometallic complexes of transition metals contained the cyclopentadienyl fragment or a derivative thereof.[1]

The iron triad metals exhibit one of the widest ranges of oxidation states. Thus, at first glance, their use should allow, with only a few elements, to have a first forecast about the behavior of a wide variety of metallic ions. Thus, one should expect that the cyclopentadienyl−

* To whom correspondence should be addressed. E-mail: maester@posta.unizar.es.

(1) Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291.

10.1021/om050272g CCC: $30.25
Publication on Web 06/22/2005

ruthenium and −osmium fragments would occupy a prominent place in the organometallic field.

Half-sandwich cyclopentadienyl−ruthenium complexes have been, in fact, one of the cornerstones in the development of organometallic chemistry. They exhibit a particularly rich chemistry, which includes interesting stoichiometric and catalytic transformations involving C−C and C−heteroatom coupling reactions.[2] However, in contrast to ruthenium, the chemistry of half-sandwich cyclopentadienyl−osmium complexes is a little known field.[3] The noticeable lack of emphasis on cyclopentadienyl−osmium chemistry has been attributed to the scarcity of convenient synthetic precursors and the greater inertness of the octahedral osmium(II) complexes in comparison with the ruthenium analogues. The latter seems to be a consequence of the dependence of the crystal field activation energy on Δ_O.

A small number of sandwich or mixed-sandwich osmium complexes containing the cyclopentadienyl or pentamethylcyclopentadienyl groups have been reported.[4] Photolysis of [Os(η^5-C_5H_5)(η^6-C_6H_6)]$^+$ in acetonitrile solution gave [Os(η^5-C_5H_5)(CH_3CN)$_3$]$^+$, but only a 30% conversion was achieved before significant photochemically induced decomposition of [Os(η^5-C_5H_5)(CH_3CN)$_3$]$^+$ occurs. Photolysis of acetonitrile solutions of [Os(η^5-C_5H_5)(η^6-C_6H_6)]$^+$ that contained biphenyl eliminated this side reaction and allowed the high-yield preparation of [Os(η^5-C_5H_5)(CH_3CN)$_3$]$^+$. Although this complex reacts with carbon monoxide, polypyrazolylborate ligands, and arenes to afford Os(η^5-C_5H_5)L_3 derivatives,[5] its chemistry does not reach the level of that of the ruthenium analogue [Ru(η^5-C_5H_5)(CH_3CN)$_3$]$^+$.[2a] A few high-valent cyclopentadienyl−osmium complexes have been also isolated. Reactions of [$OsNCl_2R_2$]$^-$ (R = CH_2SiMe_3, Ph) with NaC_5H_5 afforded neutral cyclopentadienyl−nitrido−osmium(VI) derivatives.[6] The nitrido ligand of these complexes acts as a weak Lewis base. However, the coordinatively saturated osmium center is relatively unreactive. In 1994, Girolami and co-workers reported the synthesis of the pentamethylcyclopentadienyl dimer complex (η^5-C_5Me_5)$_2Os_2Br_4$, which is allowing a slow development of the osmium chemistry with this substituted cyclopentadienyl ligand, in oxidation states between +2 and +6.[8]

A modification of these systems is the use of cyclopentadienyl ligands with a pendant donor group.[9] Due to the reversible coordination of the pendant group, these ligands stabilize highly reactive fragments, which facilitates the study of some processes.[10] Complexes with these groups have attracted increased interest in recent years. In accordance with this interest, a significant number of ruthenium complexes have been prepared,[11] while their osmium counterparts were unknown until very recently.[12]

In the long term we wish to design, à la carte, metallic homogeneous systems that are effective in the synthesis of functionalized organic molecules from basic hydrocarbon units, including alkanes. The synthesis processes would involve the entry, in a consecutive and controlled way, of organic fragments into a transition-metal complex to give an organometallic compound. The latter should react with an organic function to afford the desired compound and regenerate the initial transition-metal complex.[13] In this respect, obtaining systems that promote C−C bond formation and C−H activation is of great significance.

(2) See for example: (a) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev*. **2001**, *101*, 2067. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem*. **2001**, 571. (c) Selegue, J. P. *Coord. Chem. Rev*. **2004**, *248*, 1543. (d) Winter, R. F.; Zális, S. *Coord. Chem. Rev*. **2004**, *248*, 1565.

(3) (a) Albers, M. O.; Robinson, D. J.; Singleton, E. *Coord. Chem. Rev*. **1987**, *79*, 1. (b) Guerchais, V. *Eur. J. Inorg. Chem.* **2002**, 783. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Coord. Chem. Rev*. **2004**, *248*, 1627. (d) Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Eur. J. Inorg. Chem*. **2004**, 17.

(4) (a) Robertson, I. W.; Stephenson, T. A.; Tocher, D. A. *J. Organomet. Chem*. **1982**, *228*, 171. (b) Liles, D. C.; Shaver, A.; Singleton, E.; Wiege, M. B. *J. Organomet. Chem*. **1985**, *288*, C33. (c) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E.; Wiege, M. B.; Boeyens, J. C. A.; Levendis, D. C. *Organometallics* **1986**, *5*, 2321. (d) Droege, M. W.; Harman, W. D.; Taube, H. *Inorg. Chem*. **1987**, *26*, 1309. (e) Droege, M. W.; Taube, H. *Inorg. Chem*. **1987**, *26*, 3316. (f) O'Hare, D.; Green, J. C.; Chadwick, T. P.; Miller, J. S. *Organometallics* **1988**, *7*, 1335. (g) Rybinskaya, M. I.; Kreindlin, A. Z.; Struchkov, Yu. T.; Yanovsky, A. I. *J. Organomet. Chem*. **1989**, *359*, 233. (h) Lichtenberger, D. L.; Copenhaver, A. S. *J. Chem. Phys*. **1989**, *91*, 663. (i) Lumme, P. O.; Turpeinen, U.; Kudinov, A. R.; Rybinskaya, M. I. *Acta Crystallogr., Sect. C* **1990**, *46*, 1410. (j) Abel, E. W.; Long, N. J.; Osborne, A. G.; Hursthouse, M. B.; Mazid, M. A. *J. Organomet. Chem*. **1992**, *430*, 117. (k) Turpeinen, U.; Kreindlin, A. Z.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem*. **1992**, *441*, 109. (l) Freedman, D. A.; Matachek, J. R.; Mann, K. R. *Inorg. Chem*. **1993**, *32*, 1078. (m) Goto, M.; Yamazaki, Y.; Honda, K.; Masaki, A. *Bull. Chem. Soc. Jpn*. **1995**, *68*, 1305. (n) Freedman, D. A.; Magneson, D. J.; Mann, K. R. *Inorg. Chem*. **1995**, *34*, 2617. (o) Gassman, P. G.; Sowa, J. R., Jr.; Hill, M. G.; Mann, K. R. *Organometallics* **1995**, *14*, 4879. (p) Graf, D. D.; Mann, K. R. *Inorg. Chem*. **1997**, *36*, 150.

(5) Freedman, D. A.; Gill, T. P.; Blough, A. M.; Koefod, R. S.; Mann, K. R. *Inorg. Chem*. **1997**, *36*, 95.

(6) (a) Marshman, R. W.; Shusta, J. M.; Wilson, S. R.; Shapley, P. A. *Organometallics* **1991**, *10*, 1671. (b) Shapley, P. A.; Shusta, J. M.; Hunt, J. L. *Organometallics* **1996**, *15*, 1622. (c) Koch, J. L.; Shapley, P. A. *Organometallics* **1997**, *16*, 4071. (d) Koch, J. L.; Shapley, P. A. *Organometallics* **1999**, *18*, 814.

(7) Gross, C. L.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc*. **1994**, *116*, 10294.

(8) (a) Gross, C. L.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem*. **1995**, *34*, 2582. (b) Bayse, C. A.; Couty, M.; Hall, M. B. *J. Am. Chem. Soc*. **1996**, *118*, 8916. (c) Gross, C. L.; Girolami, G. S. *Organometallics* **1996**, *15*, 5359. (d) Herberhold, M.; Jin, G.-X.; Liable-Sands, L. M.; Rheingold, A. L. *J. Organomet. Chem*. **1996**, *519*, 223. (e) Bullock, R. M.; Song, J.-S.; Szalda, D. J. *Organometallics* **1996**, *15*, 2504. (f) Gross, C. L.; Young, D. M.; Schultz, A. J.; Girolami, G. S. *J. Chem. Soc., Dalton Trans*. **1997**, 3081. (g) Bayse, C. A.; Hall, M. B. *Inorg. Chim. Acta* **1997**, *259*, 179. (h) Gross, C. L.; Girolami, G. S. *J. Am. Chem. Soc*. **1998**, *120*, 6605. (i) Brumaghim, J. L., Girolami, G. S. *Chem. Commun.* **1999**, 953. (j) Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics* **1999**, *18*, 2139. (k) Mui, H. D.; Brumaghim, J. L.; Gross, C. L.; Girolami, G. S. *Organometallics* **1999**, *18*, 3264. (l) Glaser, P. B.; Tilley, T. D. *Eur. J. Inorg. Chem*. **2001**, 2747. (m) Cheng, T.-Y.; Bullock, R. M. *Organometallics* **2002**, *21*, 2325. (n) Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Organometallics* **2003**, *22*, 3927. (o) Glaser, P. B.; Tilley, T. D. *Organometallics* **2004**, *23*, 5799.

(9) (a) Jutzi, P.; Redeker, T. *Eur. J. Inorg. Chem*. **1998**, 663. (b) Müller, C.; Vos, D.; Jutzi, P. *J. Organomet. Chem*. **2000**, *600*, 127. (c) Siemeling, U. *Chem. Rev*. **2000**, *100*, 1495. (d) Butenschön, H. *Chem. Rev*. **2000**, *100*, 1527. (e) Qian, Y.; Huang, J.; Bala, M. D.; Lian, B.; Zhang, H.; Zhang, H. *Chem. Rev*. **2003**, *103*, 2633.

(10) See for example: (a) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2002**, *21*, 4905. (b) Esteruelas, M. A.; Fernández, F. J.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 1787. (c) Becker, E.; Mereiter, K.; Puchberger, M.; Schmid, R.; Kirchner, K.; Doppiu, A.; Salzer, A. *Organometallics* **2003**, *22*, 3164. (d) Daugulis, O.; Brookhart, M.; White, P. S. *Organometallics* **2003**, *22*, 4699. (e) Yong, L.; Hofer, E.; Wartchow, R.; Butenschön, H. *Organometallics* **2003**, *22*, 5463.

(11) See for example: (a) Chu, H. S.; Lau, C. P.; Wong, K. Y.; Wong, W. T. *Organometallics* **1998**, *17*, 2768. (b) Ayllon, J. A.; Sayers, S. F.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B.; Clot, E. *Organometallics* **1999**, *18*, 3981. (c) Matsubara, T. *Organometallics* **2001**, *20*, 19. (d) Matsubara, T.; Hirao, K. *Organometallics* **2001**, *20*, 5759. (e) Lam, Y. F.; Yin, C.; Yeung, C. H.; Ng, S. M.; Jia, G.; Lau, C. P. *Organometallics* **2002**, *21*, 1898.

(12) (a) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2004**, *23*, 3021. (b) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2004**, *23*, 5633. (c) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Inorg. Chem.* **2005**, *44*, 4094.

(13) Esteruelas, M. A.; López, A. M. In *Recent Advances in Hydride Chemistry*; Peruzzini, M., Poli, R., Eds.; Elsevier: Amsterdam, 2001; Chapter 7, pp 189−248.

For our objective, the cyclopentadienyl−osmium fragment is of particular interest. The cyclopentadienyl ligand occupies a face of the metal complex, while the other one remains free for the entry of the organic substrates. Osmium, in addition to providing catalysts for C−C bond formation,[14] affords stable models of reactive intermediates proposed in catalytic transformations with their ruthenium counterparts.[15]

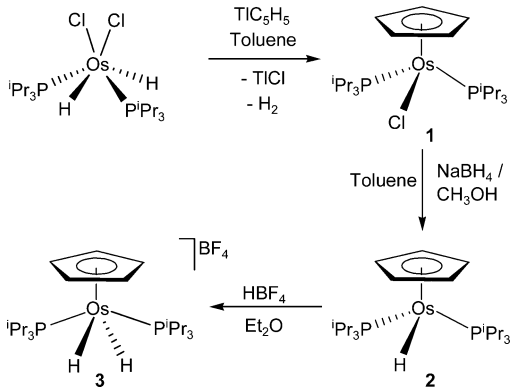
Our interest in cyclopentadienyl−osmium chemistry began in 1995. Two years later, we reported the preparation of the complex $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$.[16] The large number of observed reactions, mainly involving C−C bond formation and C−H bond activation, and new organometallic complexes synthesized in recent years using this complex as the starting point prompt us to consider it as a cornerstone in the development of cyclopentadienyl−osmium chemistry. In the following pages, we review the most important features of this rich chemistry.

Preparation of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ and Related Complexes Containing a Cyclopentadienyl Ligand with a Pendant Donor Group

The six-coordinate complex $OsH_2Cl_2(P^iPr_3)_2$ is a unique species[17] with a chemical behavior completely different from that of the compounds reported until now. It not only catalyzes the reduction of ketones, olefins, and diolefins and is a useful starting material to prepare dihydrogen, polyhydride, carbyne, diolefin, and azavinylidene derivatives of osmium(II), osmium(IV), and osmium(VI)[18] but it also serves as an entry to cyclopentadienyl−osmium chemistry. The addition of 1.0 equiv of cyclopentadienylthallium to a toluene solution of this complex resulted in formation of the cyclopentadienyl−osmium derivative $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**), which was isolated as an orange solid in 52% yield.[16] Treatment of a 1:10 mixture of **1** and $NaBH_4$ in toluene with 1.0 mL of methanol afforded the monohydride $OsH(\eta^5\text{-}C_5H_5)(P^iPr_3)_2$ (**2**) in quantitative yield. Protonation of the latter with $HBF_4{\cdot}OEt_2$ in diethyl ether gave the dihydride−osmium(IV) complex $[OsH_2(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]BF_4$ (**3**) with a transoid disposition for the hydride ligands (Scheme 1).

Complexes related to **1**−**3** with phosphine ligands smaller than triisopropylphosphine have been prepared by starting from $OsBr_2(PPh_3)_3$. The reaction of this compound with cyclopentadiene gave $Os(\eta^5\text{-}C_5H_5)Br(PPh_3)_2$,[19] which could be obtained directly from hexabromoosmic acid, triphenylphosphine, and cyclopentadiene

Scheme 1



in refluxing ethanol.[20] Reactions between $Os(\eta^5\text{-}C_5H_5)Br(PPh_3)_2$ and diphosphines or phosphines less bulky than triphenylphosphine afforded $Os(\eta^5\text{-}C_5H_5)Br(P{-}P)$ (P−P = bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane) and $Os(\eta^5\text{-}C_5H_5)Br(PR_3)_2$, respectively. Treatment of these compounds with sodium methoxide in methanol led to the corresponding monohydride compounds, which gave the dihydride complexes on protonation with HBF_4. Reactions of $OsH(\eta^5\text{-}C_5H_5)(PR_3)_2$ with HX (X = Cl, I) generated $Os(\eta^5\text{-}C_5H_5)X(PR_3)_2$, which were converted to monohydride−osmium(IV) derivatives of the type $[OsH(\eta^5\text{-}C_5H_5)X(PR_3)_2]Y$ by reaction with Brønsted acids.[21]

In toluene, complex **1** shows a high tendency to release a phosphine ligand. Under a carbon monoxide atmosphere, the formation of the carbonyl complex $Os(\eta^5\text{-}C_5H_5)Cl(CO)(P^iPr_3)$ (**4**) occurred, whereas the addition of trimethyl phosphite, methyl vinyl ketone, and dimethyl acetylenedicarboxylate to **1** afforded the derivatives $Os(\eta^5\text{-}C_5H_5)Cl\{P(OMe)_3\}(P^iPr_3)$ (**5**), $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}CH_2{=}CHC(O)CH_3\}(P^iPr_3)$ (**6**), and $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}C(CO_2Me){\equiv}C(CO_2Me)\}(P^iPr_3)$ (**7**), respectively (Scheme 2).[16] The reactions proceeded at room temperature and did not result in displacement of the second phosphine ligand, even if an excess of π-acid ligand was used.

The carbonyl complex **4** can be also obtained according to Scheme 3. The reaction of the five-coordinate compound $OsHCl(CO)(P^iPr_3)_2$[22] with cyclopentadiene in refluxing methanol afforded the monohydride cyclopentadienyl derivative $OsH(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)$ (**8**), which reacted with CCl_4 to give **4**.[23] Similarly to **2**, the protonation of **8** with $HBF_4{\cdot}OEt_2$ in diethyl ether led to the dihydride $[OsH_2(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)]BF_4$ (**9**).

The dicarbonyl complex $Os(\eta^5\text{-}C_5H_5)Br(CO)_2$ has been prepared in 40% yield by reaction of $OsBr_2(CO)_4$ with

(14) Brumahim, J. L.; Girolami, G. S. *Organometallics* **1999**, *18*, 1923. (b) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2000**, *19*, 5098. (c) Esteruelas, M. A.; Herrero, J.; López, A. M.; Oliván, M. *Organometallics* **2001**, *20*, 3202. (d) Cobo, N.; Esteruelas, M. A.; González, F.; Herrero, J.; López, A. M.; Lucio, P.; Oliván, M. *J. Catal*. **2004**, *223*, 319.

(15) (a) Sánchez-Delgado, R. A.; Rosales, M.; Esteruelas, M. A.; Oro, L. A. *J. Mol. Catal. A.: Chem*. **1995**, *96*, 231. (b) Esteruelas, M. A.; Oro, L. A. *Chem. Rev*. **1998**, *98*, 577.

(16) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657.

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

(18) See for example: Castarlenas, R.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Jean, Y.; Lledós, A.; Martín, M.; Oñate, E.; Tomàs, J. *Organometallics* **2000**, *19*, 3100 and references therein.

(19) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2376.

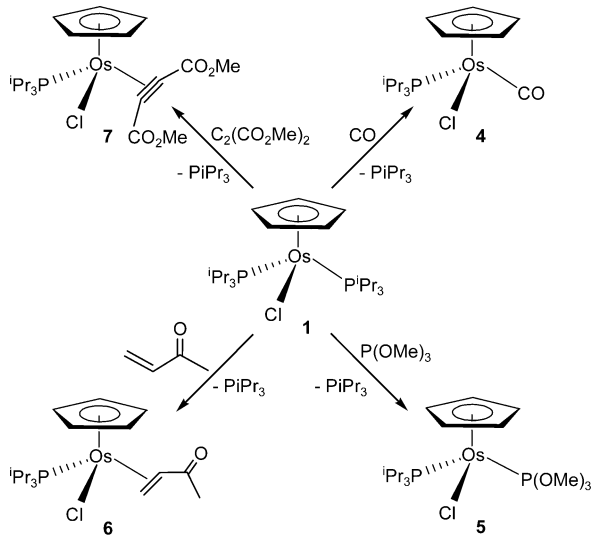
(20) (a) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem*. **1977**, *30*, 1601. (b) Wanandi, P. W.; Tilley, T. D. *Organometallics* **1997**, *16*, 4299.

(21) (a) Bruce, M. I.; Wong, F. S. *J. Organomet. Chem*. **1981**, *210*, C5. (b) Bruce, M. I.; Tomkins, B.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans*. **1982**, 687. (c) Wilczewski, T. *J. Organomet. Chem*. **1982**, *224*, C1. (d) Wilczewski, T. *J. Organomet. Chem*. **1986**, *317*, 307. (e) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc*. **1992**, *114*, 8296. (f) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc*. **1993**, *115*, 7267. (g) Angelici, R. J. *Acc. Chem. Res*. **1995**, *28*, 51. (h) Wang, D.; Angelici, R. J. *J. Am. Chem. Soc*. **1996**, *118*, 935. (i) Jia, G.; Ng, W. S.; Yao, J.; Lau, C.-P.; Chen, Y. *Organometallics* **1996**, *15*, 5039. (j) Jia, G.; Lau, C. P. *J. Organomet. Chem*. **1998**, *565*, 37.

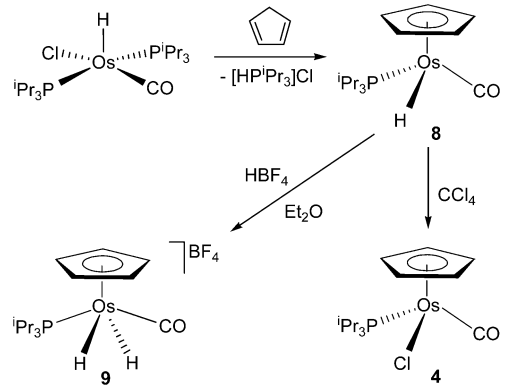
(22) (a) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem*. **1986**, *303*, 221. (b) Esteruelas, M. A.; Oro, L. A. *Adv. Organomet. Chem*. **2001**, *47*, 1.

(23) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oro, L. A. *Organometallics* **1996**, *15*, 878.

Scheme 2



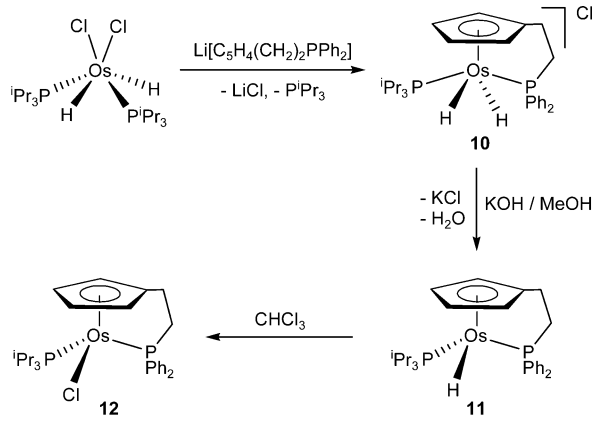
Scheme 3



dicyclopentadiene in decane under reflux. The reaction, in an autoclave, of $OsBr_2(CO)_4$ with cyclopentadienylthallium in heptane at 220 °C gave the hydride derivative $OsH(\eta^5\text{-}C_5H_5)(CO)_2$, which was isolated in 30% yield.[24] A more convenient method to obtain this monohydride is the treatment of the dimer complex $[OsCl_2(CO)_3]_2$ with cyclopentadienylsodium in diethyl ether at room temperature.[25] The reaction of $[OsCl_2(CO)_3]_2$ with $C_5H_5SiMe_3$ afforded $Os(\eta^5\text{-}C_5H_5)Cl(CO)_2$.[26] The monohydride $OsH(\eta^5\text{-}C_5H_5)(CO)_2$ can be deprotonated with strong bases. Treatment of this compound with butyllithium at −20 °C in tethahydrofuran led to the osmate derivative $[Os(\eta^5\text{-}C_5H_5)(CO)_2]^-$, which reacted with ^{t}BuSiH$_2$Cl to give $Os(\eta^5\text{-}C_5H_5)(SiH_2{}^t\text{Bu})(CO)_2$.[27]

The unsaturated complex $OsH_2Cl_2(P^iPr_3)_2$ is also useful to prepare osmium compounds with a cyclopentadienyl ligand bearing a pendant donor group.[12] At room temperature, in toluene, this compound reacted with Li[$C_5H_4(CH_2)_2PPh_2$] to give the dihydride−osmium derivative $[OsH_2\{[\eta^5\text{-}C_5H_4(CH_2)_2]PPh_2\}(P^iPr_3)]Cl$ (**10**), which was isolated in 64% yield (Scheme 4). Complex **10** can be deprotonated by methanolic potassium hydroxide. The addition of this base to a tetrahydrofuran solution

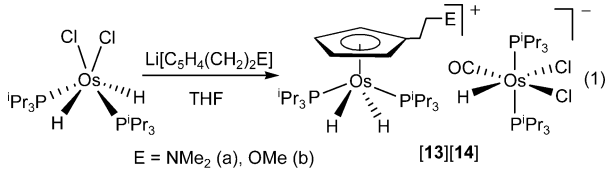
Scheme 4



of **10** gave $OsH\{[\eta^5\text{-}C_5H_4(CH_2)_2]PPh_2\}(P^iPr_3)$ (**11**), as a result of the abstraction of one of the hydride ligands. Complex **11** is unstable in chloroform and forms the chloro derivative $Os\{[\eta^5\text{-}C_5H_4(CH_2)_2]PPh_2\}Cl(P^iPr_3)$ (**12**), which is analogous to **1** but with a PR_2 phosphorus atom connected to the cyclopentadienyl ring.[12a]

The treatment of $OsH_2Cl_2(P^iPr_3)_2$ with a cyclopentadienyl derivative of an s- or p-block element is a method in general use to obtain osmium complexes containing a cyclopentadienyl ligand with a pendant donor group. However, it should be noted that such reactions and the preparation of the modified s- or p-block cyclopentadienyl derivatives must be carried out in a hydrocarbon solvent and that the use of donor solvents, in particular tetrahydrofuran, should be avoided. The latter can react with the s- or p-block cyclopentadienyl systems to give organic fragments, which promote undesired secondary reactions of the osmium precursor.

In agreement with this, it has been observed that the treatment, at room temperature, of $OsH_2Cl_2(P^iPr_3)_2$ with Li[$C_5H_4(CH_2)_2E$] (E = NMe_2, OMe) in tetrahydrofuran provides the salts $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2E\}(P^iPr_3)_2]$-$[OsHCl_2(CO)(P^iPr_3)_2]$ ([**13**][**14**] in eq 1). On the other



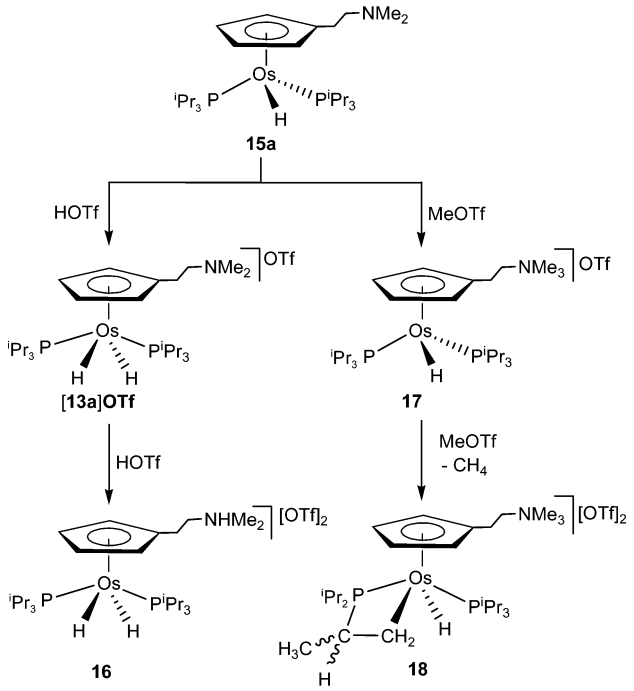
hand, when the preparations of Li[$C_5H_4(CH_2)_2E$] were carried out in pentane, and the reactions with the osmium precursor were performed in toluene, the corresponding salts [**13**]Cl were obtained in 82−85% yield.[12b]

To rationalize the formation of **14**, it has been proposed that Li[$C_5H_4(CH_2)_2E$] reacts with some amount of the tetrahydrofuran solvent to give the lithium enolate of acetaldehyde. Thus, the reaction of $OsH_2Cl_2(P^iPr_3)_2$ with this enolate generates the five-coordinate carbonyl derivative $OsHCl(CO)(P^iPr_3)_2$,[22] to which then is coordinated a chloride ligand from the salts [**13**]-Cl, to give the anion species **14**.

Cations **13** can be deprotonated by reaction with a methanol solution of KOH.[12b] The addition of this base to tetrahydrofuran solutions of **13** results in the abstraction of one of the hydride ligands and the formation

(24) Hoyano, J. K.; May, C. J.; Graham, W. A. G. *Inorg. Chem.* **1982**, *21*, 3095.
(25) Herrmann, W. A.; Herdtweck, E.; Schäfer, A. *Chem. Ber.* **1988**, *121*, 1907.
(26) Dev, S.; Selegue, J. P. *J. Organomet. Chem.* **1994**, *469*, 107.
(27) Kawano, Y.; Tobita, H.; Ogino, H. *Organometallics* **1994**, *13*, 3849.

Scheme 5

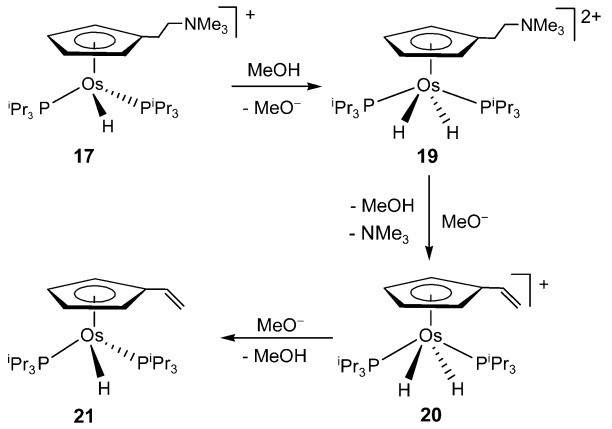


of the neutral compounds $OsH\{\eta^5\text{-}C_5H_4(CH_2)_2E\}(P^iPr_3)_2$ (E = NMe_2 (**15a**), OMe (**15b**)).

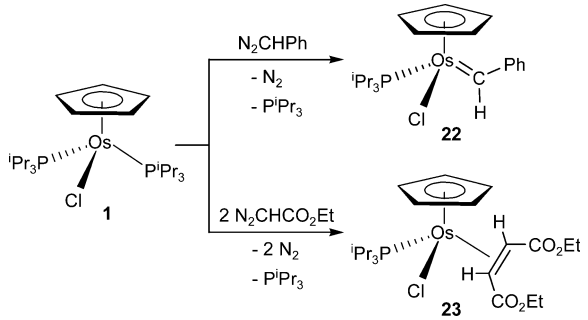
Complex **15a** has two nucleophilic centers, which can undergo attack by electrophiles such as proton and methyl. From a thermodynamic point of view, the protonation of the metal center is preferred to that of the nitrogen atom. Thus, complex **15a** reacts with trifluoromethanesulfonic acid (HOTf) to give [**13a**]OTf and $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2NHMe_2\}(P^iPr_3)_2][OTf]_2$ (**16**) in a sequential manner (Scheme 5). However, from a kinetic point of view, the addition of electrophiles to the nitrogen atom appears to be favored with regard to attack at osmium. In agreement with this, **15a** reacts with MeOTf to afford $[OsH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_3\}(P^iPr_3)_2]$-OTf (**17**), as a result of the addition of the methyl group to the nitrogen atom. Treatment of the latter complex with a second molecule of MeOTf directs the attack of the new methyl group, now to the osmium atom. As a result of this addition and the subsequent elimination of methane, the unsaturated intermediate $[Os\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_3\}(P^iPr_3)_2]^{2+}$ is formed. This short-lived species is transformed into $[OsH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_3\}\{CH_2CH(CH_3)(P^iPr_2)\}(P^iPr_3)][OTf]_2$ (**18**) by methyl C−H activation of the isopropyl group of one of the phosphine ligands.[12c]

In methanol, the metal center of **17** underwent attack by a proton from the solvent to afford the dicationic dihydride complex $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_3\}(P^iPr_3)_2]^{2+}$ (**19**) (Scheme 6). The oxidation of the osmium atom increases the acidity of the Cp−CH_2 group of the cyclopentadienyl chain, which becomes greater than that of the OsH_2 unit. Thus, the first deprotonation of dihydride **19** occurs at the Cp−CH_2 group, which results in elimination of trimethylamine from the pendant substituent and formation of the dihydride vinylcyclopentadienyl derivative $[OsH_2(\eta^5\text{-}C_5H_4CH{=}CH_2)(P^iPr_3)_2]^+$ (**20**).[12c] In contrast to **19**, the OsH_2 unit of **20** can be deprotonated. Treatment of **20** with 1.1 equiv of sodium methoxide in tetrahydrofuran afforded the monohydride $OsH(\eta^5\text{-}C_5H_4CH{=}CH_2)(P^iPr_3)_2$ (**21**).

Scheme 6



Scheme 7



Substitution of a Phosphine: Formation and Reactions of Neutral Carbene, Vinylidene, and Allenylidene Complexes

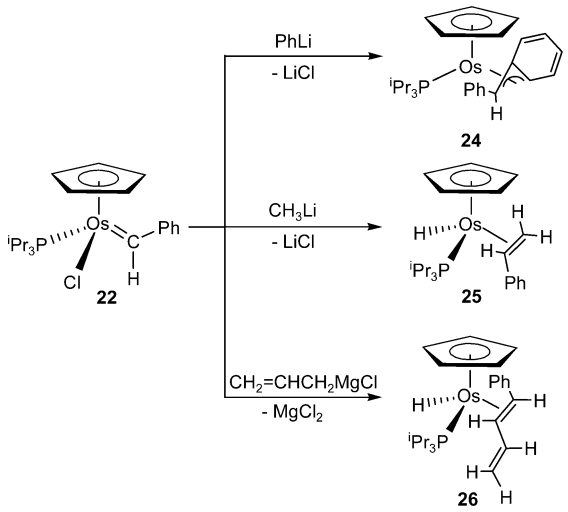
One of the phosphines of **1** can be easily replaced by η^1-carbon donor ligands to form neutral carbene, vinylidene, and allenylidene derivatives.

Treatment of a toluene solution of **1** with a toluene solution of phenyldiazomethane, at room temperature, resulted in formation of the carbene derivative $Os(\eta^5\text{-}C_5H_5)Cl(=CHPh)(P^iPr_3)$ (**22**).[28] A particularly noteworthy carbon−carbon coupling reaction took place with ethyl diazoacetate (Scheme 7). In contrast to phenyldiazomethane, the addition of 3.0 equiv of ethyl diazoacetate to toluene solutions of **1** afforded the olefin complex $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}CH(CO_2Et){=}CH(CO_2Et)\}(P^iPr_3)$ (**23**).[16]

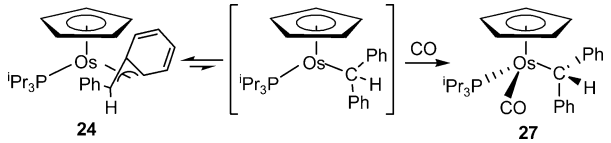
The carbene carbon atom of **22** shows a marked electrophilicity, characteristic of the Fischer-type derivatives. Thus, complex **22** reacted with main-group organometallic compounds, such as phenyllithium, methyllithium, and allylmagnesium chloride, to afford carbene plus organic fragment coupling processes (Scheme 8).[28] The addition at 0 °C of a cyclohexane/diethyl ether solution of phenyllithium to a stoichiometric amount of **22** in tetrahydrofuran gave the α-phenyl-η^3-benzyl complex $Os(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CHPhC_6H_5)(P^iPr_3)$ (**24**). At the same temperature, treatment of a tetrahydrofuran solution of **22** with a stoichiometric amount of methyllithium in diethyl ether afforded the

(28) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414.

Scheme 8



Scheme 9

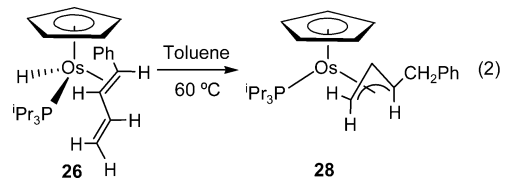


hydride styrene derivative OsH(η^5-C_5H_5)(η^2-CH_2=CHPh)(P^iPr_3) (**25**), whereas the reaction of **22** with allylmagnesium chloride in tetrahydrofuran gave the hydride η^2-phenylbutadiene compound OsH(η^5-C_5H_5){η^2-(*E*)-CHPh=CHCH=CH_2}(P^iPr_3) (**26**).

These reactions can be rationalized in terms of the addition of the nucleophilic organic fragments to the carbene carbon atom of **22**, followed by the elimination of chloride and subsequent η^1-/η^3-benzyl rearrangement in **24** or β-hydrogen abstraction in **25** and **26**. An alternative pathway involving carbene−(η^1-organic fragment)−metal species, which evolve into the same intermediates as those resulting from the direct attack of the organic fragment to the carbene carbon atom, may also be considered.

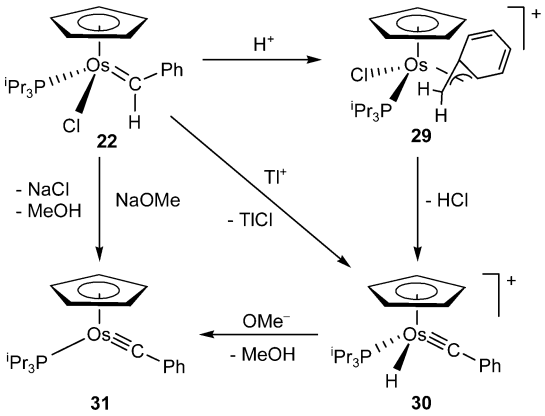
In solution the phenyl groups of **24** exchange their positions. The process takes place via an unsaturated η^1-diphenylmethyl intermediate (Scheme 9), which was trapped when a dichloromethane solution of **24** was stirred at room temperature under 1 atm of carbon monoxide. Under these conditions, complex Os(η^5-C_5H_5)($CHPh_2$)(CO)(P^iPr_3) (**27**) was formed.

In solution, at room temperature, the styrene ligand of **25** rotates around the osmium−olefin axis. Under the same conditions, the osmium−olefin bond of **26** is rigid. Attempts to force the rotation of the diene led to the formation of the allyl derivative Os(η^5-C_5H_5)(η^3-CH_2-CHCHCH_2Ph)(P^iPr_3) (**28**) as a result of the migratory insertion of the styryl unit into the Os−H bond (eq 2).

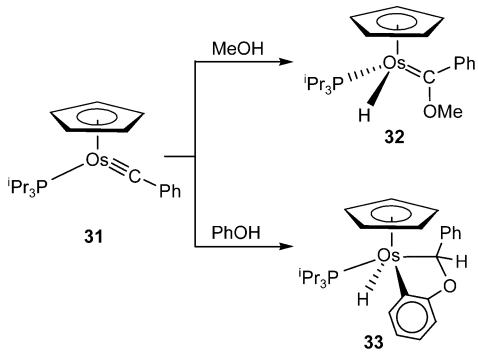


Although the reactions shown in Scheme 8 prove the electrophilicity of the carbene carbon atom of **22**, it must be pointed out that this atom also undergoes attack by electrophiles (Scheme 10). Initially, the protonation of the carbene carbon atom of **22** affords [Os(η^5-C_5H_5)(η^3-$CH_2C_6H_5$)Cl(P^iPr_3)]$^+$ (**29**), which eliminates HCl to give [OsH(η^5-C_5H_5)(≡CPh)(P^iPr_3)]$^+$ (**30**). The PF_6 salt of the latter could be obtained by treatment of an acetone solution of **22** with a stoichiometric amount of $TlPF_6$. Reaction of a tetrahydrofuran solution of **22** with sodium methoxide resulted in the deprotonation of the carbene carbon atom and the formation of the neutral carbyne derivative Os(η^5-C_5H_5)(≡CPh)(P^iPr_3) (**31**). Complex **31** also can be prepared by addition of sodium methoxide to a tetrahydrofuran solution of the cationic hydride carbyne **30**.

Scheme 10



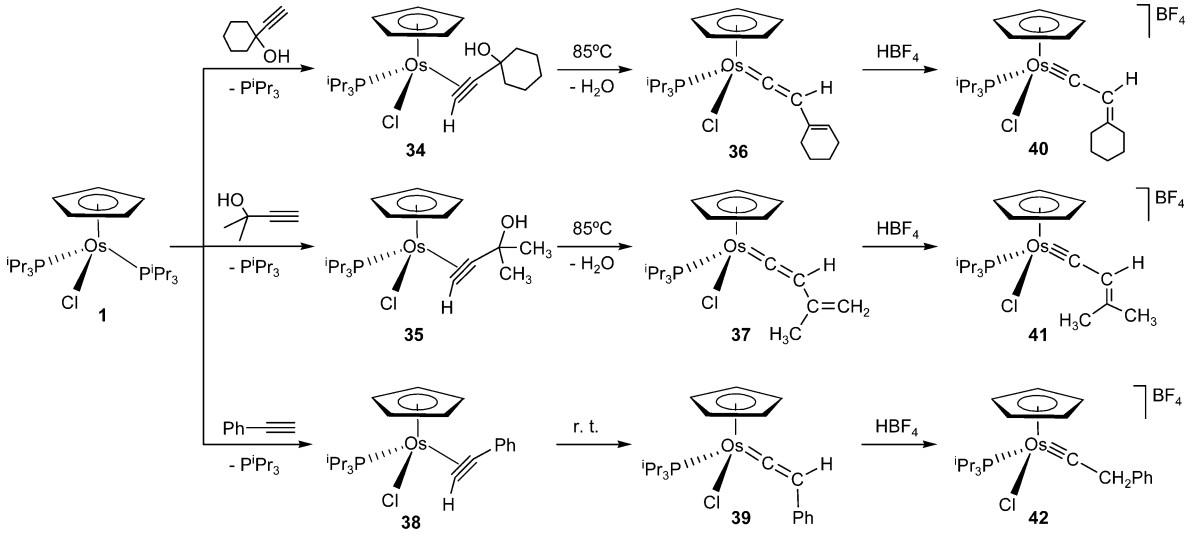
Scheme 11



In methanol, at room temperature, complex **31** was converted into the hydride alkoxycarbene derivative OsH(η^5-C_5H_5){=C(OMe)Ph}(P^iPr_3) (**32**) as a consequence of the addition of the O−H bond of the alcohol to the Os−C triple bond (Scheme 11). The reaction of **31** with phenol gave the hydride−metallacycle−osmium(IV) derivative OsH(η^5-C_5H_5){CH(Ph)OC_6H_4}(P^iPr_3) (**33**). The formation of **33** can be rationalized as a process involving the initial addition of the O−H bond of phenol to the Os−C triple bond of **31**, to give a hydride alkoxycarbene intermediate similar to that isolated from the reaction with methanol. The subsequent migration of the hydride ligand from the metal center to the C_α atom of the carbene should afford an unsaturated species, which could be converted to **33** by C−H activation of one of the ortho CH bonds of the OPh group.

In agreement with the tendency shown by **1** to release a triisopropylphosphine ligand, treatment of this compound with 1-ethynyl-1-cyclohexanol and 2-methyl-3-butyn-2-ol in pentane led to the π-alkyne compounds

Scheme 12

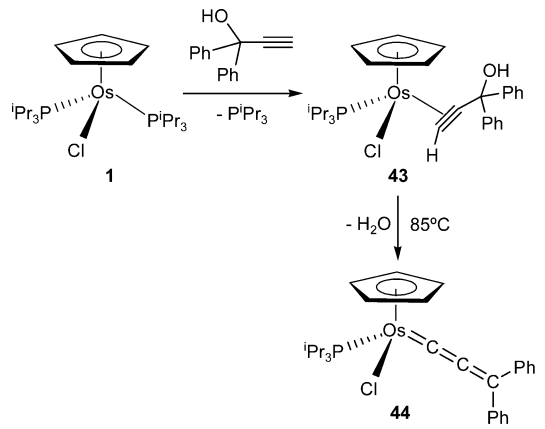


$Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}CC(OH)(CH_2)_4CH_2\}(P^iPr_3)$ (**34**) and $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}CC(OH)(CH_3)_2\}(P^iPr_3)$ (**35**), which were converted to the corresponding alkenylvinylidene derivatives $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}CHC{=}CH(CH_2)_3CH_2\}(P^iPr_3)$ (**36**) and $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}CHC(CH_3){=}CH_2\}(P^iPr_3)$ (**37**) by loss of a water molecule (Scheme 12). The formation of **36** and **37** most probably involves hydroxyvinylidene intermediates, which spontaneously undergo dehydration.[16] Complex **37** can also be prepared from 2-methyl-1-buten-3-yne. In this case, a π-alkyne intermediate related to **34** and **35** has not been detected, even at −60 °C. In contrast to the enyne, the reaction with phenylacetylene initially yielded $Os(\eta^5\text{-}C_5H_5)Cl(\eta^2\text{-}HC{\equiv}CPh)(P^iPr_3)$ (**38**), which rapidly was changed to the vinylidene $Os(\eta^5\text{-}C_5H_5)Cl(={C}={CHPh})(P^iPr_3)$ (**39**). Treatment of **36** and **37** with $HBF_4{\cdot}OEt_2$ gave the alkenylcarbyne complexes $[Os(\eta^5\text{-}C_5H_5)Cl\{{\equiv}CCH{=}C(CH_2)_4CH_2\}(P^iPr_3)]BF_4$ (**40**) and $[Os(\eta^5\text{-}C_5H_5)Cl\{{\equiv}CCH{=}C(CH_3)_2\}(P^iPr_3)]BF_4$ (**41**), respectively. Similarly, protonation of **39** afforded $[Os(\eta^5\text{-}C_5H_5)Cl({\equiv}CCH_2Ph)(P^iPr_3)]BF_4$ (**42**).

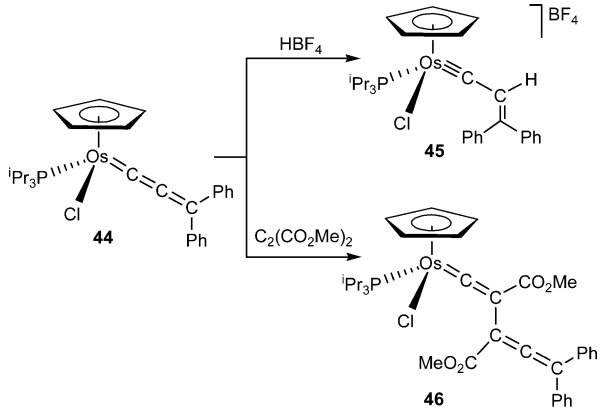
The addition of 1,1-diphenyl-2-propyn-1-ol to a pentane solution of **1** caused the displacement of a phosphine ligand and the formation of the π-alkyne complex $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}(P^iPr_3)$ (**43**), which afforded the allenylidene derivative $Os(\eta^5\text{-}C_5H_5)Cl(={C}={C}={CPh_2})(P^iPr_3)$ (**44**) in toluene at 85 °C (Scheme 13).[29]

The allenylidene ligand of **44** has a marked nucleophilic character, which was demonstrated by its inert behavior toward alcohols, diphenylphosphine, benzophenone imine, and pyrazole and in its reactions with HBF_4 and dimethyl acetylenedicarboxylate (Scheme 14), which afforded $[Os(\eta^5\text{-}C_5H_5)Cl({\equiv}CCH{=}CPh_2)(P^iPr_3)]BF_4$ (**45**) and $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}C(CO_2Me)C(CO_2Me){=}C{=}CPh_2\}(P^iPr_3)$ (**46**), respectively. The alkenylcarbyne complex **45** is the result of the attack of the proton from the acid at the C_β atom of the allenylidene ligand, whereas the formation of **46** involves the insertion of the electron-withdrawing alkyne into the $C_\alpha{-}C_\beta$ double bond of the

Scheme 13



Scheme 14

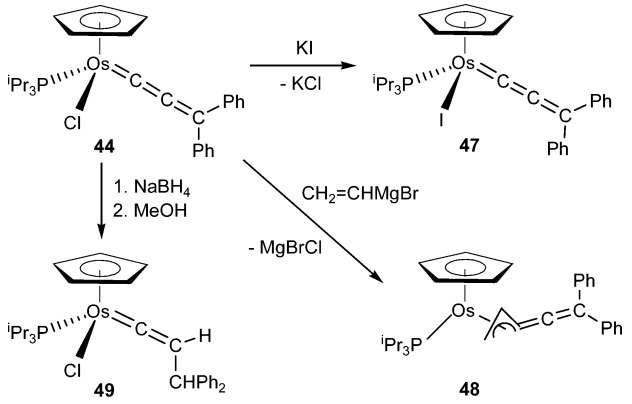


allenylidene ligand. The process has been rationalized as a stepwise cycloaddition to form a η^1-cyclobutenyl intermediate, which rapidly ring opens to give the allenylvinylidene product.

The reactivity of **44** is not limited to the nucleophilic power of the C_β atom of the allenylidene, but the chloride ligand also is activated toward nucleophilic substitution (Scheme 15), as shown by its reaction with KI to give $Os(\eta^5\text{-}C_5H_5)I(={C}={C}={CPh_2})(P^iPr_3)$ (**47**). This property is most probably responsible for the formation of the pentatrienyl derivative $Os(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2CHC{=}C{=}CPh_2)(P^iPr_3)$ (**48**), as a result of the reaction of **44**

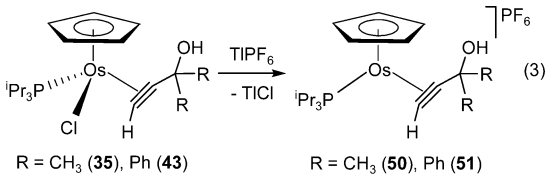
(29) Crochet, P.; Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1998**, *17*, 3479.

Scheme 15



with CH_2=CHMgBr. In this respect, complex **44** shows a behavior similar to that of MCl(=C=C=CPh_2)(P^iPr_3)$_2$ (M = Rh, Ir).[30] With regard to the mechanism of formation of the pentatrienyl ligand, it has been proposed that initially nucleophilic substitution of the chloride ligand takes place and a vinyl−metal intermediate is generated. This should rearrange by migratory insertion of the allenylidene ligand into the Os−vinyl bond to give **48**.[29] An alternative pathway involving the direct attack of the vinyl nucleophile at the C_α atom of the allenylidene followed by elimination of chloride with concomitant η^1 to η^3 rearrangement also could be considered. However, this seems less likely, since the allenylidene ligand is inert toward nucleophiles, as has been mentioned previously. Also noteworthy is the reduction of the C_β−C_γ double bond of the allenylidene ligand of **44** by the action of $NaBH_4$ and some drops of methanol, which gave the vinylidene derivative Os(η^5-C_5H_5)Cl(=C=CHCHPh_2)(P^iPr_3) (**49**).

Treatment of the π-alkyne complexes **35** and **43** with $TlPF_6$ produced the abstraction of the chloride ligand and the formation of [Os(η^5-C_5H_5){η^2-HC≡CC(OH)R_2}(P^iPr_3)]PF_6 (R = CH_3 (**50**), Ph (**51**)) according to eq 3.



The chemical bonding in transition-metal alkyne complexes can be described in a way similar to that for the transition-metal alkene complexes. The bonding is considered to arise from donor−acceptor interactions between the alkyne ligand and the transition metal (**a** and **c** in Figure 1). A major difference between alkene and alkyne complexes is that the alkyne ligand has a second occupied π orbital orhogonal to the MC_2 plane ($\pi_\perp$) which, in some cases, engages in the transition metal−alkyne bonding. In that case, the alkyne is a four-electron-donor ligand (**a**−**c** in Figure 1).

The abstraction of the chloride ligand from **35** and **43** causes the interaction between an empty d orbital of the osmium atom and the $\pi_\perp$ orbital of the alkynes.[31] As a result, the structural parameters and the spectroscopic properties of the alkynes undergo significant disturbances. The Os−alkyne distances are shortened, and in the $^{13}C\{^1H\}$ and ^1H NMR spectra, the chemical shifts of the acetylenic carbon and HC≡ hydrogen resonances are shifted toward lower field. DFT calculations on the model compounds Os(η^5-C_5H_5)Cl(η^2-HC≡CR)(PH_3) and [Os(η^5-C_5H_5)(η^2-HC≡CR)(PH_3)]$^+$ indicated that both structural and spectroscopic changes are, in fact, a consequence of the participation of the acetylenic second π ($\pi_\perp$) orbital in the bonding of **50** and **51**.

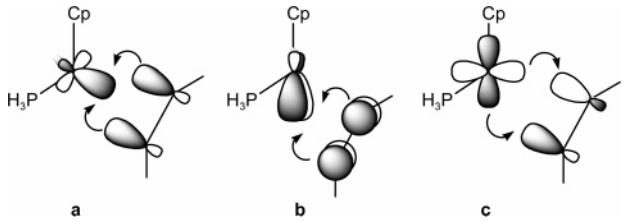
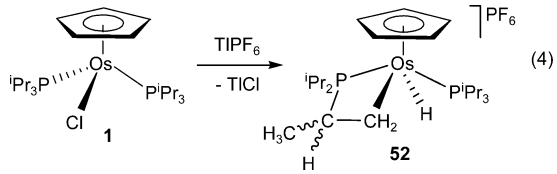


Figure 1. Schematic representation of the donative (**a** and **b**) and back-donative (**c**) interactions for metal−alkyne bonding in the complex [Os(η^5-C_5H_5)(η^2-HC≡CH)(PH_3)]$^+$.

The theoretical calculations also showed that in systems of this type the interaction between the $\pi_\perp$ orbital of the alkyne and an empty d orbital of the osmium gives rise to an increase of the dissociation energy of the alkyne and an increase of the energy of the rotation of the alkyne around the osmium−alkyne axis. The enhancement in the rotation barrier is due to the need of cleaving the $\pi_\perp$−M interaction, which makes rotation proceed via a formally unsaturated 16-electron path.

Abstraction of the Chloride Substituent: C−H and P−H Activation Reactions

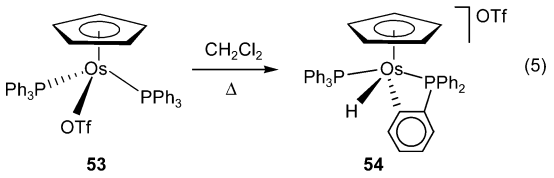
In methanol and acetone, the chloride substituent of complex **1** dissociates and the resulting unsaturated metal fragment is capable of activating a methyl C−H bond of one of the triisopropylphosphine ligands to afford a 1:1 equilibrium mixture of the two possible stereoisomers of the cationic derivative [OsH(η^5-C_5H_5)-{$CH_2CH(CH_3)P^iPr_2$}(P^iPr_3)]$^+$ (**52**). This species was isolated as the PF_6 salt (eq 4) either by addition of $NaPF_6$ to a methanol solution of **1** (61% yield) or by addition of $TlPF_6$ to an acetone solution of the same compound (86% yield).



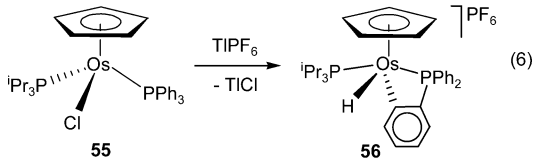
Tilley and co-workers have observed that the bis(triphenylphosphine) derivative Os(η^5-C_5H_5)(OTf)(PPh_3)$_2$ (**53**) is transformed in a similar way into the ortho-metalated species [OsH(η^5-C_5H_5)($C_6H_4PPh_2$)(PPh_3)]OTf (**54**) in dichloromethane solution and in the solid state under nitrogen (eq 5).[20b]

Although the arene C−H bond is between 14 and 8 kcal mol^{-1} stronger than the alkane C−H bond, in general, the activation of the former is kinetically and

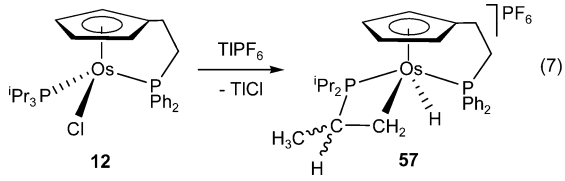
(30) Werner, H. *Chem. Commun*. **1997**, 903.
(31) Carbó, J. J.; Crochet, P.; Esteruelas, M. A.; Jean, Y.; Lledós, A.; López, A. M.; Oñate, E. *Organometallics* **2002**, *21*, 305.



thermodynamically favored. The kinetic advantage of the arene activation appears to be due to its prior η^2 coordination, while the thermodynamic preference has been largely attributed to a metal−carbon bond much stronger for aryl than for alkyl.[32] In agreement with the preferred arene C−H activation, the mixed-phosphine ligand complex Os(η^5-C_5H_5)Cl(PPh_3)(P^iPr_3) (**55**), which was obtained by addition of 1.0 equiv of triphenylphosphine to a toluene solution of **1**, reacted with $TlPF_6$ to give [OsH(η^5-C_5H_5)($C_6H_4PPh_2$)(P^iPr_3)]PF_6 (**56**) as a result of the selective activation of a phenyl ring in the presence of the alkyl groups of the triisopropylphosphine (eq 6).[33]



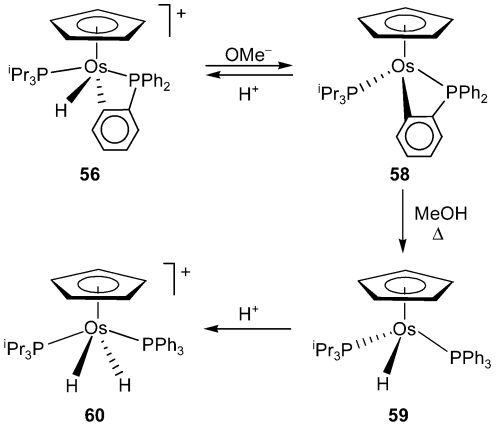
Similarly to the mixed-phosphine ligand complex **55**, the chloride ligand of **12**, which contains a PPh_2 moiety connected to the cyclopentadienyl ring, could be abstracted from the osmium atom with $TlPF_6$. The resulting metal center can activate a C−H bond of one of the substituents of the phosphine ligands. However, in this case, the C−H activation did not take place on a phenyl group, as for **55**, but on an isopropyl one (eq 7).[12a] Thus,



at room temperature, the treatment of **12** with 1.0 equiv of $TlPF_6$ in acetone afforded a 1:1 equilibrium mixture of the two possible stereoisomers of [OsH{[η^5-C_5H_4-$(CH_2)_2$]PPh_2}{$CH_2CH(CH_3)P^iPr_2$}]PF_6 (**57**).

The formation of **57** is a rare case of selective alkyl C−H activation in the presence of phenyl groups, which is in contrast with the kinetic and thermodynamic preference of the C−H arene activation over the C−H alkyl. The constriction imposed by the CH_2−CH_2 chain in the functionalized cyclopentadienyl ligand should not influence significantly the stability of the ortho-metalated ring resulting from the aryl C−H activation. Thus, it is reasonable to think that the isopropyl C−H activation in **12** is kinetic in origin. In agreement with this, it has been observed that the short-lived ruthenium(0) species Ru(η^6-C_6Me_6)(PPh_2R) (R = ^{i}Pr, ^{t}Bu), containing an alkyldiphenylphosphine ligand, initially gave cyclometalated complexes, as a result of the C−H activation of the alkyl substituent. In solution, these cyclometalated species rapidly isomerized into the thermodynamically favored aryl ortho-metalated derivatives.[34]

Scheme 16



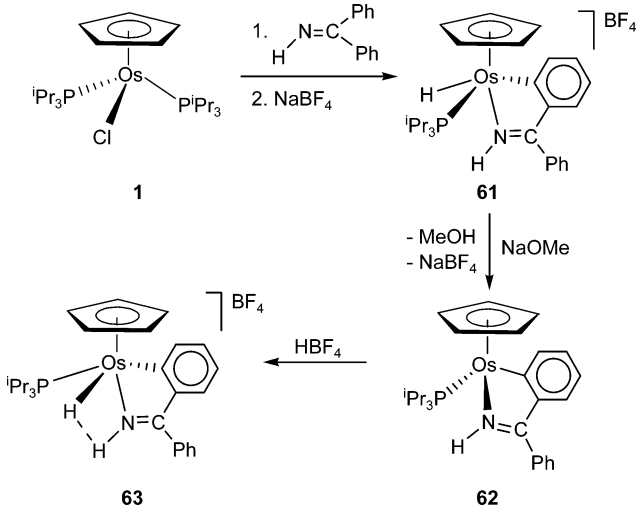
For arylphosphine ligands, the coordination of the phosphorus atom to the metal makes the η^2 coordination of the aryl group unfavorable. As a result, the barrier for the aryl activation increases with regard to the barrier for the simple arene activation. This increase can serve to locate the aryl activation barrier over the alkyl activation. In this case, the kinetic advantage for arene activation disappears and the weaker alkyl C−H bond is initially activated. In contrast to the metalated ruthenium derivatives, complex **57** does not convert into an ortho-metalated isomer. This suggests that the increase of the activation barrier for the arene activation in the case of arylphosphines is associated with the prior dissociation of the M−P bond. Thus, the strength of the Os−PPh_2 bond in the Os{[η^5-$C_5H_4(CH_2)_2$]PPh_2} moiety can explain why **57** does not change into an ortho-metalated isomer.

Treatment of a tetrahydrofuran solution of **56** with sodium methoxide caused the abstraction of the hydride ligand and the formation of the neutral complex Os(η^5-C_5H_5)($C_6H_4PPh_2$)(P^iPr_3) (**58**). The reaction is reversible (Scheme 16). The addition of 1.0 equiv of HBF_4·OEt_2 to a diethyl ether solution of **58** afforded the BF_4 salt of **56**. This suggests that the transoid disposition of the hydride ligand and the ortho-metalated group is favored not only kinetically but also thermodynamically.[33] In solution at room temperature, complex **58** is stable in toluene or benzene. However, in refluxing methanol, it is converted in quantitative yield to the monohydride OsH(η^5-C_5H_5)(PPh_3)(P^iPr_3) (**59**). Protonation of **59** with HBF_4·OEt_2 afforded the cationic dihydride [OsH_2(η^5-C_5H_5)(PPh_3)(P^iPr_3)]BF_4 (**60**).

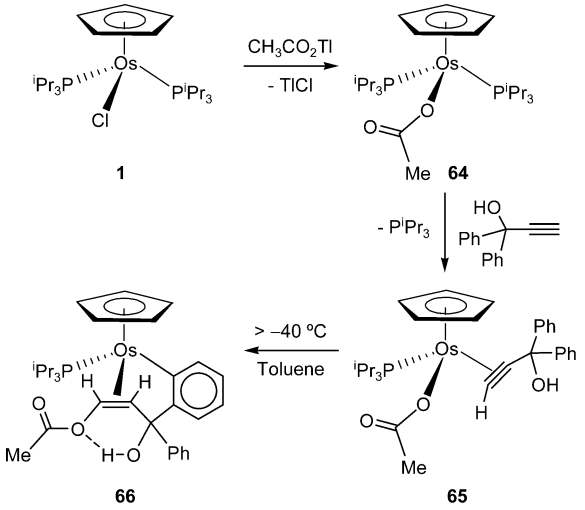
Benzophenone imine also undergoes *o*-CH activation of one of its phenyl groups. Treatment of **1** with benzophenone imine, in the presence of $NaBF_4$, gave the cationic ortho-metalated derivative [OsH(η^5-C_5H_5)-{$C_6H_4C(Ph)$=NH}(P^iPr_3)]BF_4 (**61**) that, in contrast to **56**, contains the hydride ligand and the metalated group mutally cisoid disposed. As **56**, complex **61** can be

(32) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.
(33) Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **2000**, *19*, 275.
(34) Bennet, M. A.; Huang, T.-N.; Latten, J. L. *J. Organomet. Chem.* **1984**, *272*, 189.

Scheme 17



Scheme 18



deprotonated (Scheme 17). The addition of sodium methoxide to a tetrahydrofuran solution of **61** gave the neutral compound Os(η^5-C_5H_5){$C_6H_4C(Ph)$=NH}(P^iPr_3) (**62**). Although the protonation of **62** afforded a hydride derivative, the deprotonation of **61** is not reversible. The addition of 1.0 equiv of HBF_4·OEt_2 to a diethyl ether solution of **62** led to **63**, which contains the hydride ligand and the metalated group mutually transoid disposed. In this isomer, the hydride and NH group of the imine are mutually cisoid. As a result, the separation between the hydride and NH hydrogen atom is short (about 2.5 Å), lying in the range reported for H···H interactions in four-membered rings of the type LH···H−M.[35]

The selective *o*-CH activation of one of the phenyl groups of 1,1-diphenyl-2-propyn-1-ol, along with a novel Os(η^5-C_5H_5)-mediated acetato plus 1,1-diphenyl-2-propyn-1-ol coupling has led to an interesting 2-{(*Z*)-3-acetoxy-1-hydroxy-1-phenyl-2-propenyl}aryl complex (Scheme 18).[36] Treatment of **1** with thallium acetate in dichloromethane afforded Os(η^5-C_5H_5){κ^1-OC(O)CH_3}-(P^iPr_3)$_2$ (**64**). Reaction of the latter with 1,1-diphenyl-2-propyn-1-ol yielded the π-alkyne compound Os(η^5-C_5H_5){κ^1-OC(O)CH_3}{η^2-HC≡CC(OH)Ph_2}(P^iPr_3) (**65**). In solution, complex **65** is unstable above −40 °C and rapidly is transformed into Os(η^5-C_5H_5){η^2-(*Z*)-CH[OC(O)CH_3]=CHC(OH)(Ph)C_6H_4}(P^iPr_3) (**66**).

It has been proposed that the addition of carboxylic acids to prop-2-yn-1-ols in the presence of transition-metal catalysts requires the initial π-coordination of the alkynol to the metal center, with subsequent attack of the carboxylate group at the coordinated carbon−carbon triple bond of the alkyne.[37] The reactions shown in Scheme 18 provide strong evidence in favor of this proposal.

The addition of the P−H bond of secondary phosphines to the Os(η^5-C_5H_5) fragment is favored with regard to the methyl C−H activation of triisopropylphosphine and the *o*-CH activation of an arylphosphine.[38] Similar to the reaction of **1** with triphenylphosphine, the addition of diphenylphosphine to a pentane solution of **1** afforded Os(η^5-C_5H_5)Cl($PHPh_2$)(P^iPr_3) (**67**). Treatment of **67** with $TlPF_6$ in moist acetone also caused the release of the chloride substituent. However, instead of a C−H activation reaction, the formation of [OsH_2(η^5-C_5H_5){$P(OH)Ph_2$}(P^iPr_3)]PF_6 (**68**) occurred. The generality of this reaction is evident in the synthesis of [OsH_2(η^5-C_5H_5){$P(OMe)Ph_2$}(P^iPr_3)]PF_6 (**69**), which was prepared by treatment of **67** with $TlPF_6$ in methanol (Scheme 19).

When the treatment of **67** with $TlPF_6$ was carried out in $(CD_3)_2CO$ containing D_2O and in CD_3OD, the deuterated complexes [OsHD(η^5-C_5H_5){$P(OD)Ph_2$}(P^iPr_3)]-PF_6 (**68-*d*$_2$**) and [OsHD(η^5-C_5H_5){$P(OCD_3)Ph_2$}(P^iPr_3)]-PF_6 (**69-*d*$_4$**) were obtained. The distribution of deuterium atoms in these compounds indicates that the formation of **68** and **69** takes place via the hydride phosphido intermediate [OsH(η^5-C_5H_5)(PPh_2)(P^iPr_3)]$^+$. This species is generated by intramolecular P−H oxidative addition of diphenylphosphine in the unsaturated [Os(η^5-C_5H_5)-($PHPh_2$)(P^iPr_3)]$^+$ metal fragment. Once the hydride phosphido species is formed, the RO−H addition to the Os−phosphido bond affords **68** and **69**.

Treatment of **68** with NaOMe in tetrahydrofuran resulted in its deprotonation and the formation of the dihydride−phosphinito−osmium(IV) derivative OsH_2-(η^5-C_5H_5){$P(O)Ph_2$}(P^iPr_3) (**70**). Under the same conditions **68-*d*$_2$** afforded OsHD(η^5-C_5H_5){$P(O)Ph_2$}(P^iPr_3) (**70-*d*$_1$**), which contains one deuterium atom at the hydride positions. This suggests that the deprotonation of **68** is a one-step process and occurs at the OH group of the $P(OH)Ph_2$ ligand. In contrast to **68**, treatment of **69** with sodium methoxide produced the abstraction of a hydride ligand, to form OsH(η^5-C_5H_5){$P(OMe)Ph_2$}-(P^iPr_3) (**71**).

Abstraction of the Chloride Substituent: Formation and Reactions of Cationic Vinylidene and Allenylidene Complexes

In the presence of $TlPF_6$ the C(sp)−H activation of an alkyne is favored with respect to the methyl C−H

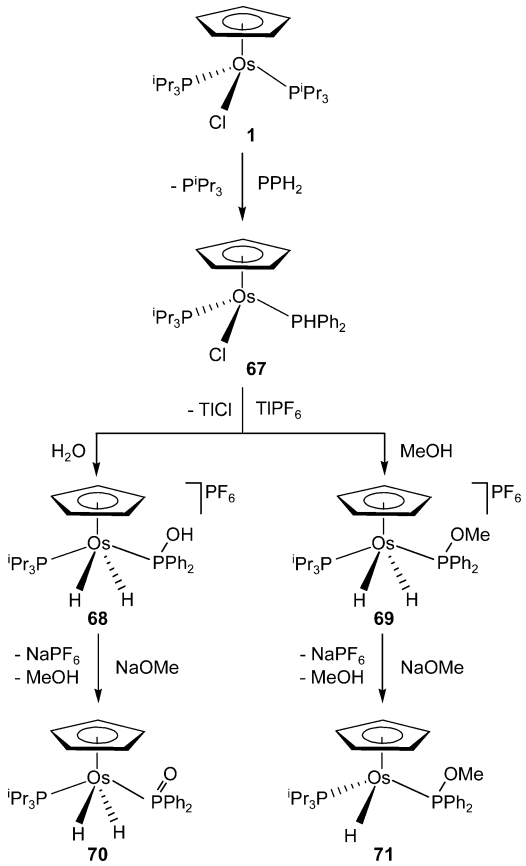
(35) Buil, M. L.; Esteuelas, M. A.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 3346.

(36) Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E. *Organometallics* **1998**, *17*, 3141.

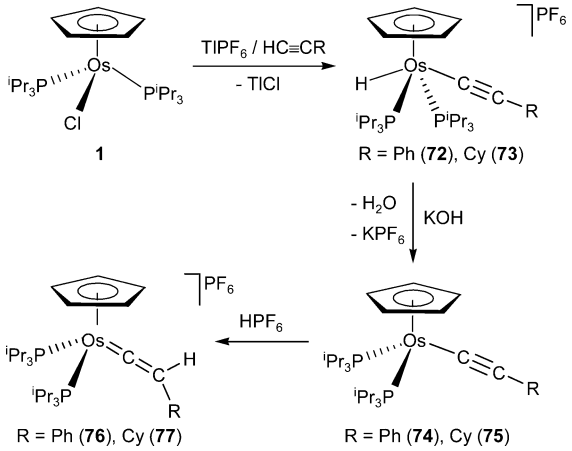
(37) Doucet, H.; Martín-Vaca, B.; Bruneau, C.; Dixneauf, P. H. *J. Org. Chem.* **1995**, *60*, 7247.

(38) Esteruelas, M. A.; López, A. M.; Tolosa, J. I.; Vela, N. *Organometallics* **2000**, *19*, 4650.

Scheme 19



Scheme 20



activation of a triisopropylphosphine ligand.[39] The combined treatment of **1** with alkynes such as phenylacetylene and cyclohexylacetylene and $TlPF_6$ gave the hydride−alkynyl−osmium(IV) complexes $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]PF_6$ (R = Ph (**72**), Cy (**73**)), as a result of C(sp)−H oxidative addition of the alkynes to the $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ metal fragment (Scheme 20). Ab initio calculations on the model complexes $[Os(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HC{\equiv}CH)(PH_3)_2]^+$ and $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CH)(PH_3)_2]^+$ showed that the π-alkyne model complex is 4.0 kcal mol^{-1} more stable than the hydride alkynyl compound.[40] This means that π-alkyne species, $[Os(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HC{\equiv}CR)(P^iPr_3)_2]^+$, are not intermediates in the formation of **72** and **73**, since they are thermodynamically more stable than the products of the oxidative addition. The formation of **72** and **73** must be rationalized by assuming that the oxidative addition of the C(sp)−H bond of the alkynes is a kinetically favored process with regard to the coordination of the carbon−carbon triple bond.[39]

Ab initio calculations also indicated that the vinylidene model complex $[Os(\eta^5\text{-}C_5H_5)(=C{=}CH_2)(PH_3)_2]^+$ is 22 kcal mol^{-1} more stable than $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CH)(PH_3)_2]^+$. However complexes **72** and **73** do not convert into the corresponding vinylidene complexes in the solid state or in solution. The formation of the vinylidenes $[Os(\eta^5\text{-}C_5H_5)(=C{=}CHR)(P^iPr_3)_2]PF_6$ (R = Ph (**76**), Cy (**77**)) requires the deprotonation of **72** and **73** with a strong base and the subsequent protonation of the resulting alkynyl−osmium(II) intermediates $[Os(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]^+$ (R = Ph (**74**), Cy (**75**)).[40]

In contrast to **72** and **73**, half-sandwich hydride−alkynyl−ruthenium(IV) compounds transform into vinylidene complexes, in solution.[41] To rationalize this finding, it has been proposed that the hydride substituent of the hydride−alkynyl−ruthenium(IV) species dissociates as a proton, yielding alkynyl−ruthenium(II) intermediates. Protonation of the latter at the C_β atom then affords the vinylidene derivatives.

The kinetic inertness of **72** and **73** has been attributed to the basicities of **74** and **75**, which are greater than those of related alkynyl−ruthenium(II) compounds, in agreement with the well-known increase of the basicity of transition-metal complexes as the metal is replaced by successively heavier metals from the same group.[42] As a consequence of the high basicity of **74** and **75**, the necessary energy for the dissociation of H^+ from **72** and **73** imposes a high activation barrier for the isomerization of the hydride−alkynyl−osmium(IV) complexes to the corresponding vinylidene derivatives.

The replacement of a triisopropylphosphine ligand and the cyclopentadienyl group by the [2-(diphenylphosphino)ethyl]cyclopentadienyl ligand increases the acidity of the hydride alkynyl intermediate.[12a] At −20 °C, treatment of **12** with phenylacetylene in the presence of $TlPF_6$ led initially to $[OsH\{[\eta^5\text{-}C_5H_4(CH_2)_2]PPh_2\}(C{\equiv}CPh)(P^iPr_3)]PF_6$ (**78**). However, in contrast to **72** and **73**, compound **78** isomerized into the vinylidene $[Os\{[\eta^5\text{-}C_5H_4(CH_2)_2]PPh_2\}(=C{=}CHPh)(P^iPr_3)]PF_6$ (**79**). In acetone at room temperature, the transformation was quantitative after 12 h (Scheme 21).

Because the rate-determining step for the isomerization of the hydride alkynyl to the vinylidene complex is the H^+ dissociation from the hydride alkynyl and, therefore, the protonation of the neutral alkynyl intermediate is very fast, the $Os\{[\eta^5\text{-}C_5H_4(CH_2)_2]PPh_2\}(C{\equiv}CPh)(P^iPr_3)$ (**80**) species was not detected during the isomerization of **78** to **79**. However, compound **80** can be prepared by deprotonation of the vinylidene ligand of **79** with potassium hydroxide in methanol. In agree-

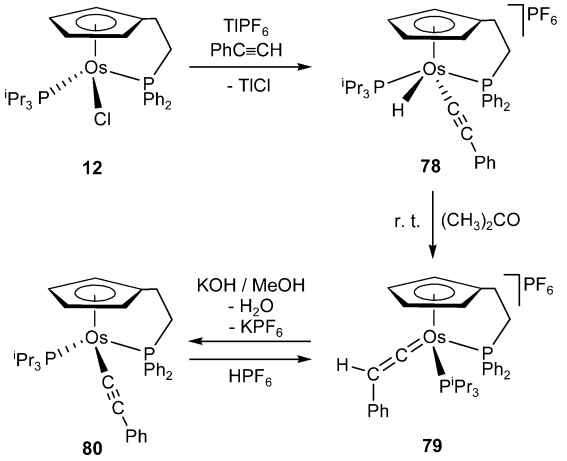
(39) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585.

(40) Baya, M.; Crochet, P.; Esteruelas, M. A.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **2001**, *20*, 4291.

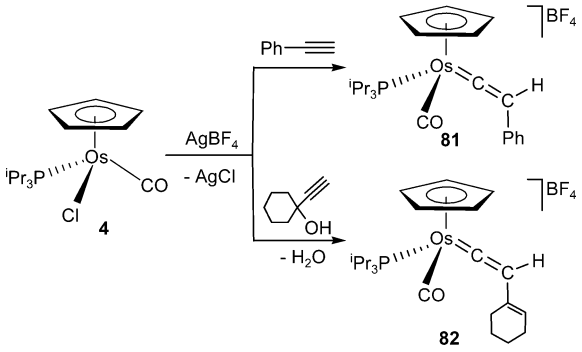
(41) (a) de los Ríos, I.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc*. **1997**, *119*, 6529. (b) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 950. (c) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4563.

(42) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc*. **2000**, *122*, 9155.

Scheme 21



Scheme 22

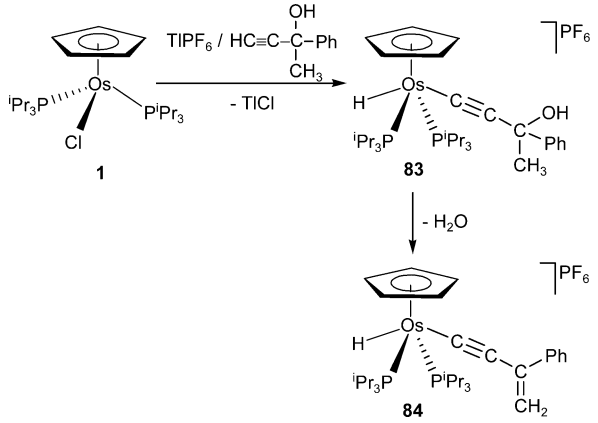


ment with the higher stability of **79** compared to **78**, the addition of 1.2 equiv of $HPF_6 \cdot H_2O$ to diethyl ether solutions of **80** produced the instantaneous precipitation of **79** in almost quantitative yield.

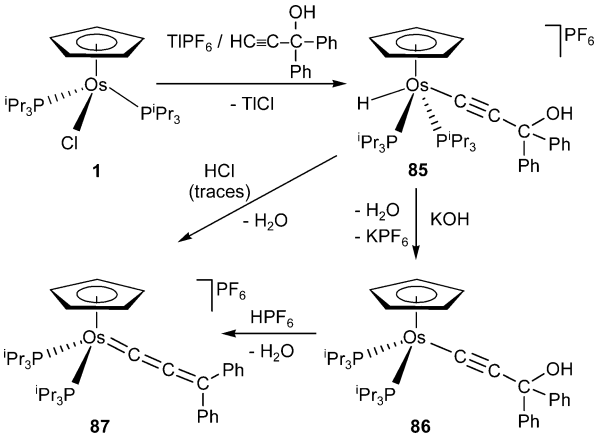
The increase in acidity of the hydride alkynyl intermediates, and therefore the falling off in stability, is a consequence of the decrease of the electron density at the metal center. Replacement of [2-(diphenylphosphino)ethyl]cyclopentadienyl by a carbonyl group and a cyclopentadienyl ligand, a more acidic combination than the cyclopentadienyl pendant phosphino moiety, produces a destabilization of the hydride−alkynyl−osmium(IV) intermediates, which were not observed during the fast formation of the vinylidene complexes. Thus, treatment of **4** with $AgBF_4$ and phenylacetylene or 1-ethynyl-1-cyclohexanol gave the stable vinylidene [Os(η^5-C_5H_5)(=C=CHPh)(CO)(P^iPr_3)]BF_4 (**81**) or alkenylvinylidene [Os(η^5-C_5H_5){=C=CHC=CH$(CH_2)_3CH_2$}(CO)(P^iPr_3)]BF_4 (**82**), respectively (Scheme 22).[23] Similarly, reactions of Os(η^5-C_5Me_5)I(CO)(PPh_3) with $AgBF_4$ and phenylacetylene or *tert*-butylacetylene gave [Os(η^5-C_5Me_5)(=C=CHR)(CO)(PPh_3)]BF_4 (R = Ph, ^{t}Bu).[43]

The reaction of **1** with 2-phenyl-3-butyn-2-ol and $TlPF_6$ resulted in formation of the hydride hydroxyalkynyl derivative [OsH(η^5-C_5H_5){C≡CC(OH)PhMe}(P^iPr_3)$_2$]PF_6 (**83**) by way of the oxidative addition of the H−C(sp) bond of the alkynol to the [Os(η^5-C_5H_5)(P^iPr_3)$_2$]$^+$ metal fragment. At room temperature, in chloroform solution, complex **83** is unstable and was converted in quantitative yield after 6 h to the hydride enynyl complex [OsH(η^5-C_5H_5){C≡CC(Ph)=CH_2}(P^iPr_3)$_2$]PF_6 (**84**), by dehydration of the hydroxyalkynyl ligand of **83** (Scheme 23). Similarly to **72** and **73**, complex **84** did not change to the corresponding alkenylvinylidene complex in the solid state or in solution.[39]

Scheme 23



Scheme 24

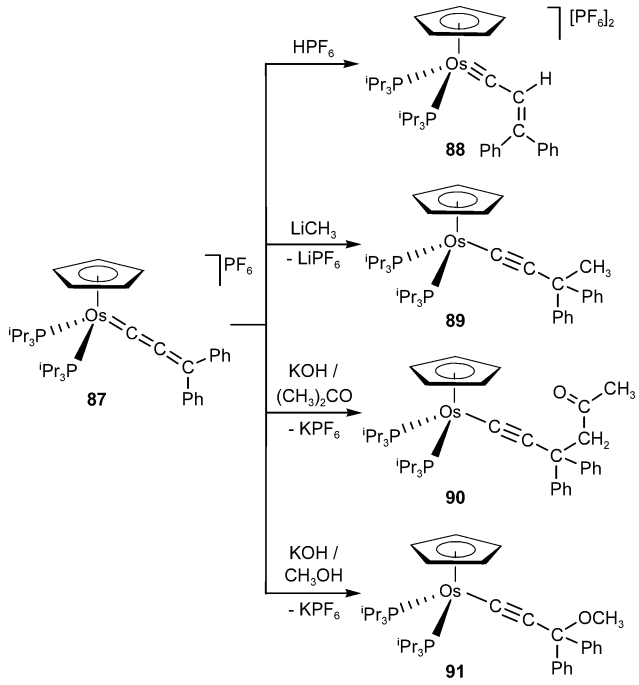


1,1-Diphenyl-2-propyn-1-ol reacted with **1** in the presence of $TlPF_6$ to give [OsH(η^5-C_5H_5){C≡CC(OH)Ph_2}(P^iPr_3)$_2$]PF_6 (**85**). In agreement with the fact that these bis(triisopropylphosphine) systems do not isomerize to the corresponding vinylidenes, complex **85** is stable in the solid state and in solution. Even the metal center can be deprotonated without affecting the alkynyl unit. Thus, the addition of KOH to a methanol solution of **85** afforded the neutral hydroxyalkynyl compound Os(η^5-C_5H_5){C≡CC(OH)Ph_2}(P^iPr_3)$_2$ (**86**). Complex **86** reacted with HPF_6 to give the allenylidene derivative [Os(η^5-C_5H_5)(=C=C=CPh_2)(P^iPr_3)$_2$]PF_6 (**87**) as a result of the protonation of the OH group of the hydroxyalkynyl ligand of **86** (Scheme 24). Complex **87** also can be obtained in a one-pot synthesis by maintaining **85** in refluxing chloroform for 6 h. The dehydration process is catalyzed by traces of HCl, which are derived from the solvent during the warming process. In accordance with this, the addition of some drops of an HCl toluene solution to **85** in dichloromethane produced instantaneous formation of **87**.

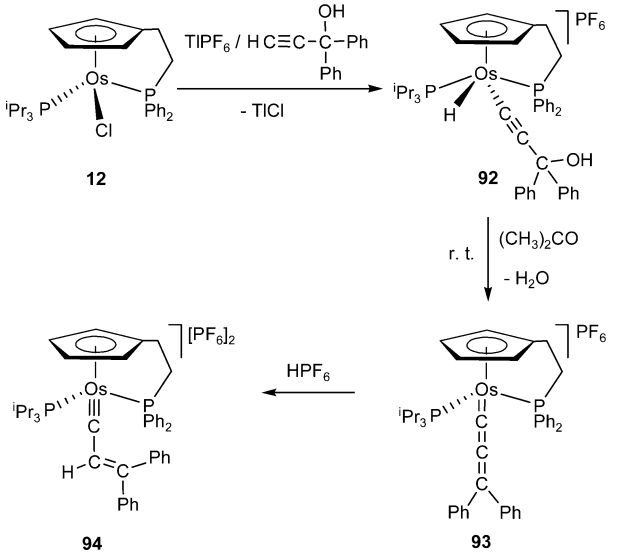
In agreement with the neutral compound **44**, the proton of HPF_6 added to the C_β atom of the C_3 chain of **87**. The addition of 1 equiv of this acid to acetone solutions of **87** gave the dicationic carbyne derivative [Os(η^5-C_5H_5)(≡CCH=CPh_2)(P^iPr_3)$_2$][PF_6]$_2$ (**88**). Complex **87** also reacted with methyllithium and with acetone

(43) Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1986**, *5*, 1337.

Scheme 25



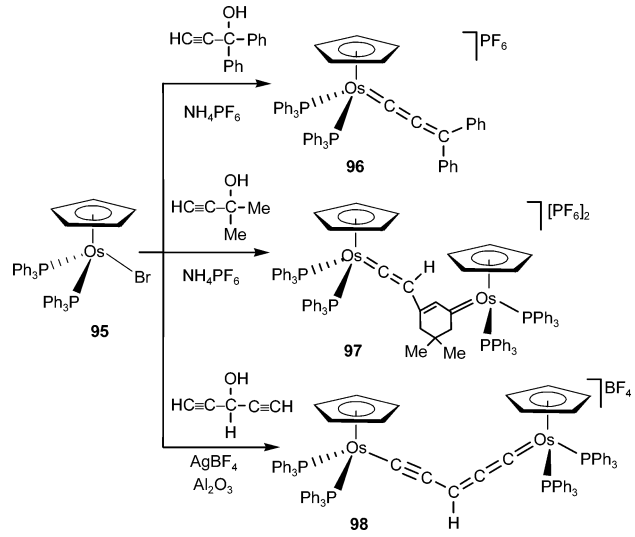
Scheme 26



and methanol solutions of KOH to give the alkynyl derivatives Os(η^5-C_5H_5){C≡CC(R)Ph_2}(P^iPr_3)$_2$ (R = CH_3 (**89**), $CH_2C(O)CH_3$ (**90**), OCH_3 (**91**)), respectively, as a result of the regioselective addition of the nucleophiles to the C_γ atom of the allenylidene ligand (Scheme 25).[39]

The replacement of the cyclopentadienyl ring and a triisopropylphosphine ligand by the [2-(diphenylphosphino)ethyl]cyclopentadienyl group also produces an increase of the acidity of the hydride−hydroxyalkynyl−osmium(IV) complexes.[12a] Treatment of an acetone solution of **12** with 1,1-diphenyl-2-propyn-1-ol and $TlPF_6$ at 10 °C led to formation of [OsH{[η^5-$C_5H_4(CH_2)_2$]PPh_2}-{C≡CC(OH)Ph_2}(P^iPr_3)]PF_6 (**92**), as a result of chloride abstraction from **12** and oxidative addition of the alkynol C(sp)−H bond to the unsaturated [Os{[η^5-C_5H_4-$(CH_2)_2$]PPh_2}(P^iPr_3)]PF_6 metal fragment (Scheme 26). In contrast to **85**, complex **92** lost a molecule of H_2O, giving the allenylidene derivative [Os{[η^5-$C_5H_4(CH_2)_2$]-PPh_2}(=C=C=CPh_2)(P^iPr_3)]PF_6 (**93**). In acetone at room temperature, the transformation was quantitative after 12 h. According to what was observed for half-sandwich ruthenium systems,[41] the dehydration of **92** to give **93** should proceed by way of a hydroxyvinylidene intermediate. Similarly to the case for **87**, complex **93** reacted with HPF_6 to afford the dicationic carbyne derivative [Os{[η^5-$C_5H_4(CH_2)_2$]PPh_2}(≡CCH=CPh_2)(P^iPr_3)][PF_6]$_2$ (**94**).

Scheme 27



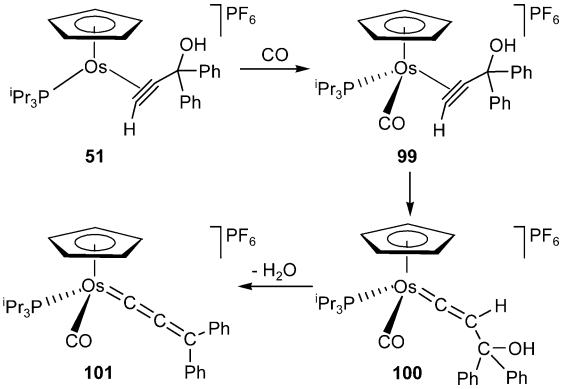
The replacement of alkylphosphines by arylphosphines certainly destabilizes the hydride−hydroxyalkynyl−osmium(IV) intermediates and facilitates the formation of the allenylidene derivatives (Scheme 27). The reaction of the bis(triphenylphosphine) complex Os(η^5-C_5H_5)Br(PPh_3)$_2$ (**95**) with 1,1-diphenyl-2-propyn-1-ol and NH_4PF_6 directly formed the allenylidene complex [Os-(η^5-C_5H_5)(=C=C=CPh_2)(PPh_3)$_2$]PF_6 (**96**). Under the same conditions 2-methyl-3-butyn-2-ol afforded a dicationic diosmium vinylidene alkylidene complex of the formula [{(η^5-C_5H_5)Os(PPh_3)$_2$}$_2$(μ-$C_{10}H_{12}$)][PF_6]$_2$ (**97**),[44] whereas treatment of **95** with $AgBF_4$, 0.5 equiv of HC≡CCH(OH)C≡CH, and Al_2O_3 gives [(η^5-C_5H_5)(PPh_3)$_2$Os=C=C=CHC≡COs(PPh_3)$_2$(η^5-C_5H_5)]BF_4 (**98**).[45] The indenyl complexes [Os(η^5-C_9H_7)(=C=C=CR_2)(PPh_3)$_2$]PF_6 (R_2 = Ph_2, C_8H_{12}) have been prepared by reaction of Os(η^5-C_9H_7)Cl(PPh_3)$_2$ with the corresponding HC≡CC(OH)-R_2 substrate and $NaPF_6$ in refluxing methanol.[46]

The four-electron alkyne complex **51** affords a general method to prepare mixed-ligand allenylidene derivatives of the type [Os(η^5-C_5H_5)(=C=C=CPh_2)L(P^iPr_3)]$^+$.[47]

Under 1 atm of carbon monoxide, complex **51** rapidly coordinated a carbon monoxide molecule to give the carbonyl intermediate [Os(η^5-C_5H_5){η^2-HC≡CC(OH)-Ph_2}(CO)(P^iPr_3)]PF_6 (**99**), according to Scheme 28. Since complex **51** is a saturated species, one might think that the first step in the formation of **99** is the transformation of the π-alkyne ligand from a four-electron to a two-electron donor. This involves the rupture of the overlap

(44) Lalrempuia, R.; Yennawar, H.; Mozharivskyj, Y. A.; Kollipara, M. R. *J. Organomet. Chem*. **2004**, *689*, 539.
(45) Xia, H. P.; Ng, W. S.; Ye, J. S.; Li, X.-Y.; Wong, W. T.; Lin, Z.; Yang, C.; Jia, G. *Organometallics* **1999**, *18*, 4552.
(46) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137.
(47) Asensio, A.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 5787.

Scheme 28



between the $\pi_\perp$ orbital of the alkyne and the corresponding metal fragment orbital, which occurs when the alkyne rotates 90°. DFT calculations gave for this process an energy of 32.7 kcal mol^{-1},[31] which is too large to be consistent with the observed reaction rate to form the carbonylation product.

Nucleophilic attack at four-electron-donor alkyne ligands is a particularly noteworthy class of reaction.[48] In this context, it should be mentioned that the $\pi_\perp$* orbital is of local a_2 symmetry (within the C_{2v} group), which prevents it from significantly interacting with the filled metal d orbitals.[31] Because the $\pi_\perp$* orbital is unoccupied, it has been proposed that the mechanism of the carbonylation of **51** involves initial attack of the carbonyl group at the alkyne and subsequent β-transfer to the metal center.

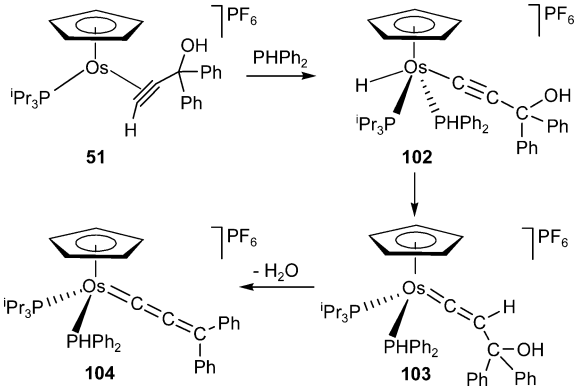
In dichloromethane at room temperature under argon, complex **99** converted to the hydroxyvinylidene derivative [Os(η^5-C_5H_5){=C=CHC(OH)Ph_2}(CO)(P^iPr_3)]PF_6 (**100**), which underwent dehydration to afford the allenylidene complex [Os(η^5-C_5H_5){=C=C=CPh_2}(CO)(P^iPr_3)]PF_6 (**101**) before the **99** to **100** change was complete.[47]

In contrast to carbon monoxide, diphenylphosphine reacted with **51** to give the hydride−hydroxyalkynyl−osmium(IV) derivative [OsH(η^5-C_5H_5){C≡CC(OH)Ph_2}($PHPh_2$)(P^iPr_3)]PF_6 (**102**). In a manner similar to that for **99**, the formation of **102** should involve the initial nucleophilic attack of the phosphine at the coordinated π-alkyne of **51** and subsequent β-transfer of $PHPh_2$ to the metal center. The resulting diphenylphosphine triisopropylphosphine intermediate could transform to **102** by C(sp)−H activation of the alkyne. In dichloromethane, complex **102** slowly changed to its hydroxyvinylidene isomer [Os(η^5-C_5H_5){=C=CHC(OH)Ph_2}($PHPh_2$)(P^iPr_3)]PF_6 (**103**). At 55 °C, complex **103** dehydrated to afford the allenylidene [Os(η^5-C_5H_5)(=C=C=CPh_2)($PHPh_2$)(P^iPr_3)]PF_6 (**104**), which was isolated after 24 h as a dark red solid in almost quantitative yield (Scheme 29).

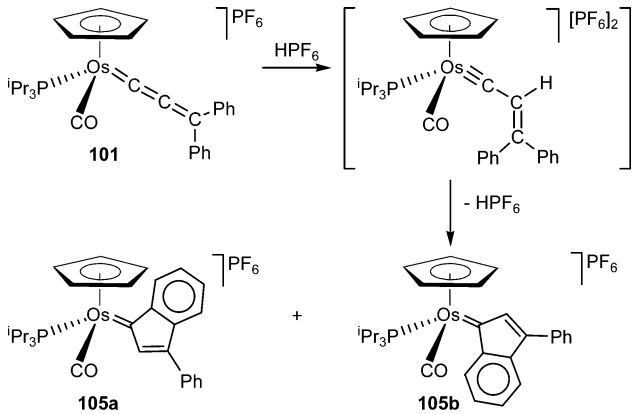
EHT-MO calculations on the model complexes [Os(η^5-C_5H_5)(=C=C=CH_2)(CO)(PH_3)]$^+$ and [Os(η^5-C_5H_5)(=C=C=CH_2)(PH_3)$_2$]$^+$ indicated that the allenylidene coordinates to the metal centers as a σ-donor and π-acceptor ligand.[39] The latter component of the bond is stronger than the first. As a result, a net charge is transferred from the metal fragment to the allenylidene.

(48) (a) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1. (b) Frohnapfel, D. S.; Templeton, J. L. *Coord. Chem. Rev.* **2000**, *206−207*, 199.

Scheme 29



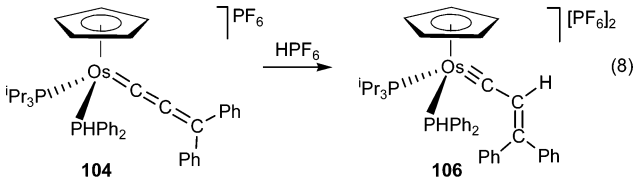
Scheme 30



The magnitude of the total charge on the allenylidene of the bis(phosphine) complex [Os(η^5-C_5H_5)(=C=C=CH_2)(PH_3)$_2$]$^+$ is about 57% higher than that on the allenylidene ligand of the carbonyl phosphine compound [Os(η^5-C_5H_5)(=C=C=CH_2)(CO)(PH_3)]$^+$. In accordance with this, there are significant differences of behavior between the carbonyl phosphine complex **101** and the diphosphine compounds **87**, **93**, and **104**.

Treatment at room temperature of dichloromethane solutions of **101** with HPF_6 gave the indenylidene derivative [Os(η^5-C_5H_5)(3-phenyl-1-indenylidene)(CO)(P^iPr_3)]PF_6 (**105**), which was isolated as a 1:1 mixture of the two possible rotamers resulting from a high barrier to the rotation of the indenylidene group around the Os−indenylidene bond. Isotope labeling experiments suggest that its formation involves the initial attack of the proton of the acid at the C_β atom of the allenylidene of **101**. The addition affords a dicationic carbyne intermediate, related to **88** and **94** (Scheme 30), which is converted to **105** by electrophilic substitution of an ortho proton of one of the phenyl groups by the C_α atom of the alkenylcarbyne unit.[47]

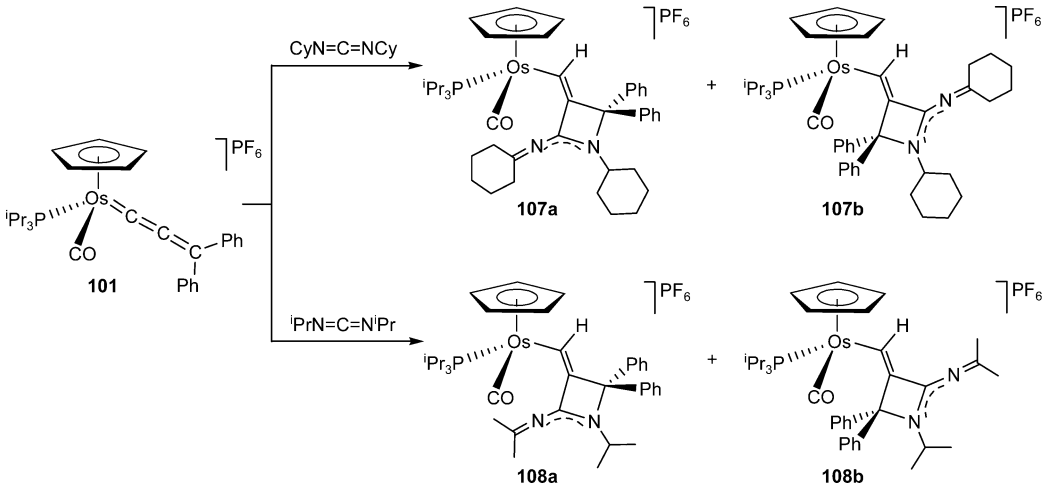
In agreement with **87** and **93**, **104** reacted with HPF_6 to give [Os(η^5-C_5H_5)(≡CCH=CPh_2)($PHPh_2$)(P^iPr_3)][PF_6]$_2$ (**106**), according to eq 8.



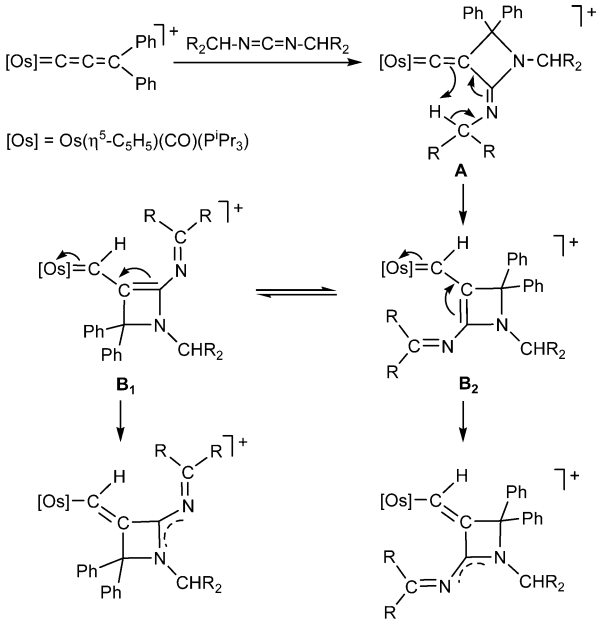
(8)

Complexes **101** and **104** show significant differences of behavior not only in the presence of HPF_6 but also in

Scheme 31



Scheme 32



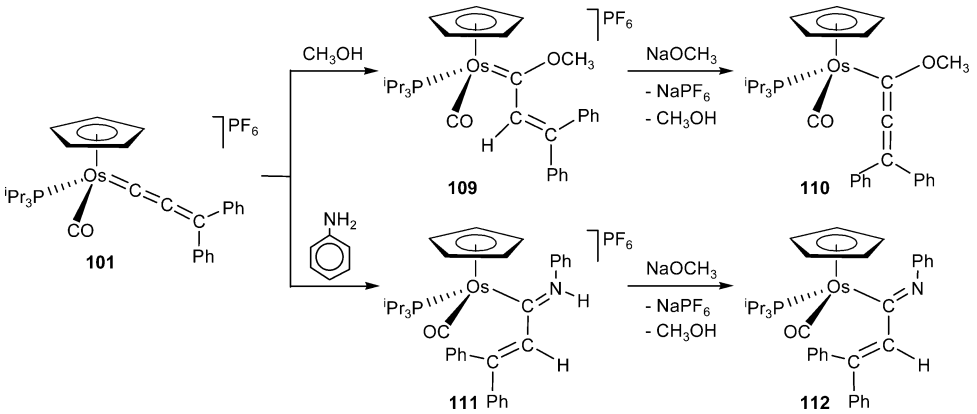
the presence of carbodiimides. While complex **101** reacted with *N*,*N*′-dicyclohexylcarbodiimide and *N*,*N*′-diisopropylcarbodiimide to give the iminiumazetidinylidene methyl derivatives $[Os(\eta^5\text{-}C_5H_5)\{CH{=}\overline{CC(Ph)_2N(Cy){=}{=}C{=}{=}N{=}C(CH_2)_4CH_2}\}(CO)(P^iPr_3)]PF_6$ (**107**) and $[Os(\eta^5\text{-}C_5H_5)\{CH{=}\overline{CC(Ph)_2N(^iPr){=}{=}C{=}{=}N{=}C(CH_3)_2}\}(CO)(P^iPr_3)]PF_6$ (**108**), respectively, which were isolated as mixtures of the isomers *Z* and *E* shown in Scheme 31, complex **104** was inert.

The formation of **107** and **108** has been rationalized as [2 + 2] cycloadditions between one of the carbon−nitrogen double bonds of the carbodiimides and the C_β−C_γ double bond of the allenylidene ligand of **101** (Scheme 32). The cycloadditions give intermediate **A**, which rapidly is changed to **B** by an Alder-ene reaction, where the C_α−C_β double bond of **A** acts as an enophile. The formation of *Z*−*E* isomeric mixtures suggests that intermediate **B** exists as a mixture in an equilibrium between the isomers $\mathbf{B}_1$ and $\mathbf{B}_2$. The [2 + 2] cycloadditions must occur via a polar mechanism, by initial attack of one of the N atoms of the carbodiimides at the C_γ atom of the allenylidene ligand. Thus, the difference in behavior between **101** and **104** could be related to the presence of a carbonyl group in **101**, which enhances the electrophilic character of the C_γ atom of the allenylidene ligand. Similar mechanisms have been proposed for the formation of the ruthenium counterpart $[Ru(\eta^5\text{-}C_5H_5)\{CH{=}\overline{CC(Ph)_2N(Cy){=}{=}C{=}{=}N{=}C(CH_2)_4CH_2}\}(CO)(P^iPr_3)]PF_6$[49] and for the cycloaddition of aromatic imines to the C_γ−C_δ double bond of the butatrienylidene ligand of the cation $[Ru(\eta^5\text{-}C_5H_5)(=C=C=C=CH_2)(CO)(PPh_3)]^+$.[50]

Complex **101** shows the typical behavior of a diarylallenylidene complex with α-electrophilic character,[51] adding RXH molecules at the C_α−C_β double bond to afford Fischer-type alkenylcarbene derivatives (Scheme 33). Thus, in methanol solution, it is converted to the α,β-unsaturated alkoxycarbene derivative $[Os(\eta^5\text{-}C_5H_5)\{{=}C(OCH_3)CH{=}CPh_2\}(CO)(P^iPr_3)]PF_6$ (**109**). Treatment of **109** with sodium methoxide in tetrahydrofuran caused deprotonation of the alkenyl group of the alkoxycarbene ligand to give the allenyl derivative $Os(\eta^5\text{-}C_5H_5)\{C(OCH_3){=}C{=}CPh_2\}(CO)(P^iPr_3)$ (**110**). Complex **101** also reacted with aniline. The reaction gave the azoniabutadienyl complex $[Os(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}NHPh\}(CO)(P^iPr_3)]PF_6$ (**111**). As for **109**, complex **111** underwent deprotonation in the presence of bases. However, the deprotonation does not take place at the $CH{=}CPh_2$ group but at the nitrogen atom. Treatment of a tetrahydrofuran solution of **111** with sodium meth-

(49) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1999**, *18*, 1606.
(50) Bruce, M. I.; Hinterding, P.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Chem. Commun*. **1997**, 715.
(51) (a) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423. (b) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826. (c) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 2297. (d) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E. *Organometallics* **1998**, *17*, 3567. (e) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *17*, 4959. (f) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1998**, *17*, 5434. (g) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Modrego, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4995. (h) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **2000**, *19*, 4. (i) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Oliván, M.; Oñate, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2000**, *19*, 4327. (j) Baya, M.; Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E.; Rodríguez, J. R. *Organometallics* **2002**, *21*, 1841. (k) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 162. (l) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 5274.

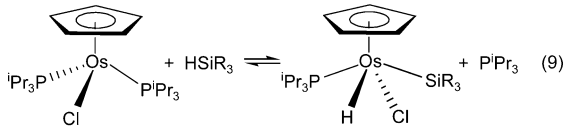
Scheme 33



oxide yielded the azabutadienyl derivative Os(η^5-C_5H_5)-{C(CH=CPh$_2$)=NPh}(CO)(P^iPr_3) (**112**).[47]

Formation and Reactions of Complexes Containing Group 14 Elements

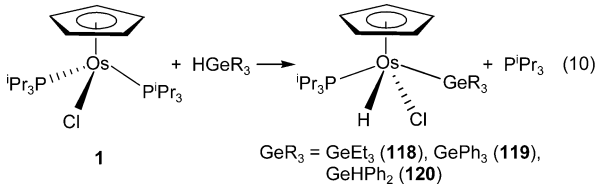
One of the phosphine ligands of **1** can be displaced by Lewis bases as weak as group 14 element hydride compounds.[52a] In the presence of silanes, equilibrium mixtures between **1** and the hydride silyl derivatives OsH(η^5-C_5H_5)Cl(SiR_3)(P^iPr_3) (SiR_3 = $SiEt_3$ (**113**), Si(CH_2-CH=CH_2)Me$_2$ (**114**), $SiPh_3$ (**115**), $SiHPh_2$ (**116**), SiH_2-Ph (**117**)) are formed (eq 9).



The constants for these equilibria increase in the sequence $HSiEt_3$ < $HSi(CH_2CH{=}CH_2)Me_2$ < $H_{4-x}SiPh_x$. This suggests that the stability of the Os−Si bond of the complexes OsH(η^5-C_5H_5)Cl(SiR_3)(P^iPr_3) is determined by the electronic nature of the substituents on the silicon atom. The more electronegative substituents appear to give the stronger metal−silicon bonds.[53] The strength of the metal−silyl bond also is determined by the cone angle of the silyl ligand. Thus, at room temperature, the addition of 1 equiv of H_2SiPh_2 to a benzene solution of **115** instantly results in quantitative formation of **116** and $HSiPh_3$.

The distribution of ligands around the osmium atom of **113**−**117** can be described as a piano-stool geometry with the phosphine and silyl ligands lying in the four-membered face, transoid disposed. This stereochemistry seems to be thermodynamically and kinetically favored and involves the approach of the Si−H bond to the osmium atom of an unsaturated Os(η^5-C_5H_5)Cl(P^iPr_3) fragment, parallel to the Cl−P vector with the Si atom on the chloride ligand side. The basis for this preference probably is steric and involves minimizing nonbonding interactions between the SiR_3 ligands and the isopropyl groups of the phosphine.[52a]

The addition of 1 equiv of $HGeEt_3$ to a benzene solution of **1** produced in quantitative yield the hydride−germyl complex OsH(η^5-C_5H_5)Cl($GeEt_3$)(P^iPr_3) (**118**). Similarly, treatment of **1** with $HGePh_3$ and H_2GePh_2 afforded OsH(η^5-C_5H_5)Cl($GePh_3$)(P^iPr_3) (**119**) and OsH-(η^5-C_5H_5)Cl($GeHPh_2$)(P^iPr_3) (**120**), respectively (eq 10).



Comparison of the yields of the reactions of **1** with $HSiEt_3$ and $HGeEt_3$ suggests that the oxidative addition of the H−Ge bond to **1** is more favored than oxidative addition of the H−Si bond. In agreement with this, addition of 1 equiv of $HGePh_3$ to a benzene solution of **115** instantly afforded **119** in quantitative yield. Since the bond enthalpy for the H−Si bond is only 1.1 times that for the H−Ge bond,[52b] these observations suggest that, in these systems, the Os−Ge bonds are significantly stronger than the Os−Si bonds. In contrast to the Os−Ge > Os−Si order, Otero and co-workers have found similar bond dissociation enthalpies for the Nb−Si and Nb−Ge bonds in complexes of the type NbH_2-(η^5-$C_5H_4SiMe_3$)$_2$(ER_3) (E = Si, Ge),[54] and Levy and Puddephatt have estimated that the Pt−EMe_3 bond dissociation energies for $PtXMe_2(EMe_3)$(bpy-$^tBu_2$) are 233 and 182 kJ mol^{-1} for E = Si, Ge, respectively.[55]

Similar to the reactions of **1** with germanes, the addition of 1 equiv of HSn^nBu_3 or $HSnPh_3$ to a benzene solution of **1** gave the hydride stannyl derivatives OsH-

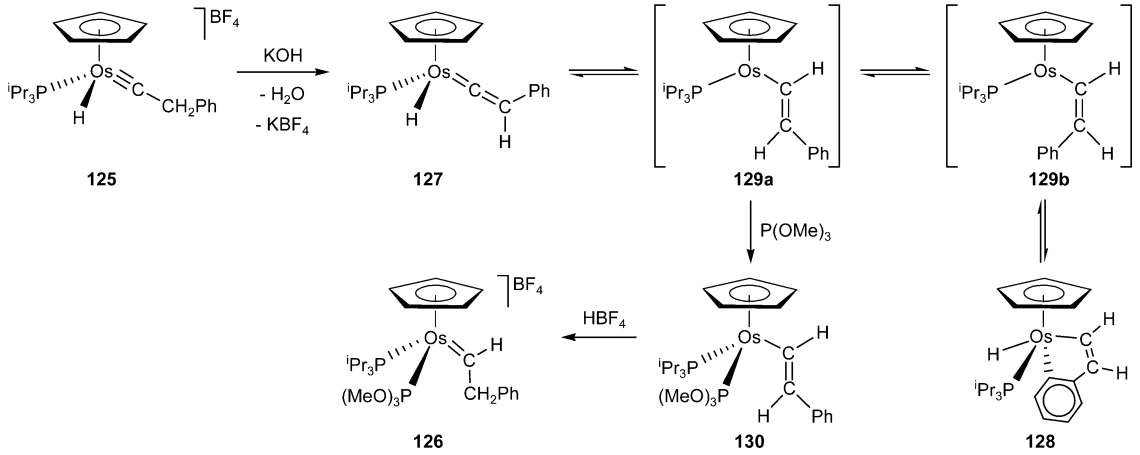
(52) (a) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Ruiz, N. *Organometallics* **1999**, *18*, 5034. (b) Jackson, R. A. *J. Organomet. Chem*. **1979**, *166*, 17.

(53) (a) Lichtenberger, D. L.; Rai-Chaudhuri, A. *J. Am. Chem. Soc*. **1991**, *113*, 2923. (b) Hübler, K.; Hunt, P. A.; Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Schwerdtfeger, P.; Wright, L. J. *Organometallics* **1997**, *16*, 5076.

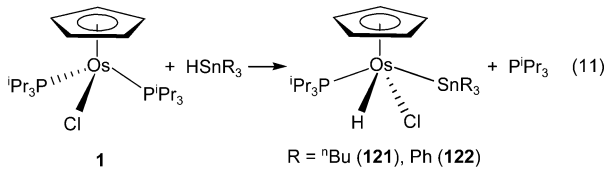
(54) Antiñolo, A.; Carrillo-Hermosilla, F.; Castel, A.; Fajardo, M.; Fernández-Baeza, J.; Lanfranchi, M.; Otero, A.; Pellinghelli, M. A.; Rima, G.; Satgé, J.; Villaseñor, E. *Organometallics* **1998**, *17*, 1523.

(55) Levy, C. J.; Puddephatt, R. J. *J. Am. Chem. Soc*. **1997**, *119*, 10127.

Scheme 34

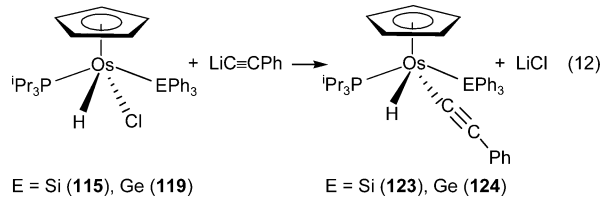


(η^5-C_5H_5)Cl(SnR_3)(P^iPr_3) (SnR_3 = Sn^nBu_3 (**121**), $SnPh_3$ (**122**)) in quantitative yield, according to eq 11.[52a]



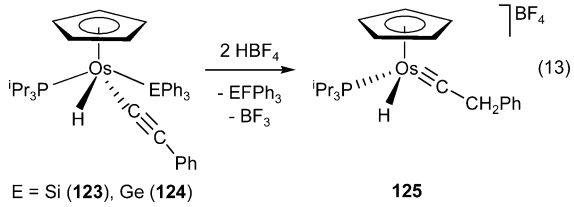
The Os−Sn bonds appear to be significantly stronger than the Os−Si bonds and slightly weaker than the Os−Ge bonds. Thus, the addition of 1 equiv of $HSnPh_3$ to a benzene solution of **115** gave **122** in quantitative yield, while under the same conditions **119** is in equilibrium with **122**.

Complexes **115** and **119** reacted with lithium phenylacetylide to give the hydride alkynyl derivatives OsH(η^5-C_5H_5)(C≡CPh)(EPh_3)(P^iPr_3) (E = Si, (**123**), Ge (**124**)), which were isolated in about 60% yield (eq 12).[56]



Species containing simultaneously hydride, alkynyl, and silyl ligands have been shown to be key intermediates in the formation of *cis*-alkenylsilanes and alkynylsilanes by hydrosilylation and dehydrogenative silylation of terminal alkynes.[57] However, only a few compounds of this type, or related complexes with stannyl or germyl instead of silyl substituents, have been isolated and characterized.[57c,58]

Complexes **123** and **124** reacted with 2.0 equiv of HBF_4·OEt_2 to give the hydride carbyne derivative [OsH(η^5-C_5H_5)(≡CCH_2Ph)(P^iPr_3)]BF_4 (**125**), according to eq 13.[59]



Complex **125** is stable in chloroform under argon, and the migration of the hydride to the C_α atom of the carbyne ligand was not observed. The addition of trimethyl phosphite to a chloroform solution of **125** gave a complex mixture of products which did not contain the carbene derivative [Os(η^5-C_5H_5)(=$CHCH_2$Ph){$P(OMe)_3$}(P^iPr_3)]BF_4 (**126**). This complex was obtained according to Scheme 34.

The CH_2 group of the carbyne ligand of **125** is fairly acidic and can easily be deprotonated. Thus, treatment of a methanol solution of **125** with KOH afforded the hydride vinylidene OsH(η^5-C_5H_5)(=C=CHPh)(P^iPr_3) (**127**) in equilibrium with its metalated isomer OsH(η^5-C_5H_5)-(C_6H_4CH=CH)(P^iPr_3) (**128**). The isomerization of **127** to **128** occurred via the spectroscopically undetected (*Z*)-alkenyl intermediate **129b**, which transformed into **128** by C−H activation of one of the *o*-CH bonds of the aryl group. Intermediate **129b** is in equilibrium with its *E* isomer **129a**. The formation of **129a** and **129b** could be the result of the migration, in **127**, of the hydride to the C_α atom of the vinylidene ligand, which should be rotating around the osmium−vinylidene axis.[60] Alternatively, the equilibrium **129a** ⇄ **129b** could be a consequence of an isomerization process via a zwitterionic carbene form. The presence of spectroscopically undetected amounts of **129a** in the isomeric mixture is strongly supported by the reaction of the latter with trimethyl phosphite, which afforded the (*E*)-styryl derivative Os(η^5-C_5H_5){(*E*)-CH=CHPh}{$P(OMe)_3$}(P^iPr_3) (**130**). As a result of a significant contribution of the zwitterionic carbene form to the structure of the alkenyl

(56) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 4875.

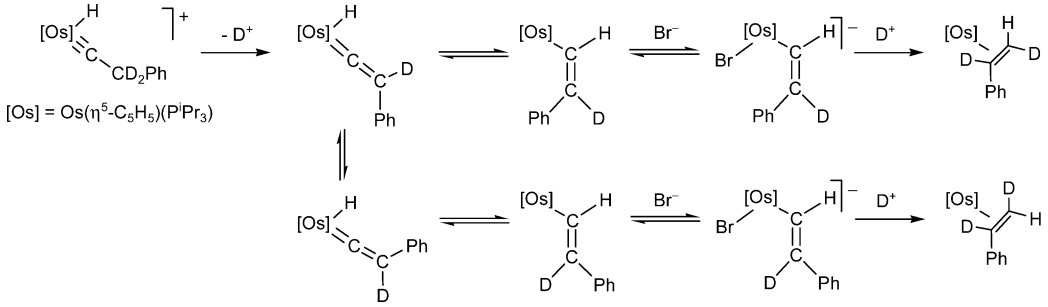
(57) (a) Esteruelas, M. A.; Oliván, M.; Oro, L. A.; Tolosa, J. I. *J. Organomet. Chem*. **1995**, *487*, 143. (b) Esteruelas, M. A.; López, A. M.; Oro, L. A.; Tolosa, J. I. *J. Mol. Catal. A: Chem*. **1995**, *96*, 21. (c) Esteruelas, M. A.; Oliván, M.; Oro, L. A. *Organometallics* **1996**, *15*, 814.

(58) (a) Esteruelas, M. A.; Lahoz, F. J.; Oliván, M.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 3486. (b) Esteruelas, M. A.; Oro, L. A. *Coord. Chem. Rev*. **1999**, *193*−*195*, 557.

(59) Baya, M.; Esteruelas, M. A. *Organometallics* **2002**, *21*, 2332.

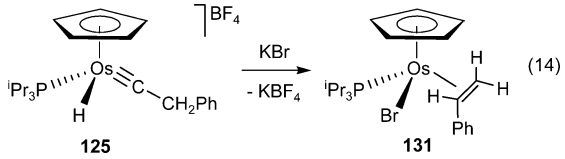
(60) (a) Bourgault, M.; Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *Organometallics* **1997**, *16*, 636. (b) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 2491.

Scheme 35



complexes, the C_β atom of the alkenyl ligands has a marked nucleophilic character.[61] In agreement with this, the addition of 1 equiv of $HBF_4 \cdot OEt_2$ to a diethyl ether solution of **130** afforded the carbene derivative **126**.

In contrast to trimethyl phosphite, bromide ion promoted the hydride carbyne to olefin transformation (eq 14). Also in contrast to the trimethyl phosphite case,

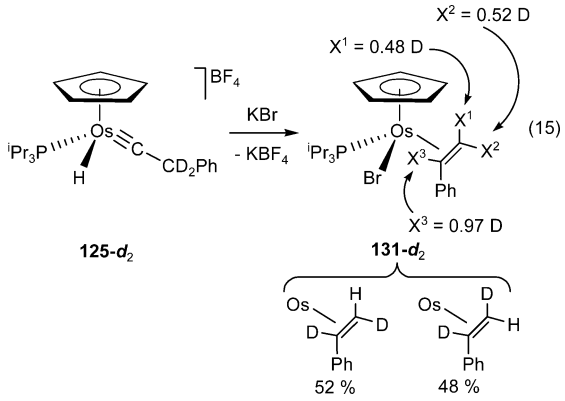


(14)

125 **131**

the transformation takes place as a one-pot synthesis. Treatment of a tetrahydrofuran solution of **125** with 6 equiv of KBr at room temperature gave, after 24 h, the π-olefin derivative Os(η^5-C_5H_5)Br{η^2-CH_2=CHPh)}(P^i-Pr$_3$) (**131**).[62]

Under the same conditions, the reaction of the dideuterated hydride carbyne complex [OsH(η^5-C_5H_5)(≡CCD_2-Ph)(P^{i}Pr$_3$)]BF_4 (**125-*d*$_2$**) with KBr gave the dideuterated π-olefin derivative Os(η^5-C_5H_5){η^2-CDH=CDPh)}(P^{i}Pr$_3$) (**131-*d*$_2$**) with the deuterium distribution, as shown in eq 15.



(15)

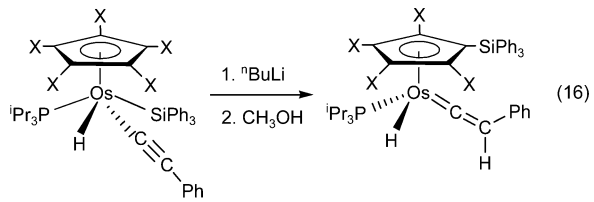
125-*d*$_2$ **131-*d*$_2$**

On the basis of the reactions shown in Scheme 34, this deuterium distribution has been rationalized according to Scheme 35. Because in **125** the benzyl group has proved to be fairly acidic, it has been proposed that the first step of the deuterated Br^--assisted hydride carbyne to olefin transformation involves the dissociation of D^+. The resulting hydride vinylidene complex exists as an equilibrium mixture of the two possible rotational isomers, that containing the deuterium atom cisoid disposed to the hydride ligand and that containing the deuterium atom transoid disposed to the hydride ligand. The migration of the hydride ligand from the metal center to the C_α atom of the vinylidene ligand should afford the corresponding unsaturated styryl intermediate, which should be stabilized by coordination of bromide. The electrophilic addition of D^+ to the C_α atom of the styryl ligand of the resulting saturated species should give the olefin.

The formation of **131** and **131-*d*$_2$** together with the preparation of **126** according to Scheme 34 show that in this cyclopentadienyl−osmium triisopropylphosphine system, the position of the nucleophilic center of the styryl ligand is strongly dependent upon the nature of the incoming ligand in the coordination vacancy of the unsaturated intermediate **129**. When the incoming ligand is a π-acceptor, such as $P(OMe)_3$, the nucleophilic center of the alkenyl group is the C_β atom. However, when the incoming ligand is a π-donor, such as bromide, the nucleophilic center is the C_α atom.

In contrast to the protonation reactions (eq 13), the group 14 element, Si or Ge, has a marked influence on the deprotonation reactions of **123** and **124**.[56]

Treatment of a tetrahydrofuran solution of OsH(η^5-C_5X_5)(C≡CPh)($SiPh_3$)(P^{i}Pr$_3$) (X = H (**123**), D (**123-*d*$_5$**)) with 3.0 equiv of *n*-butyllithium gave solutions that reacted with methanol to give OsH(η^5-$C_5X_4SiPh_3$)-(=C=CHPh)(P^{i}Pr$_3$) (X = H (**132**), D (**132-*d*$_4$**)) according to eq 16.



(16)

X = H (**123**), D (**123-*d*$_5$**) X = H (**132**), D (**132-*d*$_4$**)

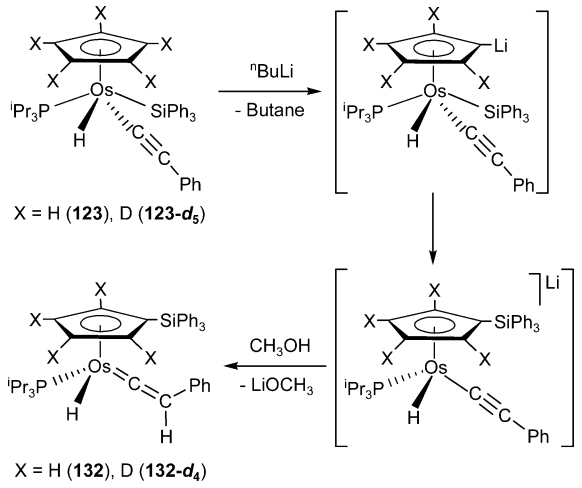
The formation of **132** and **132-*d*$_4$** indicates that the deprotonation of **123** occurs selectively at the cyclopentadienyl ligand (Scheme 36). The resulting species undergoes migration of the silyl group from the osmium atom to the cyclopentadienyl ligand to afford the anion [OsH(η^5-$C_5X_4SiPh_3$)(C≡CPh)(P^{i}Pr$_3$)]$^-$. Subsequently, the acidic proton of methanol attacks the C_β atom of the alkynyl group.

In agreement with Scheme 36, the addition of methanol-d_4 to the solution resulting from the treatment of

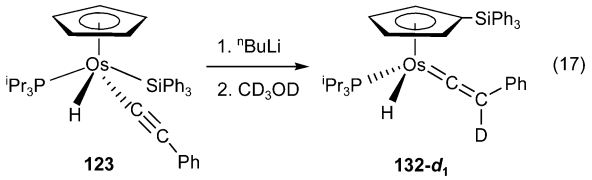
(61) (a) Esteruelas, M. A.; Liu, F.; Oñate, E.; Sola, E.; Zeier, B. *Organometallics* **1997**, *16*, 2919. (b) Buil, M. L.; Esteruelas, M. A. *Organometallics* **1999**, *18*, 1798. (c) Bohanna, C.; Buil, M. L.; Oñate, E.; Valero, C. *Organometallics* **1999**, *18*, 5176.

(62) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 5681.

Scheme 36

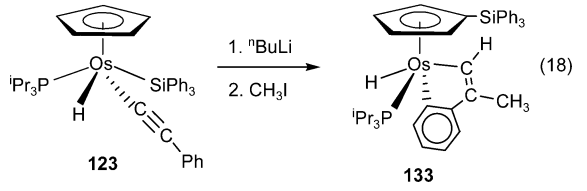


123 with ^{n}BuLi gave OsH(η^5-$C_5H_4SiPh_3$)(=C=CDPh)(P^iPr_3) (**132-*d*$_1$**), according to eq 17.



(17)

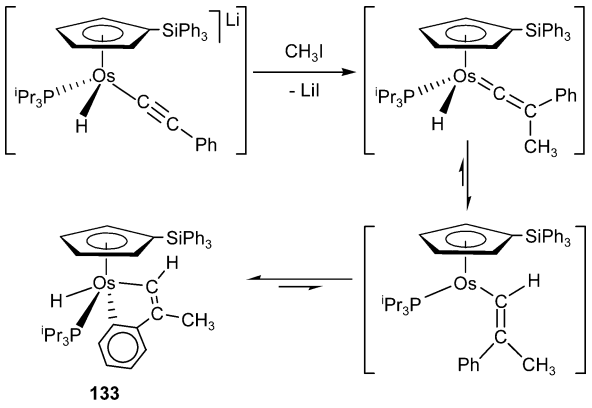
The stability of the vinylidene ligand in this type of half-sandwich complex depends on its substituents. The addition of methyl iodide to the solution resulting from the treatment of **123** with *n*-butyllithium did not give the corresponding methylphenylvinylidene, as one should expect, but instead the metalated derivative OsH(η^5-$C_5H_4SiPh_3$){$C_6H_4C(CH_3)$=CH}(P^iPr_3) (**133**) was isolated, according to eq 18.



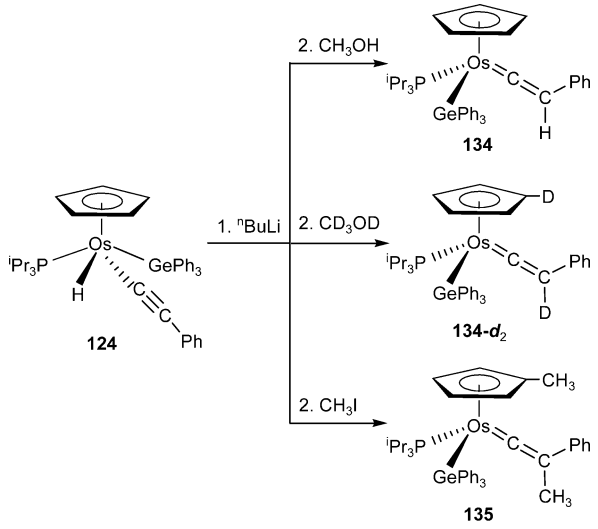
(18)

The formation of **133** has been rationalized according to Scheme 37. The anion [OsH(η^5-$C_5H_4SiPh_3$)(C≡CPh)(P^iPr_3)]$^-$, generated from the reaction of **123** with *n*-butyllithium, reacts with methyl iodide to give initially the

Scheme 37



Scheme 38



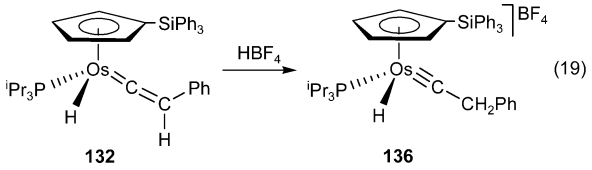
expected hydride methylphenylvinylidene OsH(η^5-$C_5H_4SiPh_3$){=C=C(CH_3)Ph}(P^iPr_3), in a manner similar to the formation of **132**. The presence of a methyl group at the C_β atom of the vinylidene ligand increases the electrophilic character of the C_α atom, favoring the migratory insertion of the vinylidene group into the Os−H bond. The insertion generates the unsaturated five-coordinate alkenyl intermediate Os(η^5-$C_5H_4SiPh_3$)-{CH=C(CH_3)Ph}(P^iPr_3), which by C−H activation of an *o*-CH aryl bond gives **133**. The activation of the phenyl instead of the methyl group of the alkenyl ligand agrees well with the kinetic and thermodynamic preference for aromatic C−H activation.

Interestingly, the treatment of a tetrahydrofuran solution of **124** with 3.0 equiv of *n*-butyllithium gave a solution that reacted with methanol, methanol-d_4, and methyl iodide to give Os(η^5-C_5H_5)($GePh_3$)(=C=CHPh)-(P^iPr_3) (**134**), Os(η^5-C_5H_4D)($GePh_3$)(=C=CDPh)(P^iPr_3) (**134-*d*$_2$**), and Os(η^5-$C_5H_4CH_3$)($GePh_3$){=C=C(CH_3)Ph}-(P^iPr_3) (**135**), respectively (Scheme 38).

The formation of **134**, **134-*d*$_2$**, and **135** indicates that treatment of **124** with *n*-butyllithium resulted in a double deprotonation: at the metal center and at the cyclopentadienyl ligand. Furthermore, in contrast to **123**, the deprotonation of the cyclopentadienyl ligand of **124** did not give way to the migration of the germyl group from the osmium atom to the cyclopentadienyl ligand, in agreement with the previously mentioned higher thermodynamic stability of the Os−Ge bond in comparison with the Os−Si one.

In these types of compounds, in addition to the M−ER_3 σ bond, there is an important π-bonding as a result of the donation of electron density from d orbitals of the metal to a linear combination of E−R σ^* orbitals.[53b] The higher acidity of the hydride of **124** with regard to the hydride of **123** suggests that the greater strength of the Os−Ge bond is a result of a more efficient π donation to $GePh_3$ than to $SiPh_3$: i.e., the $GePh_3$ group is a better π-acceptor ligand than the $SiPh_3$ group. As a result, the electron density at the metal center of **124** is lower than that at the metal center of **123**. Thus, the Os−H bond is more polarized in **124** than in **123** and, therefore, the hydride of **124** is more acidic than the hydride of **123**.

In agreement with the nucleophilic character of the C_β atom of the vinylidene ligands, complex **132** reacted with $HBF_4 \cdot OEt_2$ in diethyl ether to give the hydride carbyne [OsH(η^5-$C_5H_4SiPh_3$)(≡CCH_2Ph)(P^iPr_3)]BF_4 (**136**), related to **125** (eq 19).[56]



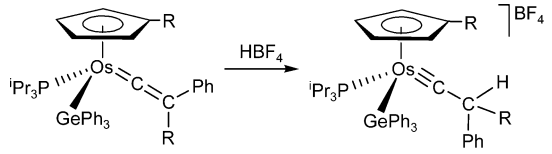
132 **136** (19)

The addition of $HBF_4 \cdot OEt_2$ to a diethyl ether solution of **133** initially gave the hydride carbyne [OsH(η^5-$C_5H_4SiPh_3$){≡$CCH(CH_3)Ph$}(P^iPr_3)]BF_4 (**137**). The formation of this complex according to Scheme 39 proves that in fact, as is shown in Scheme 37, in solution complex **133** is in equilibrium with nondetectable concentrations of the hydride vinylidene OsH(η^5-$C_5H_4SiPh_3$){=C=$C(CH_3)Ph$}(P^iPr_3). In solution, complex **137** changed into the hydride allyl isomer [OsH(η^5-$C_5H_4SiPh_3$){η^3-$CH_2C(Ph)CH_2$}(P^iPr_3)]BF_4 (**138**).

The protonation of **133** with DBF_4 afforded [OsH(η^5-$C_5H_4SiPh_3$){≡$CCD(CH_3)Ph$}(P^iPr_3)]BF_4 (**137-*d*$_1$**). Similar to **137**, in solution, **137-*d*$_1$** changed into [OsH(η^5-$C_5H_4SiPh_3$){η^3-$CH_2C(C_6H_4D)CH_2$}(P^iPr_3)]BF_4 (**138-*d*$_1$**), which contains the deuterium atom at one of the ortho carbon atoms of the phenyl group of the allyl ligand.

The deuterium atom positions in **137-*d*$_1$** and **138-*d*$_1$** indicate that although the protonation of the hydride vinylidene is kinetically favored, it is reversible, and that the protonation of **133** occurs at the metalated carbon atom of the aryl group (Scheme 40). Thus, once the unsaturated hydride alkenyl [OsH(η^5-$C_5H_4SiPh_3$){CH=$C(CH_3)Ph$}(P^iPr_3)]$^+$ is formed, the reductive elimination of the olefin afforded [Os(η^5-$C_5H_4SiPh_3$){η^2-CH_2=$C(CH_3)Ph$}(P^iPr_3)]$^+$, which, by C−H activation of the methyl group of the alkene, was converted to **138** or **138-*d*$_1$**. The reductive elimination in [OsH(η^5-$C_5H_4SiPh_3$)-{CH=$C(CH_3)Ph$}(P^iPr_3)]$^+$ is probably favored by its unsaturated character, whereas the higher stability of a M−(η^3-allyl) bond with regard to a M−aryl bond appears to be the driving force for the activation of the methyl instead the phenyl group in the intermediate [Os(η^5-$C_5H_4SiPh_3$){η^2-CH_2=$C(CH_3)Ph$}(P^iPr_3)]$^+$.[63]

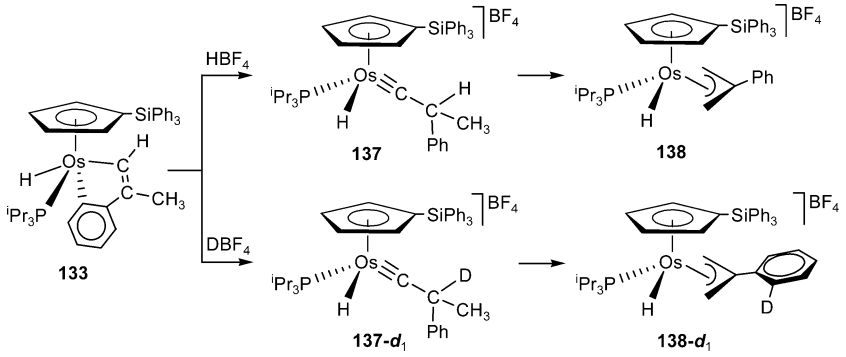
Similar to the case for **132**, the vinylidene ligands of **134** and **135** are prone to attack by electrophiles. Thus, the addition of HBF_4 to a diethyl ether solution of these compounds gave the corresponding germyl carbyne derivatives [Os(η^5-C_5H_5)($GePh_3$)(≡CCH_2Ph)(P^iPr_3)]BF_4 (**139**) and [Os(η^5-$C_5H_4CH_3$)($GePh_3$){≡$CCH(CH_3)Ph$}-(P^iPr_3)]BF_4 (**140**), respectively, as a result of the addition of the proton to the C_β atom of the vinylidene ligands (eq 20).



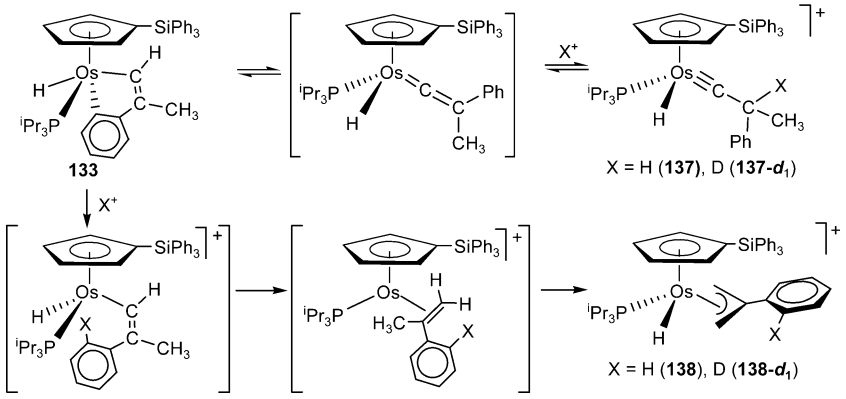
R = H (**134**), CH_3 (**135**) R = H (**139**), CH_3 (**140**) (20)

In contrast to **137**, in solution, complex **140** is stable and does not change into an allyl species related to **138**. This indicates that the migratory insertion of the methylphenylvinylidene into an Os−Ge bond is less favored than the insertion into an Os−H bond, which can be related to the lower nucleophilic power of a germyl group compared to a hydride ligand.[56]

Scheme 39



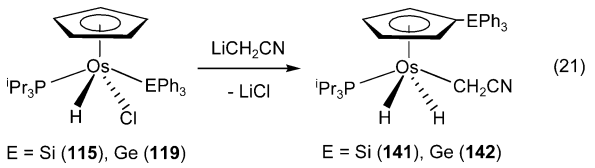
Scheme 40



Generation of Substituted Cyclopentadienyl Ligands

In addition to the processes summarized in eqs 16−18 and Scheme 38, which provide useful approaches to functionalized substituted cyclopentadienyl complexes, reactions between **115** or **119** and LiNu reagents have been developed to prepare several types of osmium(IV) derivatives.[64]

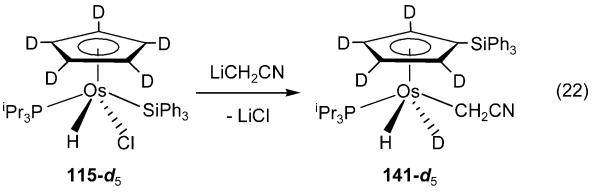
Both complexes **115** and **119** reacted with $LiCH_2CN$, in tetrahydrofuran at room temperature, to give the substituted cyclopentadienyl derivatives $OsH_2(\eta^5\text{-}C_5H_4EPh_3)(CH_2CN)(P^iPr_3)$ (E = Si (**141**), Ge (**142**)), according to eq 21.



(21)

E = Si (**115**), Ge (**119**) E = Si (**141**), Ge (**142**)

Under the same conditions, the treatment of the perdeuterated cyclopentadienyl complex $OsH(\eta^5\text{-}C_5D_5)Cl(SiPh_3)(P^iPr_3)$ (**115-*d*$_5$**) with $LiCH_2CN$ selectively gave $Os(H)(D)(\eta^5\text{-}C_5D_4SiPh_3)(CH_2CN)(P^iPr_3)$ (**141-*d*$_5$**), containing a deuterium at the osmium atom (eq 22).

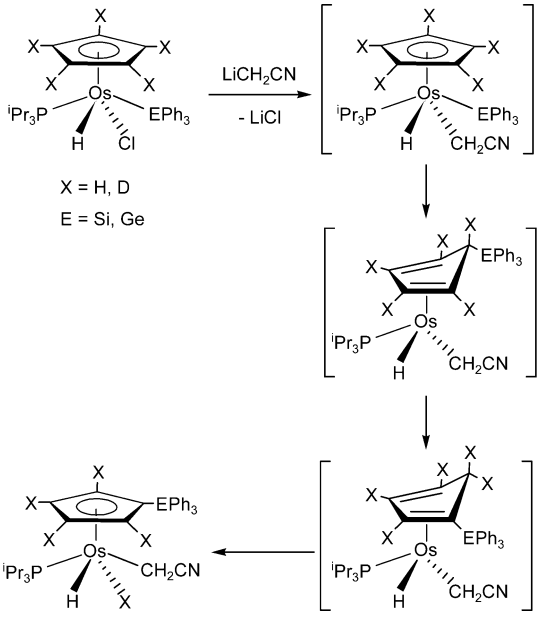


(22)

115-*d*$_5$ **141-*d*$_5$**

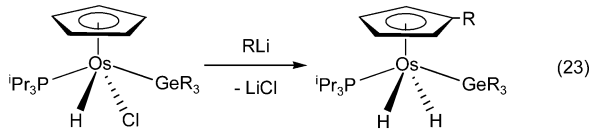
The presence of a deuteride ligand in **141-*d*$_5$** suggests that the processes shown in eqs 21 and 22 proceed via the elementary steps collected in Scheme 41. The

Scheme 41



reactions initially involve the replacement of the chloride ligand by the CH_2CN group. The spontaneous migration of EPh_3 from the osmium atom into the cyclopentadienyl ligand should afford substituted cyclopentadiene osmium(II) species with the EPh_3 groups in endo positions. Subsequently, these intermediates, by an exo-1,5-hydride (deuteride) shift, end up with a hydrogen (deuterium) atom in an endo position. Finally, the migration of this endo hydrogen (deuterium) atom from the dienes to the osmium atom affords **141**, **142**, and **141-*d*$_5$**.

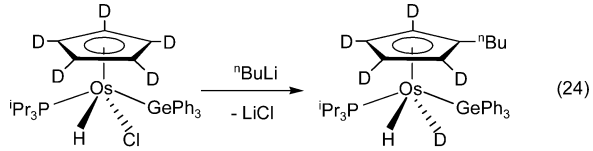
Complex **119** also reacted with MeLi, ^{n}BuLi, and ^{sec}BuLi at room temperature. The reactions gave the dihydride germyl complexes $OsH_2(\eta^5\text{-}C_5H_4R)(GePh_3)(P^iPr_3)$ (R = Me (**143**), ^{n}Bu (**144**), ^{sec}Bu (**145**)), according to eq 23.



(23)

119 R = Me (**143**), ^{n}Bu (**144**), ^{sec}Bu (**145**)

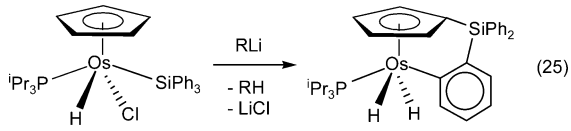
The formation of **143**−**145** involves a sequence of reactions similar to that shown in Scheme 41. However, in this case, in the $OsH(\eta^5\text{-}C_5H_5)(alkyl)(GePh_3)(P^iPr_3)$ intermediates, spontaneous migration of the alkyl group (instead of $GePh_3$) from the osmium atom to the cyclopentadienyl group has taken place. This is supported by the reaction of the perdeuterated cyclopentadienyl complex $OsH(\eta^5\text{-}C_5D_5)Cl(GePh_3)(P^iPr_3)$ (**119-*d*$_5$**) with ^{n}BuLi, which resulted in formation of $OsH(D)(\eta^5\text{-}C_5D_4{}^nBu)(GePh_3)(P^iPr_3)$ (**144-*d*$_5$**), according to eq 24.



(24)

119-*d*$_5$ **144-*d*$_5$**

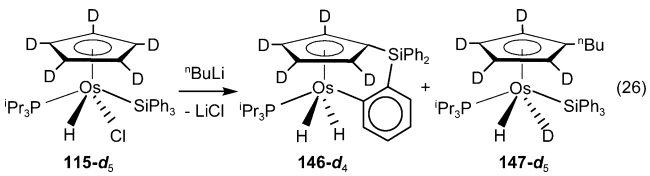
In contrast to **119**, at room temperature, complex **115** reacted with MeLi and ^{n}BuLi to give $OsH_2\{\eta^5\text{-}C_5H_4Si(C_6H_4)Ph_2\}(P^iPr_3)$ (**146**), according to eq 25.



(25)

115 **146**

Interestingly, under the same conditions, the reaction of **115-*d*$_5$** with ^{n}BuLi yielded a mixture of the deuterated compounds $OsH_2\{\eta^5\text{-}C_5D_4Si(C_6H_4)Ph_2\}(P^iPr_3)$ (**146-*d*$_4$**) and $Os(H)(D)(\eta^5\text{-}C_5D_4{}^nBu)(SiPh_3)(P^iPr_3)$ (**147-*d*$_5$**) in a 2:1 molar ratio (eq 26).



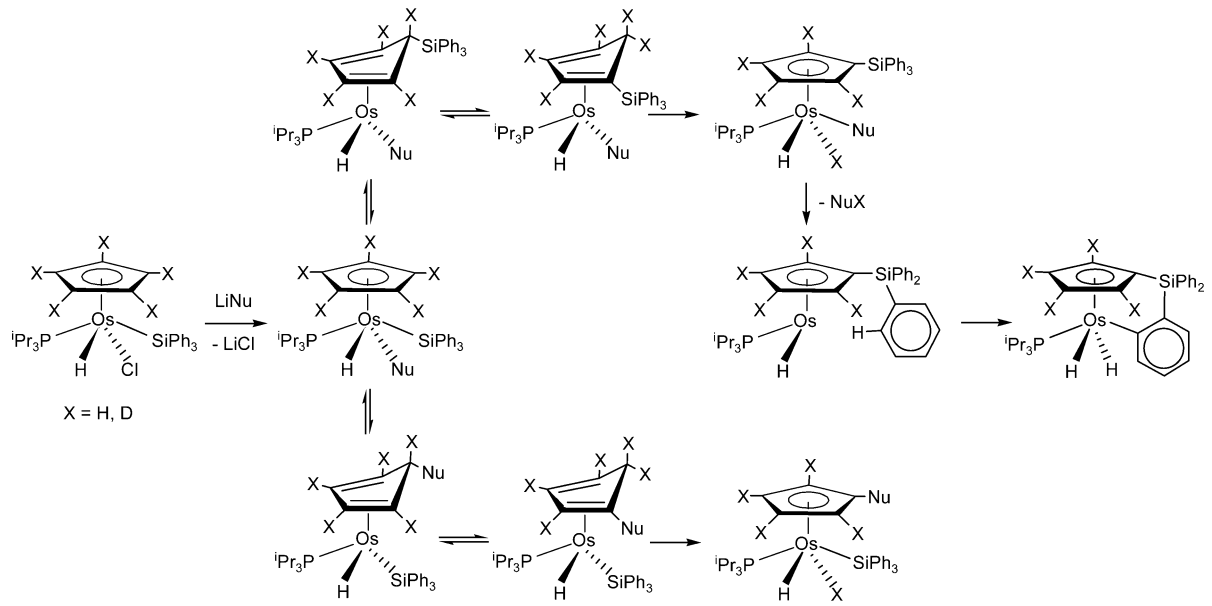
(26)

115-*d*$_5$ **146-*d*$_4$** **147-*d*$_5$**

(63) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Sola, E. *J. Am. Chem. Soc.* **1996**, *118*, 89.

(64) Baya, M.; Crochet, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 240.

Scheme 42

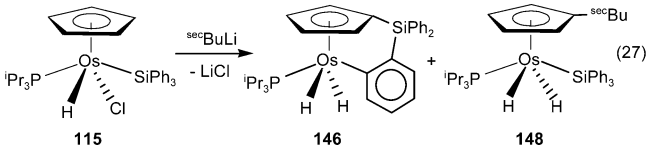


These reactions have been rationalized according to Scheme 42 (Nu = R). The formation of both **146-*d*$_4$** and **147-*d*$_5$** indicates that in the OsH(η^5-C_5X_5)(R)($SiPh_3$)(P^i-Pr_3) (X = H, D; R = alkyl) intermediates two competitive spontaneous migrations from the osmium atom to the cyclopentadienyl group can take place: the migration of the silyl group, which affords **146** or **146-*d*$_4$**, and the migration of the alkyl group, which leads to **147-*d*$_5$** by a pathway similar to that described for the formation of **143**−**145** and **144-*d*$_5$**.

According to eqs 21 and 22, the silyl migration should afford Os(H)(X)(η^5-$C_5X_4SiPh_3$)(R)(P^iPr_3) intermediates, which should be unstable toward reductive elimination of alkane (R−X). Thus, the formation of unsaturated OsH(η^5-$C_5X_4SiPh_3$)(P^iPr_3) species could give **146** and **146-*d*$_4$**, by C−H activation of a phenyl group of the silyl substituent. The absence of deuterium on the metal center of **146-*d*$_4$** indicates a kinetic or thermodynamic preference by the deuteride ligand during the reductive elimination of alkane from Os(H)(D)(η^5-$C_5D_4SiPh_3$)(R)(P^i-Pr_3), in agreement with the greater strength of the alkyl−D bond in comparison with the alkyl−H bond.

To rationalize the formation of **147-*d*$_5$**, it has been argued that the rate-determining step for the formation of **146** and **146-*d*$_4$** is the migration of X from the diene to the osmium atom, while the rate-determining step for the formation of **147-*d*$_5$** is the migration of the alkyl group from the osmium atom to the cyclopentadienyl ligand. Thus, the substitution of hydrogen by deuterium in the cyclopentadienyl ring produces an increase of the energy barrier for the formation of **146-*d*$_4$** with regard to **146** without affecting the energy barrier for the formation of **147-*d*$_5$** with regard to a nonobserved **147**.

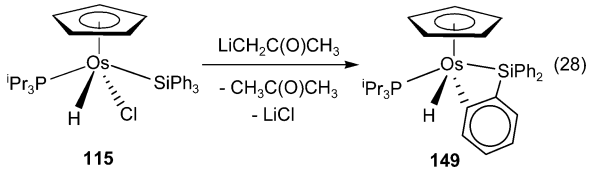
In agreement with the fact that the rate-determining step for the formation of the dihydride silyl complexes containing cyclopentadienyl ligands with an alkyl substituent is the migration of the alkyl group from the osmium atom to the cyclopentadienyl ring, the reaction of **115** with ^{sec}BuLi gave a mixture of **146** and OsH_2(η^5-$C_5H_4{}^{sec}Bu$)($SiPh_3$)(P^iPr_3) (**148**) in a 4:1 molar ratio (eq 27).



(27)

The formation of **148** is a consequence of the steric hindrance of the *sec*-butyl group, which favors the migration of the alkyl group from the osmium atom to the cyclopentadienyl ligand.

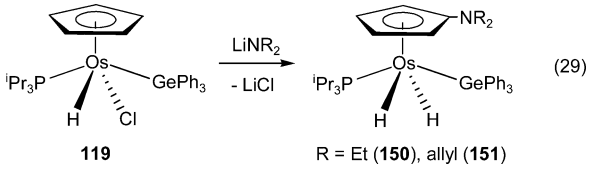
The formation of **141**−**148** took place because the OsH(η^5-C_5H_5)(EPh_3)(Nu)(P^iPr_3) intermediates were stable toward the reductive elimination of Nu−H and/or the formation of the substituted cyclopentadiene intermediates is faster than the loss of Nu−H. In contrast to $LiCH_2CN$ and RLi (R = alkyl), the enolate $LiCH_2C(O)CH_3$ did not afford substituted cyclopentadienyl compounds. The reaction of this nucleophile with **115** gave OsH(η^5-C_5H_5){Si(C_6H_4)Ph_2}(P^iPr_3) (**149**) and acetone (eq 28).



(28)

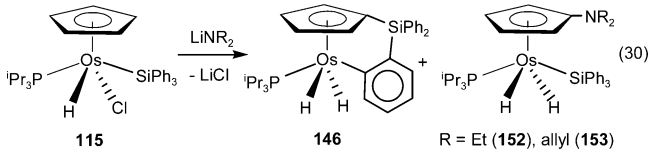
The formation of **149** involves the initial replacement of the chloride ligand by the enolate, followed by the reductive elimination of acetone to give an unsaturated Os(η^5-C_5H_5)($SiPh_3$)(P^iPr_3) intermediate. The *o*-CH activation of a phenyl group of the silyl substituent of this intermediate afforded **149**.

Complex **119** also reacted with $LiNR_2$ (R = Et, allyl). In tetrahydrofuran, at room temperature, the reactions gave OsH_2(η^5-$C_5H_4NR_2$)($GePh_3$)(P^iPr_3) (R = Et, (**150**), allyl (**151**)), where the substituent of the cyclopentadienyl group contains a nitrogen atom (eq 29).



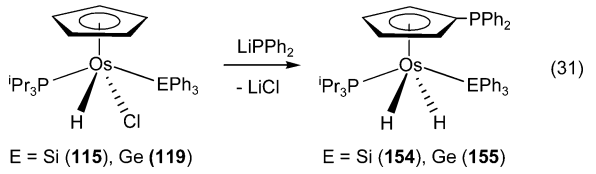
The amino group of the substituted cyclopentadienyl ligand is planar, with angles around the nitrogen atom of about 120°. This indicates that the nitrogen lone pair is largely delocalized into the aromatic ring.

Under the same conditions, the reactions of **115** with $LiNR_2$ (R = Et, allyl) afforded mixtures of **146** and the aminocyclopentadienyl complexes $OsH_2(\eta^5\text{-}C_5H_4NR_2)(SiPh_3)(P^iPr_3)$ (R = Et, (**152**), allyl (**153**)). The molar ratios of the reaction products depend on the substituents of the amide and the temperature (eq 30).



Comparison of eqs 29 and 30 indicates that in $OsH(\eta^5\text{-}C_5H_5)(EPh_3)(Nu)(P^iPr_3)$ (E = Si, Ge) intermediates the migration of the $SiPh_3$ group from the osmium atom to the cyclopentadienyl ligand is favored with regard to the migration of the $GePh_3$ group not only when Nu is alkyl but also when Nu is amide, in agreement with the greater thermodynamic stability of the Os−Ge bond in comparison with the Os−Si bond.

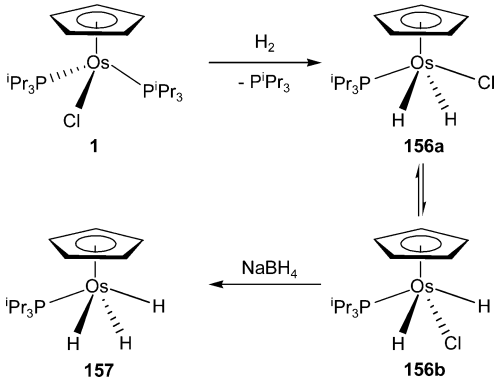
Both complexes **115** and **119** reacted with $LiPPh_2$ in tetrahydrofuran at room temperature to give the (diphenylphosphino)cyclopentadienyl derivatives $OsH_2(\eta^5\text{-}C_5H_4PPh_2)(EPh_3)(P^iPr_3)$ (E = Si, (**154**), Ge (**155**)), according to eq 31.



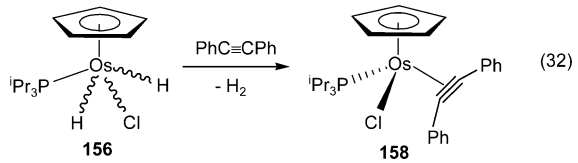
Transformations on the Remaining Phosphine: Formation and Reactions of Isopropenyldiisopropylphosphine Complexes

Bubbling molecular hydrogen through a pentane solution of complex **1** produced the displacement of a coordinated triisopropylphosphine ligand and the formation of an equilibrium mixture of the isomers *transoid*-dihydride $OsH_2(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)$ (**156a**) and *cisoid*-dihydride $OsH_2(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)$ (**156b**). Isomer **156a** has a rigid structure in solution. However, the hydride ligands of **156b** undergo a thermally activated site exchange process and show quantum exchange coupling, decreasing the H−H coupling constant from 63 to 30 Hz as the temperature decreases from 187 to 163 K. Treatment at room temperature of a toluene solution of the isomeric mixture of **156** with $NaBH_4$ and some drops of methanol led to the trihydride derivative $OsH_3(\eta^5\text{-}C_5H_5)(P^iPr_3)$ (**157**), according to Scheme 43. In solution, the *cisoid*-hydride ligands of **157** also underwent a thermally activated exchange process.[52a]

Scheme 43

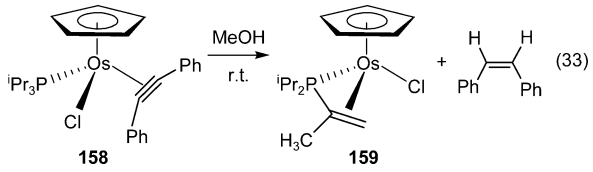


In refluxing diethyl ether and in the presence of 2.7 equiv of diphenylacetylene, the dihydride compounds of the isomeric mixture **156** lost molecular hydrogen and the resulting metal fragment coordinated a molecule of the alkyne to afford $Os(\eta^5\text{-}C_5H_5)Cl(\eta^2\text{-}PhC{\equiv}CPh)(P^iPr_3)$ (**158**), according to eq 32. During the reaction the



formation of stilbene was not observed. The direct reaction between **1** and diphenylacetylene is not a useful method to obtain **158**, since treatment of **1** with diphenylacetylene gave an equilibrium mixture of **1**, **158**, triisopropylphosphine, and diphenylacetylene.[65]

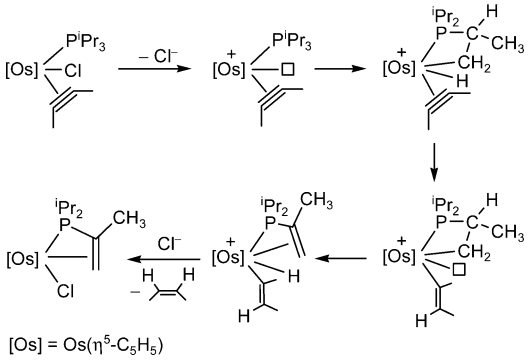
At room temperature in toluene or benzene, complex **158** is stable. However, in methanol, it was changed into the isopropenyldiisopropylphosphine derivative $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**159**) and (*Z*)-stilbene (eq 33).



The formation of **159** truly involves hydrogen transfer from an isopropyl group of the triisopropylphosphine ligand to the carbon−carbon triple bond of the coordinated alkyne in **158**. When the reaction was carried out in methanol-d_4 as solvent, neither the isopropenyldiisopropylphosphine of **159** nor the stilbene contained any deuterium atoms. The role of the methanol is to promote the dissociation of chloride from **158** (Scheme 44). Thus, the C−H activation of a methyl group of an isopropyl substituent of the phosphine, in a cationic unsaturated intermediate, followed by the migratory insertion of the alkyne into the Os−H bond of the resulting hydride afforded an unsaturated alkenyl species, containing a metalated phosphine. The β-hydrogen elimination of the metalated group of the phosphine should give a monoisopropenylphosphine hydride alkenyl intermediate, which then could undergo reductive

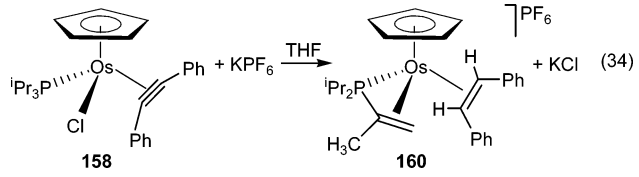
(65) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1416.

Scheme 44



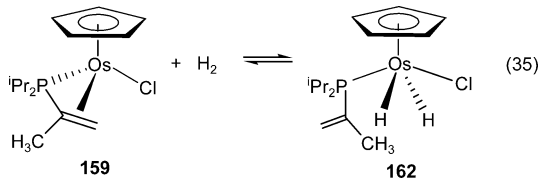
elimination of (*Z*)-stilbene and coordination of the chloride anion dissociated in the first step.

The role of methanol is in fact to promote the dissociation of chloride from **158**. In tetrahydrofuran and in the presence of KPF_6, the hydrogen transfer reaction gave the (*Z*)-stilbene derivative [Os(η^5-C_5H_5)-{η^2-(*Z*)-PhCH=CHPh}{[η^2-CH_2=C(CH_3)]P^iPr_2}]PF_6 (**160**) according to eq 34.



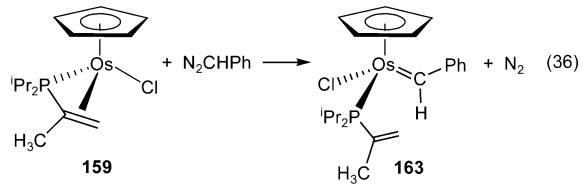
Treatment of a tetrahydrofuran solution of **160** with MeLi produced the hydride methylcyclopentadienyl derivative OsH(η^5-$C_5H_4CH_3$){η^2-(*Z*)-PhCH=CHPh}{P^i-Pr_2[C(CH_3)=CH_2]} (**161a**). The formation of this compound involves the addition of the methyl group to the metal center of the unsaturated intermediate [Os(η^5-C_5H_5){η^2-(*Z*)-PhCH=CHPh}{P^iPr_2[C(CH_3)=CH_2]}]-PF_6, followed by a CH_3(Os)/H(C_5H_5) exchange in Os(η^5-C_5H_5)(CH_3){η^2-(*Z*)-PhCH=CHPh}{P^iPr_2[C(CH_3)=CH_2]} (Scheme 45). Complex **161a** is unstable and was converted into the (*E*)-stilbene derivative OsH(η^5-C_5H_4-CH_3){η^2-(*E*)-PhCH=CHPh}{P^iPr_2[C(CH_3)=CH_2]} (**161b**). The *Z*−*E* transformation is favored by the presence of a hydride ligand in **161a**. Thus, the insertion of the (*Z*)-stilbene ligand into the Os−H bond, followed by rotation around the C−C single bond of the resulting alkyl group, and subsequent β-elimination of hydrogen afford **161b**.

The isopropenyldiisopropylphosphine of **159** has also hemilabile character. This property was revealed in the presence of molecular hydrogen. Under an atmosphere of H_2, complex **159** is in equilibrium with the dihydride derivative OsH_2(η^5-C_5H_5)Cl{P^iPr_2[C(CH_3)=CH_2]} (**162**), which contains a monodentate-phosphorus isopropenylphosphine ligand (eq 35). The reaction of Os(η^5-C_5-



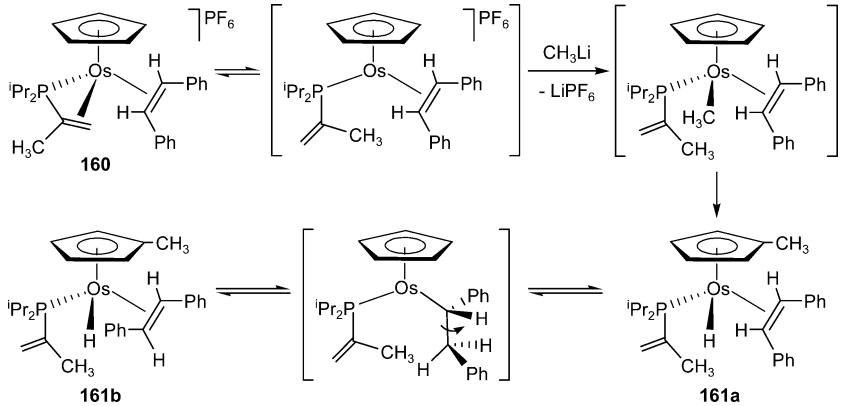
Me_5)Br(P^iPr_3) with K[B(C_6F_5)$_4$] in tetrahydrofuran−dichloromethane afforded the related dihydride pentamethylcyclopentadienyl osmium cation [OsH_2(η^5-C_5-Me_5){[η^2-CH_2=C(CH_3)]P^iPr_2}][B(C_6F_5)$_4$], which could be deprotonated with KN($SiMe_3$)$_2$ to give the neutral monohydride OsH(η^5-C_5Me_5){[η^2-CH_2=C(CH_3)]P^iPr_2}.[8o] Other isopropenyldiisopropylphosphine complexes include $OsCl_2$(η^4-diolefin){[η^2-CH_2=C(CH_3)]P^iPr_2} (diolefin = COD, NBD, TFB),[66] OsH_3($SnClPh_2$){[η^2-CH_2=C(CH_3)]-P^iPr_2}(P^iPr_3),[67] and [OsH(η^4-$C_4H_4Ph_2$){[η^2-CH_2=C(CH_3)]-P^iPr_2}($P^iPr_2{}^nPr$)]BF_4.[68]

In agreement with the hemilabile character of the α-alkenylphosphine of **159**, treatment at room temperature of a toluene solution of this compound with phenyldiazomethane in toluene gave the olefin carbene derivative Os(η^5-C_5H_5)Cl(=CHPh){P^iPr_2[C(CH_3)=CH_2]} (**163**), which is the result of the displacement of the α-alkenylphosphine olefin group from the coordination sphere of the metal by the carbene ligand (eq 36).[69]

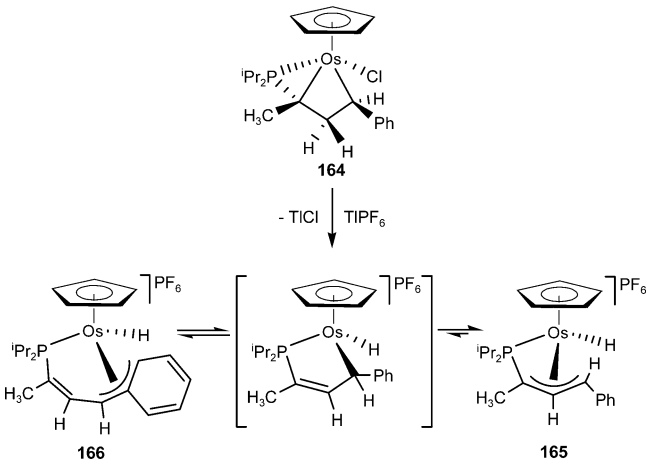


In toluene, complex **163** was converted to the osmaphosphabicyclopentane derivative Os(η^5-C_5H_5)Cl{[CH-(Ph)CH_2C(CH_3)]P^iPr_2} (**164**). The exclusive formation of the diastereomer shown in eq 37 proves that the reaction is diastereoselective and involves a [2+2] cycloaddition process between the C−C double bond of the phosphine and the Os−C double bond in the rotamer

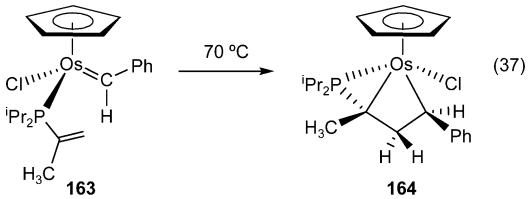
Scheme 45



Scheme 46



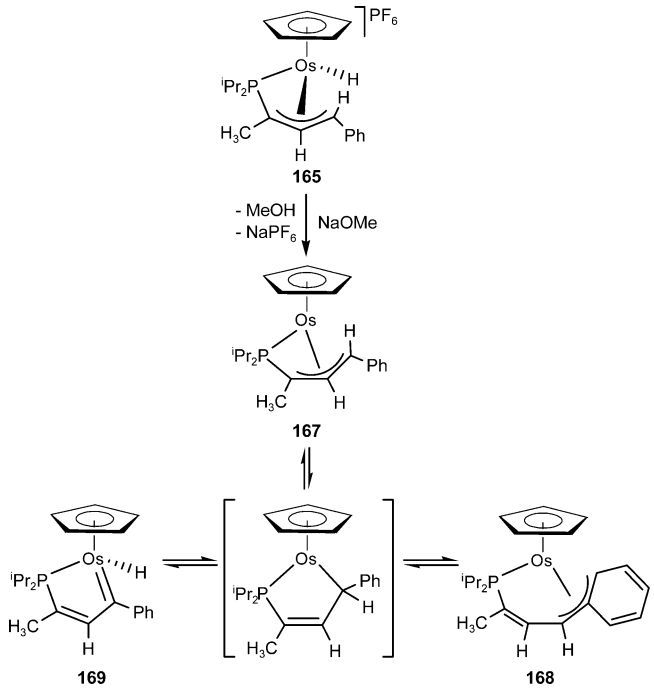
of **163** containing the phenyl group directed toward the cyclopentadienyl ligand.



The abstraction of the chloride ligand from **164** provoked the destruction of the bicycle (Scheme 46). At room temperature, treatment of an acetone solution of **164** with $TlPF_6$ gave a 1:1 mixture of the α-allylphosphine complex $[OsH(\eta^5\text{-}C_5H_5)\{[\eta^3\text{-}CH(Ph)CHC(CH_3)]P^iPr_2\}]PF_6$ (**165**) and its α-alkenyl-γ-(η^3-benzyl)phosphine isomer $OsH(\eta^5\text{-}C_5H_5)\{[\eta^3\text{-}C_6H_5CHCH{=}C(CH_3)]P^iPr_2\}]PF_6$ (**166**). The transformation initially afforded the hydride η^1-allylphosphine intermediate $OsH(\eta^5\text{-}C_5H_5)\{[CH(Ph)CH{=}C(CH_3)]P^iPr_2\}]PF_6$, as a result of the Os−C(CH_3)P bond cleavage and a β-hydrogen elimination reaction in the CH_2 group of the bicycle. From a thermodynamic point of view, complex **165** is more stable than **166**. Thus, heating the mixture in tetrahydrofuran at 66 °C resulted in the isomerization of **166** to **165**. The osmaphosphabicyclopentane−allylphosphine transformation indicates that a β-H elimination rather than a metathesis process, driven by the presence of a vacant site, is favored in the metallacyclobutane of the osmaphosphabicyclopentane.

It has been proposed that an intramolecular [2 + 2] cycloaddition reaction in olefin−carbene−metal complexes and the subsequent transformation of the resulting metallacyclobutane into hydrido−η^3-allyl−metal derivatives are the key steps for the catalytic formation of C_n olefins, by addition of diazoalkanes to C_{n-1} olefins.[70] The reactions shown in eqs 36 and 37 and the formation of **165** according to Scheme 46 are strong evidence in favor of this proposal.

Scheme 47

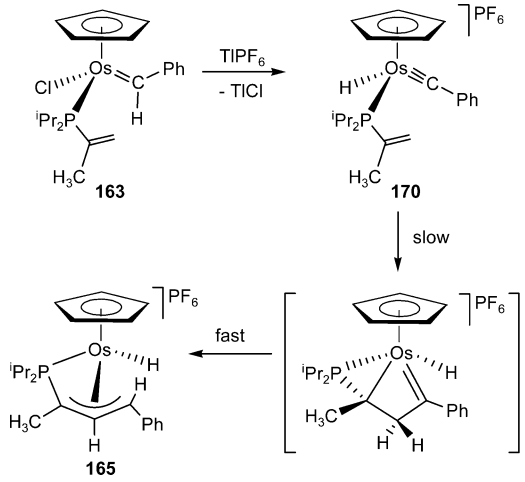


The hydride ligand of **165** is fairly acidic. Its deprotonation resulted in an equilibrium mixture of the neutral osmium(II) α-allylphosphine $Os(\eta^5\text{-}C_5H_5)\{[\eta^3\text{-}CH(Ph)CHC(CH_3)]P^iPr_2\}$ (**167**), α-alkenyl-γ-(η^3-benzyl)-phosphine $Os(\eta^5\text{-}C_5H_5)\{[\eta^3\text{-}C_6H_5CHCH{=}C(CH_3)]P^iPr_2\}$ (**168**), and α-alkenyl-γ-carbenephosphine $Os(\eta^5\text{-}C_5H_5)\text{-}\{[{=}C(Ph)CH{=}C(CH_3)]P^iPr_2\}$ (**169**) isomers.[69] The formation of these compounds has been rationalized according to Scheme 47. The deprotonation of **165** initially affords **167**. The $\eta^3-\eta^1$ conversion of the allyl moiety of the phosphine ligand of **167** should lead to the intermediate $Os(\eta^5\text{-}C_5H_5)\{[CH(Ph)CH{=}C(CH_3)]P^iPr_2\}$, where the η^1-allyl unit also is an η^1-benzyl moiety. Thus, the $\eta^1-\eta^3$ conversion of the benzyl group could yield **168**. The intermediate $Os(\eta^5\text{-}C_5H_5)\{[CH(Ph)CH{=}C(CH_3)]\text{-}P^iPr_2\}$ is an unsaturated osmaphosphacyclopentene species with H_α and H_β hydrogen atoms with regard to the σ Os−C bond. As a consequence of the rigidity imposed by the sp^2 hybridization of the CH_β carbon atom of the metallacycle, the H_β hydrogen atom points in the opposite direction of the metal center and, therefore, β-hydrogen elimination is disfavored with regard to the α-hydrogen elimination reaction. The migration of the H_α hydrogen from the CPh carbon atom to the osmium should yield isomer **169**.

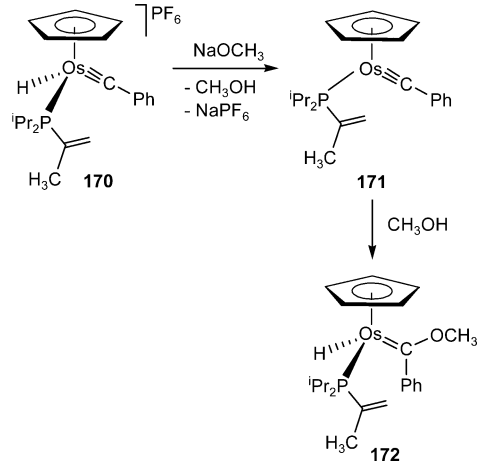
The abstraction of the chloride ligand from **163** provoked the migration of the hydrogen atom of the carbene from the carbon atom to the metal center. As a result, the hydride carbyne derivative $[OsH(\eta^5\text{-}C_5H_5)(\equiv CPh)\{P^iPr_2[C(CH_3){=}CH_2]\}]PF_6$ (**170**) was formed (Scheme 48). In acetone, complex **170** selectively was changed to **165**. The rearrangement is a first-order process with activation parameters of $\Delta H^\ddagger = 23 \pm 3$ kcal mol^{-1} and $\Delta S^\ddagger = -4 \pm 4$ cal K^{-1} mol^{-1}, which are consistent with an intramolecular [2 + 2] cycloaddition

(66) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 1316.
(67) Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oliván, M.; Oñate, E.; Tajada, M. A.; Tomàs, J. *Organometallics* **2003**, *22*, 2087.
(68) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2003**, *22*, 2472.
(69) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2004**, *23*, 4858.
(70) (a) Werner, H. *J. Organomet. Chem*. **1995**, *500*, 331. (b) Baratta, W.; Herrmann, W. A.; Kratzer, R. M.; Rigo, P. *Organometallics* **2000**, *19*, 3664. (c) Le Paih, J.; Dérien, S.; Özdemir, I.; Dixneuf, P. H. *J. Am. Chem. Soc.* **2000**, *122*, 7400. (d) Priya, S.; Balakrishna, M. S.; Mobin, S. M.; McDonald, R. *J. Organomet. Chem.* **2003**, *688*, 227.

Scheme 48



Scheme 49



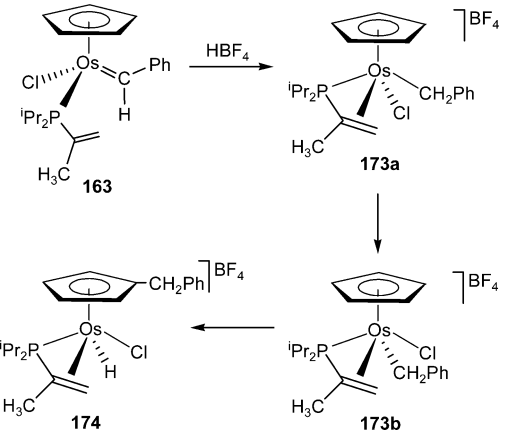
process between the isopropenyl substituent of the phosphine and the carbyne ligand. The cycloaddition led to the short-lived intermediate [OsH(η^5-C_5H_5){[=C(Ph)-CH_2C(CH_3)]P^{i}Pr$_2$}]PF_6, which rapidly afforded **165**, by a 1,2-hydrogen shift from the CH_2 group to the C_α(sp^2) atom of the bicycle.

The hydride ligand of **170** is fairly acidic, as the hydride of **30**. Thus, similarly to the latter, the addition of 2.0 equiv of sodium methoxide to a tetrahydrofuran solution of **170** resulted in its deprotonation, to afford the neutral carbyne derivative Os(η^5-C_5H_5)(≡CPh){P^i-Pr$_2$[C(CH_3)=CH_2]} (**171**). In methanol at room temperature, complex **171** was changed to the hydride alkoxycarbene derivative OsH(η^5-C_5H_5){=C(OMe)Ph}{P^{i}Pr$_2$-[C(CH_3)=CH_2]} (**172**), as a consequence of the addition of the O−H bond of the alcohol to the Os−C triple bond (Scheme 49).

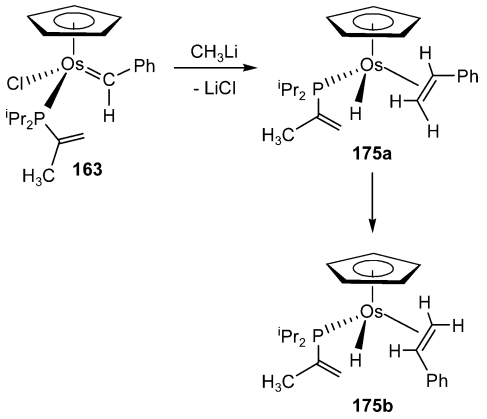
The carbene carbon atom of **163** has amphiphilic character, as does that of **22**, reacting with both nucleophiles and electrophiles. However, between **163** and **22** there are marked differences in the nature of the resulting products of the H^+ addition, which depend on the substituents of the phosphine. The differences are related to the stronger coordinating power of an isopropenyl group with regard to an isopropyl substituent.

At −40 °C, the addition of 1.0 equiv of HBF_4 to a dichloromethane solution of **163** resulted in the instantaneous formation of the benzyl−osmium(IV) complex [Os(η^5-C_5H_5)(CH_2Ph)Cl{[η^2-CH_2=C(CH_3)]P^{i}Pr$_2$}]-BF_4 (**173a**), as a result of the addition of the proton of the acid to the C_α atom of the carbene ligand, and the coordination of the isopropenyl substituent of the phosphine to the osmium atom (Scheme 50). At room temperature, complex **173a** rapidly isomerized into **173b**. The isomerization probably involves the decoordination of the isopropenyl group in **173a**, which lies between the phosphorus atom and the benzyl ligand, and its subsequent coordination between the phosphorus and chlorine atoms. The driving force for the isomerization seems to be the greater size of the benzyl group with regard to the chlorine atom, which makes the isopropenyl−benzyl cisoid disposition unfavorable with regard to the isopropenyl−chlorine cisoid disposition. The benzyl group of **173b** and one of the hydrogen atoms of the cyclopentadienyl ring slowly exchange their positions, resulting in a second isomerization to afford [OsH(η^5-$C_5H_4CH_2$Ph)Cl{[η^2-CH_2=C(CH_3)]P^{i}Pr$_2$}]-BF_4 (**174**).

Scheme 50



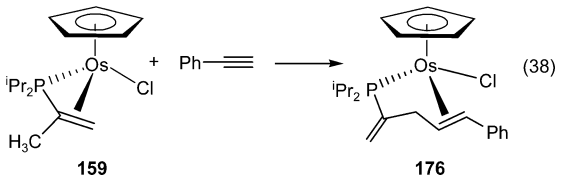
Scheme 51



The carbene carbon atom of **163**, like that of **22**, also shows a marked electrophilicity. Treatment at 0 °C of a tetrahydrofuran solution of **163** with a stoichiometric amount of MeLi afforded the hydride styrene derivative OsH(η^5-C_5H_5)(η^2-CH_2=CHPh){P^{i}Pr$_2$[C(CH_3)=CH_2]} (**175a**) containing the phenyl group of the styrene ligand cisoid-anti with regard to the phosphorus atom of the phosphine. In benzene at 80 °C complex **175a** isomerized to **175b**, with the phenyl group cisoid-anti with regard to the hydride ligand (Scheme 51). Complexes **175a** and **175b** are diastereoisomers resulting

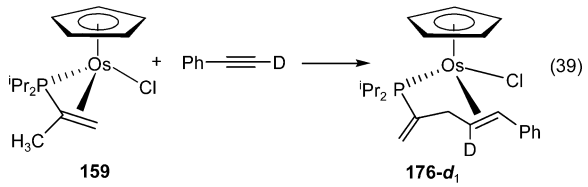
from the chirality of the osmium atom and the prochirality of the olefin. The conversion of **175a** into **175b** involves the decoordination of the styrene ligand and its subsequent recoordination at the other face.

Complex **159** also reacted with phenylacetylene to give the dienylphosphine derivative Os(η^5-C_5H_5)Cl{[η^2-(*E*)-CH(Ph)=CHCH$_2$C(=CH$_2$)]P^{i}Pr$_2$} (**176**), according to eq 38.[71]



The formation of **176** has been rationalized as an ene-type reaction between the isopropenyl substituent of the phosphine of **159** and the alkyne. The high regioselectivity of the process is noteworthy. Although three stereoisomers are feasible, only the one with the smallest steric hindrance between the initial organic moieties is formed.

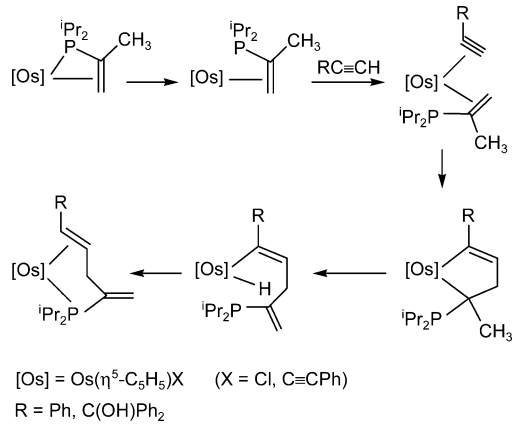
It is generally believed that this type of reaction proceeds via a metallacyclopentene intermediate that is generated by oxidative coupling between the olefin and the alkyne substrates.[2a,72] The *E* configuration at the coordinated double bond of **176** and the disposition of the phenyl group away from the osmium atom are consistent with this proposal. In favor of the formation of an osmacyclopentene unit, by coupling of coordinated π-olefin and π-alkyne ligands, it has been also observed that **159** reacts with PhC≡CD to afford exclusively Os(η^5-C_5H_5)Cl{[η^2-(*E*)-CH(Ph)=CDCH$_2$C(=CH$_2$)]P^{i}Pr$_2$} (**176-*d*$_1$**), according to eq 39.



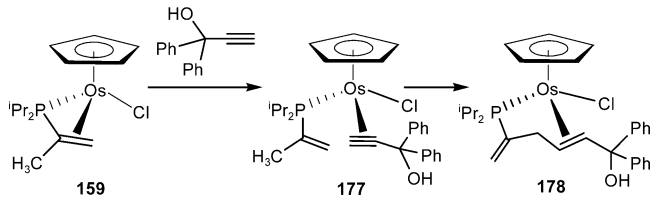
Scheme 52 summarizes the elementary steps proposed in the formation of **176**. The hemilabile properties of the isopropenyldiisopropylphosphine ligand should involve not only the isopropenyl group but also the phosphorus atom. Thus, decoordination of the latter in **159** should afford an unsaturated intermediate, which by coordination of the alkyne could give the key π-olefin−π-alkyne species. The oxidative coupling of these unsaturated ligands should afford the osmacyclopentene intermediate, which then could undergo a hydrogen β-elimination reaction in the methyl substituent at the $C_\alpha(sp^3)$ atom of the metallacycle. The β-elimination reaction should lead to a hydride alkenyl intermediate. Thus, the subsequent reductive elimination of olefin followed by the coordination of the phosphorus atom to the metal center could finally generate **176**.

The ene-type reaction shown in eq 38 has been extended to alkynols.[71] In contrast to the formation of **176**, the process is a two-step procedure (Scheme 53).

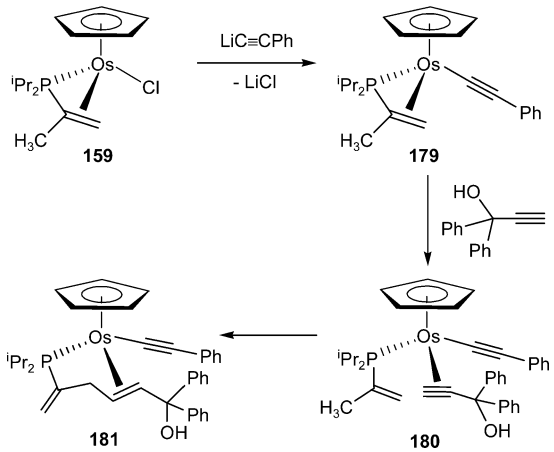
Scheme 52



Scheme 53



Scheme 54



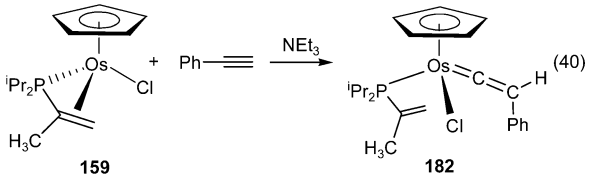
The addition, at room temperature, of 1,1-diphenyl-2-propyn-1-ol to a diethyl ether solution of **159** gave the π-alkynol derivative Os(η^5-C_5H_5)Cl{η^2-HC≡CC(OH)Ph$_2$}{P^{i}Pr$_2$[C(CH$_3$)=CH$_2$]} (**177**). In refluxing toluene, complex **177** was converted to Os(η^5-C_5H_5)Cl{[η^2-(*E*)-C(OH)Ph$_2$CH=CHCH$_2$C(=CH$_2$)]P^{i}Pr$_2$} (**178**). The process showed the same level of regioselectivity as the formation of **176**. This suggests that the products of these reactions are formed under thermodynamic control.

The replacement of the chloride ligand in the fragment Os(η^5-C_5H_5)Cl by a phenylacetylide group did not appear to have a significant influence on this type of reaction. Thus, it has been observed that the isopropenyldiisopropylphosphine-1,1-diphenyl-2-propyn-1-ol coupling shown in Scheme 53 is also promoted by the fragment Os(η^5-C_5H_5)(C≡CPh) (Scheme 54). The alkynyl complex Os(η^5-C_5H_5)(C≡CPh){[η^2-CH$_2$=C(CH$_3$)]-P^{i}Pr$_2$} (**179**) was prepared by treatment of a tetrahydrofuran solution of **159** with lithium phenylacetylide. The addition, at room temperature, of 1,1-diphenyl-2-propyn-1-ol to a diethyl ether solution of **179** afforded

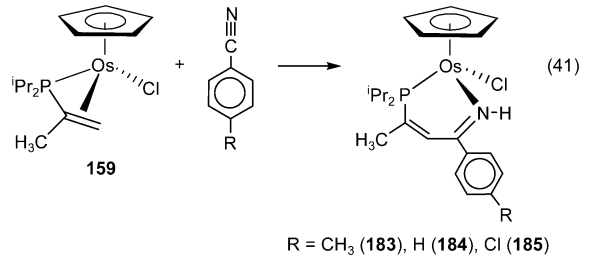
(71) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 2030.
(72) Chen, H.; Li, S. *Organometallics* **2005**, *24*, 872.

Os(η^5-C_5H_5)(C≡CPh){η^2-HC≡CC(OH)Ph_2}{P^iPr_2-[$C(CH_3)$=CH_2]} (**180**). In a manner similar to that for **177**, in refluxing toluene, complex **180** gave the ene reaction product Os(η^5-C_5H_5)(C≡CPh){[η^2-(*E*)-C(OH)Ph_2-CH=CHCH_2C(=CH_2)]P^iPr_2} (**181**).

Triethylamine inhibited the ene-type reaction between isopropenyldiisopropylphosphine and alkynes. In contrast to the reaction shown in eq 38, in the presence of 6.0 equiv of triethylamine, treatment of **159** with phenylacetylene led to the vinylidene complex Os(η^5-C_5H_5)Cl(=C=CHPh){P^iPr_2[$C(CH_3)$=CH_2]} (**182**), according to eq 40.

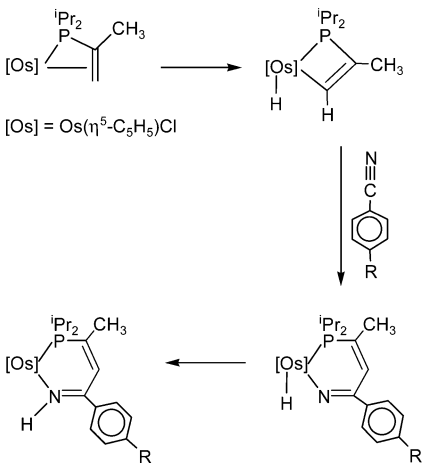


In refluxing toluene, complex **159** reacted with *p*-tolunitrile, benzonitrile, and *p*-chlorobenzonitrile to give the corresponding iminophosphine derivatives Os(η^5-C_5H_5)Cl{[NH=C(*p*-C_6H_4R)CH=$C(CH_3)$]P^iPr_2} (R = CH_3 (**183**), H (**184**), Cl (**185**)), formed by addition of one of the C(sp^2)−H bonds of the isopropenyl substituent of the phosphine of **159** to the carbon−nitrogen triple bond of the nitriles. The coupling is regiospecific and involves the formation of new carbon−carbon and nitrogen−hydrogen bonds (eq 41).[73]



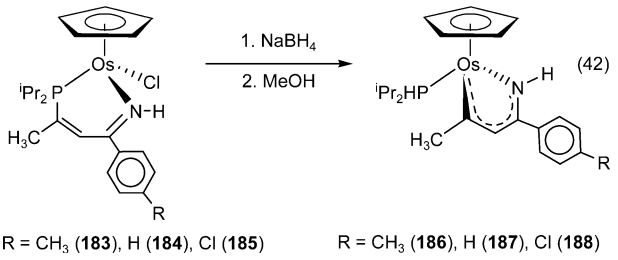
The formation of **183**−**185** has been rationalized according to Scheme 55. Initially, the activation of one of the C(sp^2)−H bonds of the isopropenyl substituent of the phosphine of **159** should afford a hydride alkenyl intermediate. Thus, the insertion of the carbon−nitrogen triple bond of the nitriles into the Os−C(sp^2) bond, followed by subsequent migration of the hydride

Scheme 55



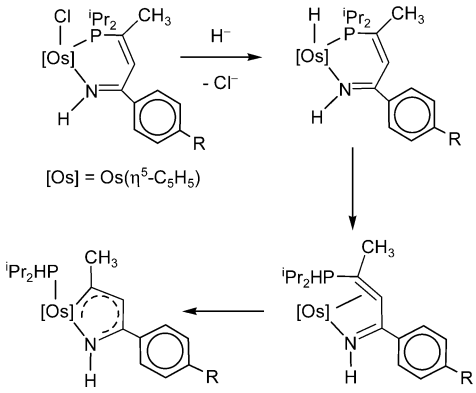
from the metal center to the nitrogen atom, could give the iminophosphine derivatives.

The fragments resulting from the addition of the C(sp^2)−H bond of the isopropenyl substituent of the phosphine to the carbon−nitrogen triple bond of the nitriles can be removed from the phosphine group by reaction with $NaBH_4$ (eq 42). Treatment at room temperature of a toluene solution of **183**−**185** with approximately 8 equiv of $NaBH_4$ and 1 mL of methanol resulted in the cleavage of the P−C(CH_3) bond of the iminophosphine ligands and the formation of the corresponding osmapyrrole derivatives Os(η^5-C_5H_5){NH···C-(*p*-C_6H_4R)···CH···C(CH_3)}(PH^iPr_2) (R = Me (**186**), H (**187**), Cl (**188**)).



Scheme 56 summarizes the elementary steps proposed to the formation of **186**−**188**. The replacement of the chloride by hydride in the starting compounds should afford hydride iminophosphine derivatives which should change by elimination of [NH=C(*p*-C_6H_4R)CH=$C(CH_3)$$PH^iPr_2$]$^+$.[74] These cations could stabilize the metal center by means of the coordination of the nitrogen atom and the carbon−carbon double bond. Finally, the activation of the P−C(CH_3) bond of these cations should give the osmapyrrole compounds.

Scheme 56

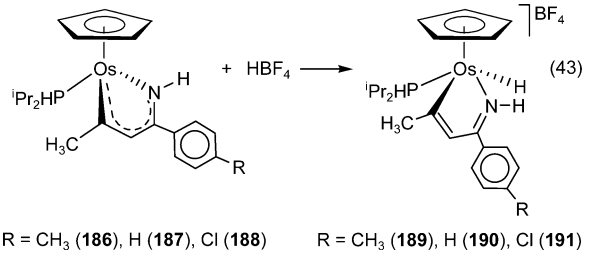


Complexes **186**−**188** reacted with HBF_4·OEt_2. The addition at 0 °C of the acid to a diethyl ether solution of these compounds gave the corresponding hydride−azabutadienyl−osmium(IV) derivatives [OsH(η^5-C_5H_5)-{NH=C(*p*-C_6H_4R)CH=C(CH_3)}(PH^iPr_2)]BF_4 (R = CH_3

(73) Baya, M.; Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2005**, *24*, 1225.

(74) (a) Esteruelas, M. A.; Lahoz, F. J.; Martín, M.; Oñate, E.; Oro, L. A.; Oñate, E. *Organometallics* **1997**, *16*, 4572. (b) Esteruelas, M. A.; Lahoz, F. J.; Martín, M.; Martínez, A.; Oro, L. A.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **1999**, *577*, 265.

(**189**), H (**190**), Cl (**191**)), as a result of the addition of the proton of the acid to the metal center of **186**−**188** (eq 43).



R = CH_3 (**186**), H (**187**), Cl (**188**) R = CH_3 (**189**), H (**190**), Cl (**191**)

Concluding Remarks

We started this account by pointing out that the noticeable lack of emphasis on the cyclopentadienyl−osmium complexes has been attributed to the scarcity of convenient synthetic precursors and the inertness of the octahedral osmium(II) species. The results summarized in the previous pages show a useful access to cyclopentadienyl−osmium chemistry and prove that any inertness can be overcome by the hard work of creative Ph.D. students.

A method of general use to obtain osmium complexes containing a cyclopentadienyl ligand involves the reaction between the known dihydride dichloro complex $OsH_2Cl_2(P^iPr_3)_2$ and a cyclopentadienyl derivative of an s- or p-block element. Treatment of $OsH_2Cl_2(P^iPr_3)_2$ with TlC_5H_5 gave $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$, which has been the starting point for the preparation of about 200 new complexes during the last few years and for the development of novel and interesting reactions.

The chemical behavior of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ seems to be the result of two factors: the large steric hindrance due to the triisopropylphosphine ligands, which are disposed mutally cis, and the strong nucleophilic character of the metal center. The latter is a consequence of the high Lewis basicity of the phosphines, the large π-donor power of the chlorine substituent, and the intrinsically high basicity of the osmium atom. In hydrocarbon solvents (pentane or toluene) the cleavage of an Os−P bond is favored. One of the phosphine ligands of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ is easily displaced by unsaturated organic species such as a carbene, an alkyne, and an alkynol. The substitution reactions afford complexes containing an Os−C double bond, including carbene, vinylidene, and allenylidene derivatives. The Os−C double bond of these compounds can be transformed into single and triple bonds. The C-donor ligands generated on the metal center in this way can grow by means of C−C and C−heteroatom coupling reactions. In the presence of chlorine abstractors the rupture of the Os−Cl bond is favored, and the resulting metal fragment is capable of activating $C(sp^3)$−H, $C(sp^2)$−H, C(sp)−H, and P−H bonds.

The C(sp)−H activation of terminal alkynes is the key step in the formation of cationic half-sandwich vinylidene− and allenylidene−osmium compounds. The cumulene ligands result from the dissociation of the hydride as a proton, from hydride−alkynyl−osmium(IV) intermediates, and the subsequent protonation of the alkynyl−osmium(II) species. A general method to prepare mixed-ligand allenylidene derivatives of the type $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)L(P^iPr_3)]^+$ involves the addition of Lewis bases to the four-electron alkyne complex $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}(P^iPr_3)]^+$. In agreement with its ruthenium counterpart, the allenylidene ligand of the carbonyl derivative $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]^+$ is a weak nucleophile and a strong electrophile. Thus, it isomerizes to 3-phenyl-1-indenylidene in the presence of acid, affords iminiumazetidinylidenemethyl derivatives by reaction with carbodiimides, and adds RXH (X = O, NR) molecules at the C_α−C_β double bond to give Fischer-type alkenylcarbene complexes.

One of the phosphine ligands of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ even can be displaced by Lewis bases as weak as group 14 element hydride compounds. The displacement products are $OsH(\eta^5\text{-}C_5H_5)Cl(ER_3)(P^iPr_3)$ (E = Si, Ge, Sn). Complexes of the type $OsH(\eta^5\text{-}C_5H_5)Cl(EPh_3)(P^iPr_3)$ (E = Si, Ge) react with lithium phenylacetylide to give the hydride alkynyl derivatives $OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)(EPh_3)(P^iPr_3)$ (E = Si, Ge), which have been protonated and deprotonated. The protonation of both species affords the hydride carbyne complex $[OsH(\eta^5\text{-}C_5H_5)(\equiv CCH_2Ph)(P^iPr_3)]^+$. The hydride and carbyne ligands of the latter can be transformed into olefin or carbene ligands by the action of Lewis bases, via ionic mechanisms. The π-acceptor groups favor the transformation into a carbene, while the π-donor ligands favor the formation of an olefin. In contrast to the protonation, the group 14 element, Si or Ge, has a marked influence on the deprotonation of $OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)(EPh_3)(P^iPr_3)$ (E = Si, Ge). While the deprotonation of the silyl derivative with *n*-butyllithium occurs selectively at the cyclopentadienyl ligand, the deprotonation of the germyl compound takes place both at the cyclopentadienyl group and at the metal center. Furthermore, the deprotonation of $OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)(SiPh_3)(P^iPr_3)$ is accompanied by the migration of the silyl group from the osmium atom to the cyclopentadienyl ligand. The reactions of the resulting anions with electrophiles transform the acetylide ligand of the starting compounds into vinylidene, carbyne, osmacyclopentadiene, or allyl units.

The transformations on the coordination sphere of the metal center involve not only organic fragments external to the $Os(\eta^5\text{-}C_5H_5)(P^iPr_3)$ skeleton but also its own skeleton. Treatment of a tetrahydrofuran solution of $OsH(\eta^5\text{-}C_5H_5)Cl(EPh_3)(P^iPr_3)$ (E = Si, Ge) with LiNu reagents (Nu = CH_2CN, $CH_2C(O)CH_3$, alkyl, NR_2, PPh_2) produces the replacement of the chloride ligand of the starting compounds by the Nu group, to afford unstable $OsH(\eta^5\text{-}C_5H_5)(Nu)(EPh_3)(P^iPr_3)$ intermediates. These species are converted to the final products in three different manners, depending on the nature of E and the Nu group, to give four different types of compounds: $OsH_2(\eta^5\text{-}C_5H_4EPh_3)(Nu)(P^iPr_3)$, $OsH_2(\eta^5\text{-}C_5H_4Nu)(EPh_3)(P^iPr_3)$, $OsH_2\{\eta^5\text{-}C_5H_4Si(C_6H_4)Ph_2\}(P^iPr_3)$, and $OsH(\eta^5\text{-}C_5H_5)\{Si(C_6H_4)Ph_2\}(P^iPr_3)$. The formation of these derivatives can be rationalized on the basis of the tendency of the EPh_3 and Nu ligands of $OsH(\eta^5\text{-}C_5H_5)(Nu)(EPh_3)(P^iPr_3)$ to exchange their positions with the hydrogen atoms of the cyclopentadienyl ring (PPh_2 > $N(allyl)_2$ > NEt_2 > $SiPh_3$ > ^{sec}Bu > $GePh_3$ > H, D, CH_2CN, $CH_2C(O)CH_3$) and on the basis of the stability of these species and $OsH_2(\eta^5\text{-}C_5H_4EPh_3)(Nu)(P^iPr_3)$ toward reductive elimination of H−Nu.

There is great interest in the preparation of novel functionalized phosphines by their connection with homogeneous catalysis.[75] In this context, the Os(η^5-C_5H_5)(P^iPr_3) unit can play an important role in the functionalization of triisopropylphosphine. Although the addition of a C(sp^3)−H bond to an organic species is difficult, the remaining triisopropylphosphine of the complex Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ is easily converted to isopropenyldiisopropylphosphine in a three-step procedure, involving the oxidative addition of molecular hydrogen to Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$, the subsequent reaction of the resulting dihydride complex with diphenylacetylene to afford Os(η^5-C_5H_5)Cl(η^2-PhC≡CPh)(P^iPr_3), and, finally, the reduction of the coordinated alkyne by hydrogen transfer from an isopropyl substituent of the phosphine ligand that is dehydrogenated. In contrast to the C(sp^3)−H bonds, the reactions involving C(sp^2)−H bonds are promising processes with regard to synthetic applications. Thus, the isopropenyldiisopropylphosphine ligand of the resulting Os(η^5-C_5H_5)Cl{[η^2-CH_2═C(CH_3)]-P^iPr_2} can be converted to α-allylphosphines by reaction with diazoalkanes via [2 + 2] cycloaddition reactions, to iminophosphines by insertion of the C−N triple bond of benzonitriles into one of the C(sp^2)−H bonds of the isopropenyl group, to dienylphosphines by ene-type reactions between the isopropenyl group and the C−C triple bond of alkynes, and even to dienylphosphines functionalized with a hydroxy group when the ene-type reaction involves an alkynol.

The cyclopentadienyl−osmium moiety, in addition to its capacity to promote the functionalization of alkylphosphines, also is useful in the study of the behavior of guiding alkane models. Alkanes are very weak Lewis bases and, therefore, *blind* molecules. They generally need the assistance of a coordination auxiliary to approach the transition metal. The use of a coordination assistance strategy to functionalize alkanes involves the rupture of the carbon−assistant bond after the functionalization, as an additional step within the overall synthetic process. The reactions of Os(η^5-C_5H_5)Cl{[NH═C(p-C_6H_4R)CH═C(CH_3)]P^iPr_2} with $NaBH_4$ to afford Os(η^5-C_5H_5)Cl{[NH┈C(p-C_6H_4R)┈CH┈C(CH_3)}-(PH^iPr_2) show how, in the cyclopentadienyl−osmium chemistry, the resulting fragment from the addition of a previously dehydrogenated isopropyl group to a benzonitrile easily can be removed from the P^iPr_2 coordination assistant.

In conclusion, complex Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ is a versatile starting material, which is allowing a rapid development of cyclopentadienyl−osmium chemistry. Its reactivity is not only limited to the fission of the Os−Cl bond and the dissociation of one of the phosphine ligands but also involves the cyclopentadienyl ring and the remaining phosphine ligand. As a consequence of the latter, a promising future can be envisaged for this chemistry.

Acknowledgment. We thank first and foremost J. I. Tolosa (1998), M. Baya (2002), and A. I. González (2005), who have developed their Ph.D.'s in this field. Moreover, we acknowledge the indispensable contribution of other members of our group (P. Crochet, N. Ruiz, N. Vela, M. L. Buil, E. Royo, E. Oñate, and A. Asensio). It is a pleasure to collaborate with Professor Agustí Lledós and his group, as well as with Professor Enrique Gutiérrez-Puebla and Dr. J. Modrego. Financial support from the MCYT of Spain (Proyect BQU2002-00606) is also acknowledged.

OM050272G

(75) (a) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed*. **2001**, *40*, 680. (b) Braunstein, P.; Boag, N. M. *Angew. Chem., Int. Ed*. **2001**, *40*, 2427.