isomorphous structures of pentakis(trimethylphosphine oxide)-magnesium perchlorate[15] and pentakis(trimethylarsine oxide)-magnesium perchlorate.[16] They both have a square-pyramidal coordination geometry. Thus it appears that enolase represents the first known trigonal-bipyramidal environment of Mg^{2+} ions. With the known propensity of Mg^{2+} for octahedral coordination, it is interesting to analyze how 5-fold coordination is achieved. It seems that the carboxylic ligands form a relatively rigid frame with the side chains of Glu295 and Asp320 stabilized by ion pairs formed with Lys396 and Lys345, respectively (Figure 1), and Asp246 by a hydrogen bond to Ala248 N. In the equatorial plane, in addition to OE1 of Glu295, there are two water molecules: WAT1 and WAT2. It would seem that these waters could adjust their position and create room for an additional water molecule ligand. The clue to the stability of the observed structure is most probably two strong H bonds, both 2.6 Å long, formed by WAT1 to the carboxylic groups of Asp246 and Asp296. They force the Glu295 OE1–Zn^{2+}–WAT1 angle of 120°, which leaves room for only one more oxygen atom in the equatorial plane. WAT1 has a very low temperature factor, $B = 7$ Å^2, and its position is conserved in apoenolase, and in the complexes of enolase with nonactivating metal ions Ca^{2+} and Sm^{3+} which have an octahedral coordination geometry.[17] The other water molecule ligand, WAT2, has a significantly higher temperature factor, $B = 22$ Å^2. It is probably the H_2O molecule that is replaced by the hydroxyl group of 2-phosphoglycerate in the forward reaction and that attacks C3 of the phosphoenolpyruvate molecule in the reverse reaction. The lower-resolution, 2.2-Å, studies of ternary complex enolase–Mg^{2+}–2-phosphoglycerate suggest such a mechanism.[12,17]

In solution, where hexaaquo complexes are the predominant form of Mg^{2+} ions, substitution of inner-sphere water occurs[18] at a rate of $10^{5.2}$ s^{-1}. In enzymes with the same coordination geometry, the ligand substitution should be slower. Thus, for Mg^{2+} enzymes, substrate dissociation could be the rate-limiting step. We propose that in enolase the unstable 5-fold coordination of the metal ion allows much faster ligand exchange than would be possible with the normal octahedral coordination.

In the structures of the Ca^{2+} and Sm^{3+} complexes of enolase, the metal-ion binding site is shifted 0.5 Å from the Zn^{2+} binding site approximately toward WAT2. This shift and the larger ionic radii of the nonactivating metal ions create sufficient space at the metal ion to accommodate the third, additional water molecule. The resulting coordination is octahedral.

Despite the high concentration of Zn^{2+} (25 mM), we did not find any evidence, in the final difference Fourier map, of metal-ion binding in the inhibitory site. It is possible that the inhibitory site is created only in the presence of substrate. We think so because at pH = 6.0 the crystals of yeast enolase survive soaking in 100 mM Mg^{2+} and 20 mM 2-phosphoglycerate solution but shatter in 20 mM Zn^{2+} and 20 mM 2-phosphoglycerate solution.

Overall, the structures of apo- and holoenolase in crystals seem to be almost identical, especially taking into account the pH and ionic strength differences.

The fact that we do not see conformational changes between apo- and holoenolase is probably due to the pH = 5.0 of studied apoenolase and the protonation of some of the metal carboxylic ligands. The conformational change observed upon divalent cation binding was reported at pH = 7.8.[19]

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Ortho-Vinylation and Alkylation of Coordinated Triarylphosphines by Reaction of Olefins with Osmium Polyhydrides

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Although cyclometalation of coordinated arylphosphine ligands is a reaction of widespread occurrence, examples of directly observed functionalization of the resulting metal carbon bonds are still somewhat limited.[1] We report here a distinctive example of such a reaction involving the coupling of an olefin to the metal-bonded carbon atom of a cyclometalated triarylphosphine ligand to form a stable complex in which the resulting vinyl substituent is bonded to the metal.

Our studies relate to the reactions of OsH_4L_3 and $[OsH_5L_3]^+$ (L = tri-*p*-tolylphosphine) depicted in the schemes. Treatment of a dichloromethane solution of OsH_4L_3 with 1 equiv of HBF_4 at −78 °C yields the cationic pentahydride $[OsH_5L_3]^+$, whose ^1H and ^{31}P NMR spectra[2] are similar to those of the known pentahydrides $[OsH_5(PPh_3)_3]^{+3}$ and $[OsH_5(PMe_2Ph)_3]^{+}$.[4] The rapid displacement of H_2 by Br$^-$ and I$^-$ to form OsH_3L_3Br and OsH_3L_3I obeys pseudo-first-order kinetics, suggestive of rate-determining dissociation of H_2. This is consistent with other observations that protonated polyhydrides lose H_2 more readily than their neutral precursors.[5] The rate constant for H_2 dissociation from $[OsH_5L_3]^+$ at −20 °C, 5.8×10^{-4} s^{-1}, is more than 6 orders of magnitude greater than that from OsH_4L_3, 2.4×10^{-10} s^{-1}.[6]

$[OsH_5L_3]^+$ reacts rapidly with excess ethylene at −20 °C to form the coordinately unsaturated complex $[OsHL_3(\eta^2-C_2H_4)]^+$ (1) and 2 mol of ethane in greater than 90% yield (^1H NMR).[7,8] The rate constant, 4.8×10^{-4} s^{-1}, independent of $[C_2H_4]$, is consistent with rate-determining dissociation of H_2. Above −20 °C, 1 is converted under C_2H_4 to the orthometalated complex $[OsL_2\{P(p-tolyl)_2(p-CH_3C_6H_3)\}(\eta^2-C_2H_4)]^+$ (2), characterized by ^1H and ^{31}P NMR spectroscopy.[7] 1 and 2 are related to the neutral complexes $OsH_2L_3(\eta^2-C_2H_4)$ (3) and $OsHL_2\{P(p-tolyl)_2(p-CH_3C_6H_3)\}(\eta^2-C_2H_4)$ (4) derived from the corresponding reactions of OsH_4L_3 with excess ethylene. 3 and 4 were isolated as white crystals and characterized by NMR spectroscopy and elemental analyses.[7] Protonation of either 3 or 4 at −60 °C under ethylene results in immediate conversion to 1 (Scheme I).

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(2) NMR data for $[OsH_5L_3]^+BF_4^-$: ^1H (CDCl$_3$, 25 °C) δ −5.85 (quart, J_{HP} = 4 Hz, 5 H, MH); T_1 (min) = 82 ms (500 MHz, −32 °C); $^{31}P\{^1H\}$ δ 7.24 (s). The low T_1 value suggests that this complex *may* have a "nonclassical" structure, possibly $[L_3Os(H_2)H_3]^+$. Such a formulation has been proposed by Hamilton and Crabtree for the related complex $[(Ph_3P)_3OsH_5]^{+}$.[3] Because of the uncertainty in the precise partitioning of hydrogens between terminal and η^2 ligands, we prefer to use the "generic" designation "OsH_5L_3". No particular structural formulation is intended.
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(6) Deduced from the rates of the reaction OsH_4L_3 + *t*-BuNC → $OsH_2L_3($*t*-BuNC$)$ + H_2 between 55 and 85 °C. ΔH^* = 25.4 kcal/mol and ΔS^* = −2 cal/mol-K.
(7) NMR, analytical, and mass spectral data are listed in the supplementary material.
(8) While the presence of coordinated dichloromethane or an agostic phenyl–hydrogen interaction cannot be excluded, it is noteworthy that neither changing the solvent from CD$_2$Cl$_2$ to CDCl$_3$ nor changing the anion from BF$_4^-$ to CF$_3$SO$_3^-$ affected the NMR spectrum of $[OsHL_3(C_2H_4)]^+$ appreciably. The fact that both 1 and the orthometalated analogue, 2, are intensely red-brown both in solution and in the solid state, whereas all the coordinately saturated osmium complexes that we have prepared are colorless or pale yellow, also supports the coordinately unsaturated formulation.

Scheme I

L = (P-TOLYL)$_3$ P
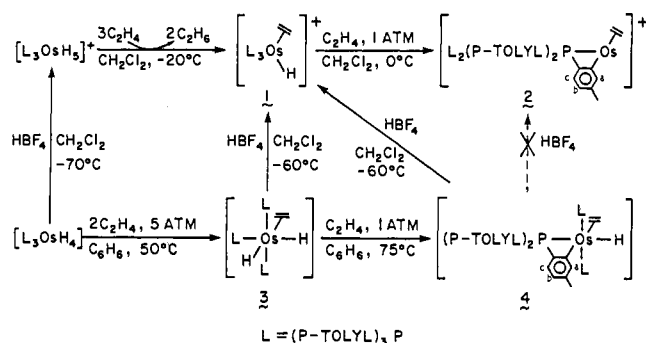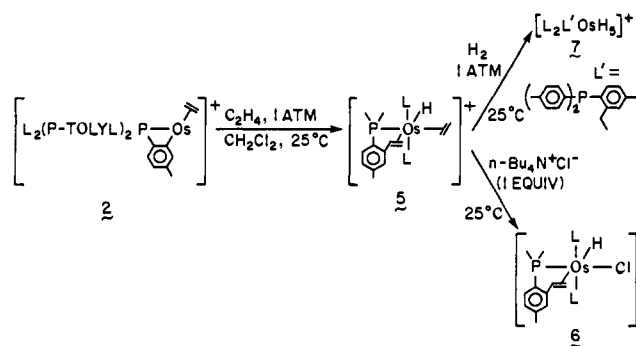
Scheme II

At 25 °C, reaction with excess ethylene converts **2** to [OsHL$_2${P(p-tolyl)$_2$(p-CH$_3$-o-CH$_2$=CHC$_6$H$_3$)}(η^2-C$_2$H$_4$)]$^+$ (-**5**), which contains an o-vinyl substituent on one of the aryl rings, coordinated in an η^2 manner to the osmium atom (Scheme II). **5** was isolated as white crystals of the BF$_4$ salt under ethylene and characterized by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy.[9] This compound loses ethylene readily above −20 °C ($k_{obsd} = 1 \times 10^{-3}$ s^{-1} at 0 °C). However, reaction with 1 equiv of n-Bu$_4$N$^+$Cl$^-$ yields the neutral complex OsHL$_2${P(p-tolyl)$_2$(p-CH$_3$-o-CH$_2$=CHC$_6$H$_3$)}Cl (**6**), which is stable indefinitely at 25 °C and was isolated as yellow crystals. The resonances due to the ortho-substituted phenyl ring and a coordinated vinyl group are clearly evident in both the ^{1}H and ^{13}C NMR spectra.[7]

5 reacts with H$_2$ at 0 °C to yield the pentahydride [OsH$_5$L$_2${P(p-tolyl)$_2$(p-CH$_3$-o-C$_2$H$_5$C$_6$H$_3$)}]$^+$ (**7**), containing an ethyl substituent on one of the ortho positions of a tri-p-tolylphosphine ligand.[7] The unique phosphine ligand of **7** was labile, and displacement by reaction with chloride ion and 1 equiv of tri-p-tolylphosphine yielded OsH$_3$L$_3$Cl and the ethylated phosphine isolated at a white solid by column chromatography and characterized by ^{1}H NMR (which clearly reveals the presence of an o-ethyl substituent) and ^{31}P NMR spectroscopy, as well as mass spectrometry.[7]
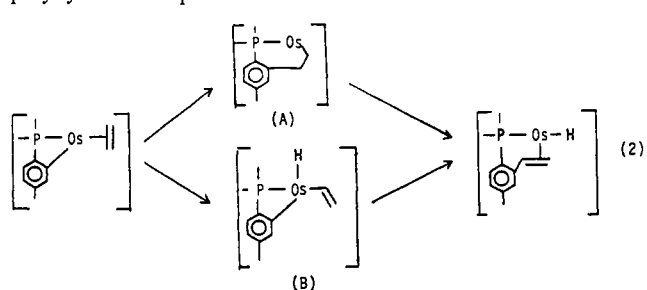
At 25 °C, 1 atm of H$_2$, [OsH$_5$L$_3$]$^+$ catalyzes the hydrogenation of ethylene and other olefins (with rates approaching 100 turnovers/h for styrene). The rate of phosphine ethylation is slow compared with that of ethylene hydrogenation. The relation of ethylation to the hydrogenation process and the effect on the rate of hydrogenation currently are being investigated.

Such ortho-alkylation of osmium triarylphosphine complexes appears to be a reaction of some generality, which we now have observed for other olefins and for neutral osmium polyhydride complexes, for example, under the conditions of the transfer hydrogenation reaction, eq 1. Although the osmium-containing species involved in this catalysis have yet to be characterized, the alkylated phosphine **8** was isolated from catalytically active solutions as a white solid and characterized by NMR and mass

spectrometries.[7] This identifies yet another possible route of deactivation of phosphine-containing homogeneous catalysts.[10]
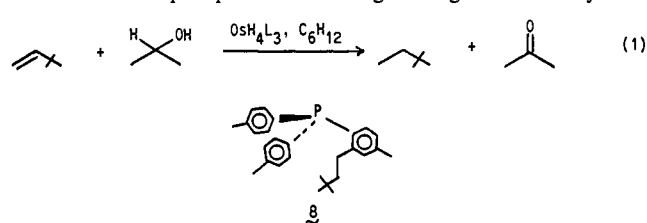
Two plausible mechanisms of the ortho-vinylation reactions are depicted in eq 2. Intermediate A finds parallels in recently reported insertion reactions of olefins into ruthenium–aryl[11] and nickel–aryl[12] bonds, as well as in the intermediates of postulated mechanisms of palladium-mediated aryl–olefin coupling reactions (Heck reaction).[13] On the other hand, the reductive elimination step of route B finds parallels in the postulated mechanisms of various nickel-, palladium-, and platinum-catalyzed aryl, vinyl, and alkynyl cross-coupling reactions.[14] At this stage the evidence is insufficient to select among these alternative mechanisms, and further studies on this theme, as well as on the scope of the chemistry uncovered by this investigation, are in progress. These observations serve, as do other recent studies, to call attention to the rich and novel chemistry that is exhibited by transition-metal polyhydride complexes.[15,3,5a]

Supplementary Material Available: NMR data for **1–8** and P(p-tolyl)$_2$(p-CH$_3$-o-C$_2$H$_5$C$_6$H$_3$), analytical data for **3** and **4**, and mass spectral data for **8** and P(p-tolyl)$_2$(p-CH$_3$-o-C$_2$H$_5$C$_6$H$_3$) (2 pages). Ordering information is given on any current masthead page.

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(9) ^{13}C{^{1}H} NMR (sample prepared by using ^{13}C$_2$H$_4$): δ 62.42 (dd, J_{CC} = 40 Hz, J_{CP} = 19 Hz, 1 C, vinyl CH), 52.36 (br s, 2 C, η^2-C$_2$H$_4$), 45.64 (d, J_{CC} = 40 Hz, 1 C, vinyl CH$_2$). Other data are in supplementary material.