Articles

Synthesis and Structure of New Osmium−PCP Complexes. Osmium-Mediated C−C Bond Activation

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The new complex Os{1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}(Cl)(PPh$_3$) (**2**) was obtained from the reaction between the diphosphine {1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_4$} (**1**) and OsCl$_2$(PPh$_3$)$_3$. **2** reacts with H$_2$ to yield the dihydrido species Os{1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}(H)$_2$(Cl)(PPh$_3$) (**3**). Addition of 1 equiv of carbon monoxide to **2** led to the formation of Os{1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}(CO)(Cl)(PPh$_3$) (**4**), while in the presence of excess CO, the bis-carbonyl complex Os{1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}(CO)$_2$-(Cl) (**5**) was formed. Both **2** and **5** were structurally characterized by X-ray diffraction studies. The reaction of OsCl$_2$(PPh$_3$)$_3$ (under hydrogen pressure) and OsHCl(PPh$_3$)$_3$ with the diphosphine {1,3,5-(CH$_3$)$_3$-2,6-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H} (**6**) led to the formation of the C−C activation products Os{3,5-(CH$_3$)-2,6-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H}(H$_2$)(Cl)(PPh$_3$) (**7**) and Os{3,5-(CH$_3$)-2,6-(^{i}Pr$_2$-PCH$_2$)$_2$C$_6$H}(Cl)(PPh$_3$) (**8**), respectively.

Introduction

Since their first use by Shaw and co-workers in the 1970s,[1] pincer ligands bearing a PCP donor set have attracted considerable attention. Upon coordination to transition metals, the rigid bis-chelated framework may confer on such complexes interesting reactivities, as well as allow the stabilization of uncommon species.[2] Efficient catalytic transformations by PCP-containing systems have also been reported.[3] Although a variety of late transition metals have been complexed with PCP ligands, of the iron triad only the ruthenium derivatives have been the subject of thorough studies.[4] To our knowledge, only two examples of osmium−PCP complexes have been reported.[5] Following our interest in the exploration of the chemistry of the PCP complexes, in particular regarding their potential in the field of strong bonds activation,[6] we describe here the synthesis and structure of new osmium complexes bearing the PCP ligand {1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}$^-$, as well as our first results regarding the intramolecular activation of carbon−carbon bonds with osmium.

Results and Discussion

The complex Os{1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}(Cl)(PPh$_3$) (**2**) was obtained as a green solid from the reaction between the diphosphine {1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_4$} (**1**) and the dichloride complex OsCl$_2$(PPh$_3$)$_3$[7] (Scheme 1). The cyclometalation occurs at room temperature and requires the use of triethylamine as a base. In its absence, the reaction proceeds sluggishly.

The geometry of complex **2** in the solid state was determined by an X-ray diffraction study (Figure 1).

The structure of the compound, similar to the one recently reported for Os{1,3-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$}(Cl)-(PPh$_3$),[5a] is of the distorted square-pyramidal type. The

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(1) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

(2) Some examples: (a) Vigalok, A.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 477. (b) Vigalok, A.; Rybtchinski, B.; Shimon, L. J. W.; Ben-David Y.; Milstein, D. *Organometallics* **1999**, *18*, 895. (c) Rybtchinski, B.; Ben-David Y.; Milstein, D. *Organometallics*, **1997**, *16*, 3786. (d) van der Boom, M. E.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 6652. (e) Ashkenazi, N.; Vigalok, A.; Parthiban, S.; Ben-David, Y.; Shimon, L. J. W.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 8797.

(3) (a) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687. (b) Jensen, C. M. *Chem. Commun.* **1999**, 2443. (c) Morales-Morales, D.; Redon, R.; Yung, C.; Jensen, C. M. *Chem. Commun.* **2000**, 1620. (d) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; Van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 743.

(4) (a) Karlen, T.; Dani, P.; Grove, D. M.; Steenwinkel, P.; van Koten, G. *Organometallics* **1996**, 15, 5687. (b) Jia, G.; Lee, H. M.; Xia, H. P.; Williams, I. D. *Organometallics* **1996**, *15*, 5453. (c) Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317. (d) Steenwinkel, P.; Kolmschot, S.; Gossage, R. A.; Dani, P.; Veldman, N.; Spek, A. L.; van Koten, G. *Eur. J. Inorg. Chem.* **1998**, 477. (e) van der Boom, M. E.; Kraatz, H.-B.; Hassner, L.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 3873.

(5) (a) Wen, T. B.; Cheung, Y. K.; Yao, J.; Wong, W.-T.; Zhou, Z. Y.; Jia, G. *Organometallics* **2000**, *19*, 3803. (b) For an earlier example of a PCP−Os complex formed by successive electrophilic additions of a carbene on PPh$_3$ ligands, see: Hoskins, S. V.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1984**, 1000.

(6) (a) For a review on C−C bond activation with a particular emphasis on PCP systems, see: Rybtchinski B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (b) C−O activation: van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531. van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Vigalok, A.; Milstein, D. *Angew. Chem., Int. Ed.* **1997**, *36*, 625.

(7) (a) Hoffmann, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221. (b) Elliott, G. P.; McAuley, N. M.; Roper W. R. *Inorg. Synth.* **1989**, *26*, 184.

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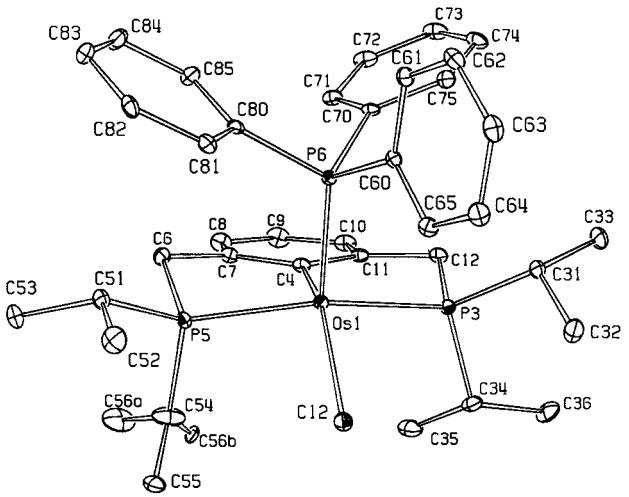
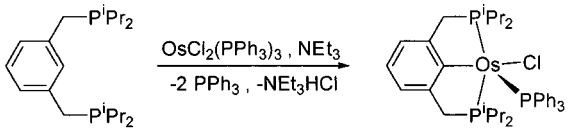


Figure 1. ORTEP drawing of **2** (30% probability). Selected bonds lengths (Å): Os(1)−C(4) = 2.064(3); Os(1)−Cl(2) = 2.4146(11); Os(1)−P(3) = 2.3322(10); Os(1)−P(5) = 2.3495(11); Os(1)−P(6) = 2.2189(9). Selected bond angles (deg): C(4)−Os(1)−Cl(2) = 144.49(8); P(3)−Os(1)−P(5) = 156.31(3); C(4)−Os(1)−P(3) = 82.04(8); C(4)−Os(1)−P(5) = 80.66(8); C(4)−Os(1)−P(6) = 89.63(8); P(6)−Os(1)−Cl(2) = 125.74(3).

Scheme 1



1 **2**

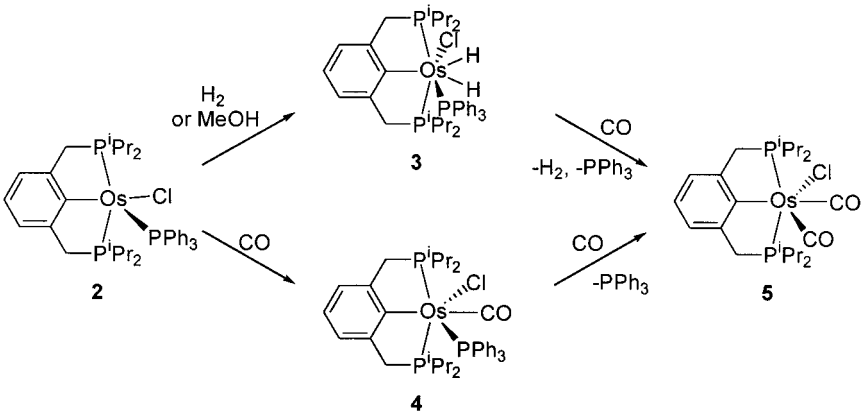
basal plane comprises the PCP ligand and the chlorine atom, while the apical position is occupied by the PPh_3 ligand. Noteworthy, the methyl groups of the isopropyl substituents on the PCP are pointing away from the triphenylphosphine, to reduce the steric interactions. The bond distances and angles are within the expected ranges. More particularly, the osmium−aryl bond distance, 2.064(3) Å, is comparable to the corresponding distance of the phenyl phosphine PCP analogue (2.04(1) Å).[5a] However, the PCP bite angle (P(3)−Os(1)−P(5)) of 156.31(3)° is slightly larger than the one reported for Os{1,3-$(Ph_2PCH_2)_2C_6H_3$}(Cl)(PPh_3) (149.9(1)°), probably due to the larger steric hindrance generated by the bulkier isopropyl substituents. The spectroscopic features of **2** in solution are in agreement with the crystal structure. The $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 at room temperature consists of a doublet and a triplet in a 2:1 ratio, centered at 33.88 and 5.17 ppm, respectively, with a coupling constant of 12.1 Hz. The ^1H NMR exhibits two sets of doublets of virtual triplets at 2.85 and 1.98 ppm, the consequence of the diastereotopicity of the methylene protons. Moreover, the ipso carbon of the pincer ligand resonates at 153.20 ppm as a triplet with a $^2J_{PC}$ coupling constant of 7.8 Hz. The multiplicity of this signal and the low value of the coupling constant indicates the absence of a phosphorus trans to the osmium-bound carbon, thus confirming the position of the triphenylphosphine at the apex of the coordination polyhedron.

The formal electronic unsaturation of the 16-electron complex **2** is demonstrated by its reactivity toward small donor molecules such as dihydrogen and carbon monoxide. Flushing of a green benzene solution of **2** with H_2 leads to a rapid color change to yellow. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR indicate the quantitative formation of Os{1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}(H)$_2$(Cl)(PPh_3) (**3**, Scheme 2). The spectroscopic features of **3** in deuterated benzene comprise in the $^{31}P\{^1H\}$ NMR the expected doublet and triplet at 29.61 and −6.91 ppm, respectively, for the PCP and PPh_3 ligands, as well as in ^1H NMR two sets of doublets of virtual triplets for the CH_2 groups, at 3.95 and 3.03 ppm. Moreover, the presence of two equivalent hydrogen ligands is confirmed by the observation of a doublet of triplets centered at −12.11 ppm. The low T_1 value of 132 ms at 213 K (C_7D_8) obtained for the hydride in **3** is borderline between a H_2 adduct and a dihydride.[8] To determine the nature of the H_2 moiety, we generated the complex **3-*d*** by reaction between **2** and HD for the determination of the $^1J_{HD}$ value. However, the ^1H NMR spectrum of the new complex merely exhibits a high-field signal similar to the one observed for **3**, but differing in its intensity relative to the other peaks (1H instead of 2H for **3**). The signal obtained on the $^1H\{^{31}P\}$ NMR spectrum is a singlet, and no splitting due to proton−deuterium coupling was observed. This suggests a structure of the dihydride type, i.e., a seven-coordinated species with two equivalent hydrides. Leaving a sample of **3-*d*** in C_6D_6 solution at room temperature for a few hours resulted in an increase of the intensity of the hydride signal. The ^2H NMR spectrum reveals a statistical redistribution of the deuterium between the hydride and the ortho protons of the aromatic rings of the triphenylphosphine at 8.06 ppm, thus showing the existence of a scrambling process that exchanges those protons, similarly to what was reported for RuHCl(PPh_3)$_3$.[9] An NOE experiment carried out at 243 K (C_7D_8, 400 MHz) indicates that the hydrides are located cis to the triphenylphosphine ligand. Moreover, the absence of a large coupling constant between the C_{ipso} of the PCP and the phosphorus nucleus of the PPh_3 is indicative that the latter lies in a cis position relative to the Os−C bond. Thus, it can be assumed that in this heptacoordinate complex the two hydrides are pseudo-trans to the PCP C_{ipso}, in the meridional plane defined by the Os−PCP framework, with the chloride trans to the triphenylphosphine. Slow loss of hydrogen gradually converts **3** back to **2**, both in solution and in the solid state. Noteworthy, **3** is also slowly formed by reaction between **2** and MeOH, most probably by dehydrogenation of the primary alcohol. Such a process is reminiscent of a key step in the catalytic hydrogen transfer reaction from alcohols to unsaturated substrates.[3d,10] No decarbonylation was observed (no carbonyl complex was detected by infrared spectroscopy).

In a similar fashion, **2** reacts at room temperature in benzene with 1 equiv of CO to yield quantitatively (by NMR) the carbon monoxide adduct Os{1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}(CO)(Cl)(PPh_3) (**4**). The carbonyl ligand gives rise to a characteristic absorption band in the IR spectrum at 1921 cm^{-1}. NMR data confirm the formulation, with notably the expected A_2B system in the $^{31}P\{^1H\}$ spectrum (doublet centered at 25.81 ppm for the

(8) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.
(9) Stolzenberg, A. M.; Muetterties, E. L. *Organometallics* **1985**, *4*, 1739.
(10) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *95*, 1051.

Scheme 2



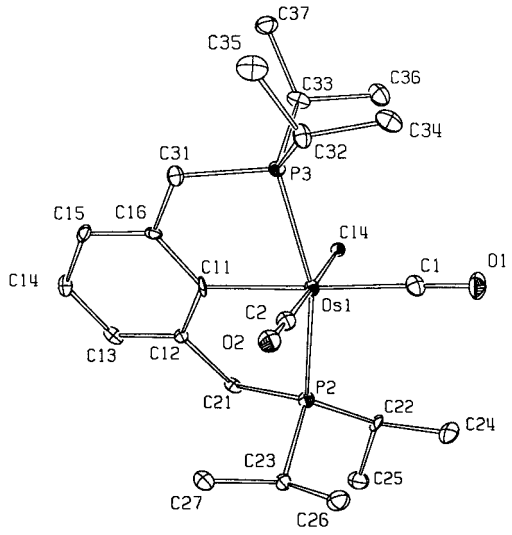


Figure 2. ORTEP drawing of **5** (30% probability). Selected bonds lengths (Å): Os(1)−C(1) = 1.941(8); Os(1)−C(2) = 1.855(15); Os(1)−C(11) = 2.154(6); Os(1)−Cl(4) = 2.474(2); Os(1)−P(2) = 2.3798(18); Os(1)−P(3) = 2.3816(17); C(1)−O(1) = 1.136(8); C(2)−O(2) = 1.16(2). Selected bond angles (deg): P(2)−Os(1)−P(3) = 160.59(6); C(2)−Os(1)−C(1) = 90.9(3); C(2)−Os(1)−C(11) = 92.8(3); C(11)−Os(1)−Cl(4) = 84.76(17).

PCP ligand, triplet at 3.71 ppm for the PPh_3, with respective intensities 2:1) and the two sets of doublets of virtual triplets for the diastereotopic methylene PCP protons at 4.00 and 3.14 ppm in the ^1H NMR spectrum. In the $^{13}C\{^1H\}$ NMR the ipso carbon resonates at 150.51 ppm, with a $^2J_{PC}$ coupling constant of 7.8 Hz, which is consistent with the absence of a phosphine in the position trans to the metal−aryl bond of the octahedral complex. The CO ligand appears in the $^{13}C\{^1H\}$ spectrum at 194.80 ppm as a doublet of triplets. The low coupling constant with the triphenylphosphine phosphorus allows us to conclude on a mutual cis postion of the CO and PPh_3 ligands. We can then conclude that in the octahedral complex **4** the chloride and the triphenylphosphine occupy the positions cis to the PCP ipso carbon, the carbonyl being coordinated trans to the metal−aryl bond. **4** reacts further with an additional equivalent of CO to give the bis-carbonyl complex Os{1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}(CO)$_2$(Cl) (**5**), with elimination of the triphenylphosphine ligand. **5** can be directly generated by pressurizing **2** with 3 bar CO or from the reaction of **3** with CO under mild conditions. Slow evaporation of a concentrated pentane solution of the reaction mixture led to the formation of colorless single crystals of the bis-carbonyl compound. An X-ray diffraction study unambiguously confirmed the formulation (Figure 2). The geometry around the osmium is distorted octahedral, with the PCP ligand coordinating in a meridional fashion, and two carbonyls occupying mutually cis positions.

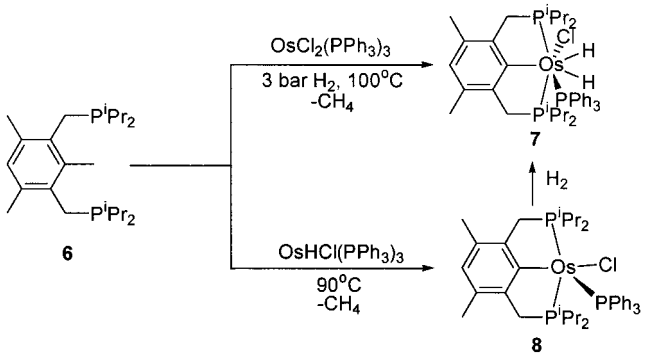
The PCP bite angle (P(2)−Os(1)−P(3)) of 160.59(6)° is significantly larger than in **2**, which could originate from the lesser distortion of the PCP framework in the pseudo-octahedral complex **5**. The Os−C_{aryl} bond length (Os(1)−C(11) = 2.154(6) Å) is longer than in **2**, as expected from the strong trans influence of the carbonyl ligand. It is similar to the value of 2.162(5) Å found in the isostructural complex Os(2-naphthyl)(Cl)(CO)$_2$(PPh$_3$)$_2$,[11] but shorter than the corresponding distance in Os{(*o*-PPh$_2$C$_6$H$_4$)$_2$(CH)}(Cl)(CO)$_2$[5b] (2.215(8) Å), as expected for a switch from a Os−C sp^2 to Os−C sp^3 bond. However, the osmium−carbonyl bond distances are very similar: 1.941(8) and 1.855(5) Å for **5**, 1.939(7) and 1.855(7) Å for Os(2-naphthyl)(Cl)(CO)$_2$(PPh$_3$)$_2$, and 1.918(10) and 1.878(10) Å for Os{(*o*-PPh$_2$C$_6$H$_4$)$_2$(CH)}(Cl)(CO)$_2$, for the CO ligands respectively trans and cis to the Os−C_{PCP} bond. Infrared spectroscopy shows two characteristic carbonyl absorption bands at 2001 and 1922 cm^{-1} of equal intensity, indicating a C(1)−Os(1)−C(2) angle of 90°, in agreement with the X-ray structure. The NMR features of **5** in C_6D_6 solution are those expected for the solid state structure, namely a singlet in $^{31}P\{^1H\}$ NMR at 46.63 ppm, and two sets of doublets of virtual triplets for the methylenic protons at 3.95 and 3.03 ppm, the latter as a result of the lack of equatorial symmetry in the PCP framework. The two different *C*O give rise to two triplets centered at 187.90 and 180.30 ppm in the $^{13}C\{^1H\}$ spectrum.

Having shown that osmium−PCP complexes were stable and synthetically accessible via C−H bond acti-

(11) Baker, L.-J.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. *J. Organomet. Chem.* **1998**, *551*, 247.

(12) C−C cleavage by β-alkyl elimination in a Os complex has been postulated: (a) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, A. M.; Onate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 1316. For C−C activation by Os clusters, see: (b) Chi, Y.; Chung, C.; Chou, Y. C.; Su, P. C.; Chiang, S. J.; Peng, S. M.; Lee, G. H. *Organometallics* **1997**, *16*, 1702. (c) Adams, R. D.; Qu, X. S. *Organometallics* **1995**, *14*, 4172. (d) Park, T. J.; Woo, B. W.; Chung, J. H.; Shim, S. C.; Lee, J. H.; Lim, S. S.; Suh, I. H. *Organometallics* **1994**, *13*, 3384. (e) Deeming, A. J.; Felix, M. S. B.; Nuel, D. *Inorg. Chim. Acta* **1993**, *213*, 3.

Scheme 3



vation, we chose to study the ability of this metal to promote intramolecular cleavage of C−C bonds.

We have recently reported such a reaction in the case of ruthenium,[4e] while osmium insertion into a strong, nonstrained C−C bond[12] has not been reported yet. Heating of an equimolar mixture of the complex $OsCl_2(PPh_3)_3$ and the diphosphine {1,3,5-$(CH_3)_3$-2,6-($^iPr_2PCH_2)_2C_6H$} (**6**) under 3 bar of hydrogen leads to the formation of the pincer complex Os{3,5-(CH_3)-2,6-($^iPr_2PCH_2)_2C_6H_3$}$(H)_2(Cl)(PPh_3)$ (**7**) in 80% yield by NMR (Scheme 3).

Separation of the products from the reaction mixture, especially from the residual triphenylphosphine, was prevented by the very similar solubilities of those compounds in organic solvents. However, the similarity of the spectroscopic features of **7** and **3**, from which it differs only by the presence of the two methyl groups on the PCP aromatic moiety, is in agreement with the formulation. The $^{31}P\{^1H\}$ NMR spectrum consists of a doublet at 29.65 ppm and a triplet at −7.33 ppm in a 2:1 respective proportion. The ^1H NMR spectrum exhibits notably a doublet of triplets at −12.09 ppm for the two osmium-bound hydrides, along with two doublets of triplets centered at 3.89 and 3.02 ppm for the CH_2 groups. The two methyls on the PCP aromatic ring resonate as a singlet at 2.36 ppm. This new osmium complex results from the selective activation of the $C_{sp2}-C_{sp3}$ Ar−CH_3 bond located between the two phosphine arms.

No activation of the two other analogous $C_{sp2}-C_{sp3}$ bonds was detected. This tends to indicate that the C−C activation requires an initial bis-coordination of the diphosphine substrate, as in the similar ruthenium system.[4e]

CH_4 formation was confirmed by GC analysis of the reaction gas phase. This product most probably originates from the reaction of a chelated diphosphine−osmium hydride species, in which the irreversible cleavage of the aryl−methyl bond yields a cyclometalated complex and CH_4. Indeed, it is known that $OsCl_2(PPh_3)_3$ reacts with hydrogen to yield hydride-containing complexes.[13]

A similar reaction is obtained by heating an equimolar mixture of the hydridochloride complex Os(H)(Cl)$(PPh_3)_3$[13] and the diphosphine (**6**) in the absence of hydrogen in a closed vessel. In this case, we observed the formation of the pincer complex Os{3,5-(CH_3)-2,6-($^iPr_2PCH_2)_2C_6H$}$(Cl)(PPh_3)$ (**8**) in 65% yield by NMR (Scheme 3). GC analysis of the gas phase showed methane formation. **8** has spectroscopic features very similar to those of **2**. The $^{31}P\{^1H\}$ displays a doublet and a triplet at 37.60 (2P) and 3.01 (1P) ppm, respectively, and the ^1H NMR is almost identical, with the notable exception of the singlet at 2.25 ppm for the two methyl groups on the PCP backbone. The methylene protons resonate at 2.86 and 1.73 ppm as doublets of virtual triplets. Placing a solution of **8** under hydrogen cleanly converted it to **7**, as expected from the reactivity of **2** with H_2.

(13) Ferrando, G.; Caulton, K. G. *Inorg. Chem.* **1999**, *38*, 4168.

Summary

New osmium complexes bearing a bulky PCP ligand have been synthesized, and two of them have been structurally characterized by X-ray diffraction. Moreover, we have reported the first example of osmium insertion into an unstrained strong aryl−C bond in solution. Our efforts are currently directed toward the broadening of the scope of this reaction, as well as toward mechanistic understanding of this process.

Experimental Section

General Procedures. All reactions were carried out under an inert atmosphere in a glovebox or using standard Schlenk techniques. Solvents were dried, distilled, and degassed before use. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ spectra were recorded on a Bruker AMX400 spectrometer at 400, 162, and 100 MHz, respectively, or on a Bruker DPX250 spectrometer at 250, 101, and 62 MHz, respectively. NMR solvent is C_6D_6. ^1H and ^{13}C chemical shifts are reported in ppm downfield from TMS and referenced to the residual solvent h_1 (7.15 ppm for benzene-d_6) and all-*d* solvent peaks (128.00 ppm for benzene), respectively. ^{31}P NMR chemical shifts are in ppm downfield from H_3PO_4 and referenced to an external 85% H_3PO_4 sample. All measurements were performed at 20 °C. Assignments of ^1H and $^{13}C\{^1H\}$ NMR signals were done with $^1H\{^{31}P\}$ and ^{13}C-DEPT-135 NMR, respectively. Infrared spectra were collected on a Nicolet Protégé 460 spectrometer. GC analyses were performed on a Hewlett-Packard HP6890 gas chromatograph equipped with a molecular sieves column. Elemental analyses were carried out at the Hebrew University, Jerusalem, and by H. Kolbe, Mülheim an der Ruhr, Germany. Mass spectroscopy analyses were carried out at the Ludwig-Maximilians Universität, München, Germany.

Os{1,3-($^iPr_2PCH_2)_2C_6H_3$}(Cl)(PPh_3) (2). To a deep green solution of 253 mg (0.241 mmol) of $OsCl_2(PPh_3)_3$ and 50 μL (0.359 mmol) of NEt_3 in 10 mL of benzene was added a solution of 82 mg (0.243 mmol) of **1** in 5 mL of benzene. Stirring the mixture overnight at room temperature caused the precipitation of NEt_3HCl out of the emerald green supernatant. Filtration and evaporation to dryness followed by repeated washings of the resulting green solid with pentane led to the isolation of 182 mg of the desired complex (yield: 91%). X-ray quality crystals were obtained by slow evaporation of a THF solution of the complex. ^1H NMR (250 MHz): δ 7.60 (m, 6H, PPh_3), 7.05 (d, J = 7.1 Hz, CH_{meta} PCP), 6.95 (m, 9H, PPh_3), 6.84 (t, J = 7.3 Hz, 1H, CH_{para} PCP), 2.85 (dvt, $^2J_{HH}$ = 16.6 Hz, $^vJ_{HP}$ = 5.0 Hz, 2H, ArC*H*HP), 2.76 (m, 2H, CH ^{i}Pr), 1.98 (dvt, $^2J_{HH}$ = 16.6 Hz, $^vJ_{HP}$ = 4.0 Hz, 2H, ArCH*H*P), 1.41 (m, 6H, CH_3 ^{i}Pr), 1.26 (m, 2H, CH ^{i}Pr), 1.23 (m, 6H, CH_3 ^{i}Pr), 1.09 (m, 6H, CH_3 ^{i}Pr), 0.75 (m, 6H, CH_3 ^{i}Pr). $^{31}P\{^1H\}$ NMR (100 MHz): δ 33.88 (d, $^2J_{PP}$ = 12.1 Hz, 2P, PCP), 5.17 (t, $^2J_{PP}$ = 12.1 Hz, 1P, PPh_3). $^{13}C\{^1H\}$ NMR (62 MHz): δ 153.20 (t, J_{PC} = 7.8 Hz, C_{ipso} PCP), 135.22−120.66 (C Ar), 37.89 (vt, $^vJ_{PC}$ = 15.0 Hz, $ArCH_2P$), 28.01 (vt, $^vJ_{PC}$ = 11.5 Hz, CH ^{i}Pr), 26.41 (vt, $^vJ_{PC}$ = 10.4 Hz, CH ^{i}Pr), 20.65 (CH_3 ^{i}Pr), 20.25 (CH_3 ^{i}Pr),

19.19 (CH_3 ^{i}Pr), 18.00 (CH_3 ^{i}Pr). Anal. Found (calcd): C, 55.51 (55.29); H, 5.91 (6.11).

Os{1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}(H)$_2$(Cl)(PPh$_3$) (3). A 30 mg (0.036 mmol) sample of **2** was dissolved in 5 mL of benzene. Hydrogen was bubbled through the solution, whose color turned rapidly from deep green to yellow. Evaporation to dryness yielded an analytically pure pale yellow solid in quantitative yield. ^{1}H NMR (400 MHz): δ 8.06 (m, 6H, PPh_3), 7.4−7.0 (m, 12H, H Ar), 3.95 (dvt, $^2J_{HH}$ = 15.7 Hz, J_{HP} = 3.7 Hz, 2H, ArC*H*HP), 3.03 (dvt, $^2J_{HH}$ = 15.7 Hz, J_{HP} = 3.7 Hz, 2H, ArCH*H*P), 2.20 (m, 2H, CH ^{i}Pr), 1.41 (m, 2H, CH ^{i}Pr), 1.04 (m, 6H, CH_3 ^{i}Pr), 0.75 (m, 1H, CH_3 ^{i}Pr), −12.11 (dt, $^2J_{PH}$ = 16.2 Hz, $^2J_{PH}$ = 13.0 Hz, 2H, Os(H)$_2$). ^{31}P{^{1}H} NMR (162 MHz): δ 29.61 (d, $^2J_{PP}$ = 12.4 Hz, 2P, PCP), −6.91 (t, $^2J_{PP}$ = 12.4 Hz, 1P, PPh_3). ^{13}C{^{1}H} NMR (100 MHz): δ 147.48 (dt, $^2J_{PC}$ = 7.1 Hz, 1.3 Hz, C_{ipso} PCP), 140.82−120.99 (C Ar), 39.86 (dvt, J_{PC} = 16.4 Hz, 6.0 Hz, ArCH_2P), 25.19 (vt, J_{PC} = 13.3 Hz, CH ^{i}Pr), 24.32 (vt, J_{PC} = 10.8 Hz, CH ^{i}Pr), 20.47 (vt, J_{PC} = 1.9 Hz, CH_3 ^{i}Pr), 20.06 (CH_3 ^{i}Pr), 19.19 (CH_3 ^{i}Pr), 18.90 (CH_3 ^{i}Pr). Anal. Found (calcd): C, 55.04 (55.16); H, 6.26 (6.33).

Os{1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}(CO)(Cl)(PPh$_3$) (4). To 96 mg (0.115 mmol) of **2** dissolved in 10 mL of benzene in a closed vessel was added with a syringe 2.8 mL (0.116 mmol) of CO. The green solution turned gradually to yellow. Evaporation to dryness followed by repeated washing with 10 mL portions of pentane led to the isolation of 84 mg of analytically pure **4** (yield: 86%). ^{1}H NMR (250 MHz): δ 7.55 (m, 6H, PPh_3), 6.90 (m, 12H, H Ar PCP + PPh_3), 4.00 (dvt, $^2J_{HH}$ = 15.1 Hz, $^vJ_{HP}$ = 4.6 Hz, 2H, ArC*H*HP), 3.68 (m, 2H, CH ^{i}Pr), 3.14 (dvt, $^2J_{HH}$ = 15.0 Hz, $^vJ_{HP}$ = 3.1 Hz, 2H, ArCH*H*P), 1.54 (m, 6H, CH_3 ^{i}Pr), 1.15 (m, 6H, CH_3 ^{i}Pr), 1.00 (m, 2H, CH ^{i}Pr), 0.87 (m, 6H, CH_3 ^{i}Pr), 0.61 (m, 6H, CH_3 ^{i}Pr). ^{31}P{^{1}H} NMR (162 MHz): δ 25.81 (d, $^2J_{PP}$ = 8.6 Hz, 2P, PCP), 3.71 (t, $^2J_{PP}$ = 8.6 Hz, 1P, PPh_3). ^{13}C{^{1}H} NMR (62 MHz): δ 194.80 (dt, $^2J_{PC}$ = 9.5 Hz, 4.8 Hz, *C*O), 150.51 (t, $^2J_{PC}$ = 7.8 Hz, C_{ipso} PCP), 138.57−121.73 (C Ar), 42.02 (vt, J_{PC} = 17.2 Hz, CH_2 PCP), 26.46 (vt, J_{PC} = 10.1 Hz, CH ^{i}Pr), 25.22 (vt, J_{PC} = 13.2 Hz, CH ^{i}Pr), 21.07 (CH_3 ^{i}Pr), 20.50 (CH_3 ^{i}Pr), 20.12 (CH_3 ^{i}Pr), 19.79 (CH_3 ^{i}Pr). IR (NaCl, film, cm^{-1}): 1921, ν_{CO}. Anal. Found (calcd): C, 54.75 (54.89); H, 5.87 (5.91).

Os{1,3-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}(CO)$_2$(Cl) (5). Stirring benzene solutions of **2**, **3**, or **4** under CO pressure (3 bar) at room temperature for 3 h yielded yellow solutions of **5**. Evaporation to dryness gave yellow solids containing both the expected complex and free triphenylphosphine. Analytically pure material was obtained by recrystallization from diethyl ether at −30 °C. Colorless single crystals of **5** were formed by slow evaporation of a concentrated pentane solution. ^{1}H NMR (250 MHz): δ 7.00 (m, 3H, CH Ar PCP), 3.66 (dvt, $^2J_{HH}$ = 15.8 Hz, $^vJ_{HP}$ = 4.7 Hz, 2H, ArC*H*HP), 3.19 (dvt, $^2J_{HH}$ = 15.8 Hz, $^vJ_{HP}$ = 3.7 Hz, 2H, ArCH*H*P), 2.94 (m, 2H, CH ^{i}Pr), 2.00 (m, 2H, CH ^{i}Pr), 1.26 (m, 6H, CH_3 ^{i}Pr), 1.05 (m, 6H, CH_3 ^{i}Pr), 0.95 (m, 12H, CH_3 ^{i}Pr). ^{31}P{^{1}H} NMR (100 MHz): δ 46.63 (s, PCP). ^{13}C{^{1}H} NMR (62 MHz): δ 187.89 (t, $^2J_{PC}$ = 4.9 Hz, Os*C*O), 180.30 (t, $^2J_{PC}$ = 7.8 Hz, Os*C*O), 149.19 (t, $^2J_{PC}$ = 7.4 Hz, C_{ipso} PCP), 138.06−122.17 (C Ar), 41.34 (vt, $^vJ_{PC}$ = 17.3 Hz, Ar*C*H$_2$P), 26.04 (vt, $^vJ_{PC}$ = 13.2 Hz, CH ^{i}Pr), 23.6 (vt, $^vJ_{PC}$ = 13.9 Hz, CH ^{i}Pr), 20.30 (CH_3 ^{i}Pr), 19.87 (CH_3 ^{i}Pr), 19.48 (CH_3 ^{i}Pr), 17.98 (CH_3 ^{i}Pr). IR (NaCl, film, cm^{-1}): 2001, 1922, ν_{CO}. Anal. Found (calcd): C, 42.60 (42.68); H, 5.63 (5.70).

Os{3,5-(CH$_3$)-2,6-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H}(Cl)(H)$_2$(PPh$_3$) (7). In a Fischer−Porter bottle, 66 mg (0.063 mmol) of $OsCl_2(PPh_3)_3$ and 24 mg (0.063 mmol) of **6** were dissolved in 5 mL of THF. The solution was pressurized with 3 bar of hydrogen and heated at 100 °C for 16 h. The gas phase was collected by regular Schlenk techniques, and the resulting yellow solution was evaporated to dryness. NMR showed the presence of **7** as the major species. Attempts to separate this product from excess PPh_3 were not successful due to the very similar solubility properties of these compounds in organic solvents such as pentane, diethyl ether, or ethanol. Chromatography attempts led to decomposition of **7**. ^{1}H NMR (400 MHz): δ 8.07 (m, 6H, PPh_3), 7.00 (9H, PPh_3), 6.81 (s, 1H, H_{para} PCP), 3.89 (dvt, $^2J_{HH}$ = 15.3 Hz, $^vJ_{HP}$ = 3.4 Hz, 2H, ArC*H*HP), 3.02 (dvt, $^2J_{HH}$ = 15.3 Hz, J_{HP} = 3.3 Hz, 2H, ArCH*H*P), 2.36 (s, 6H, Ar*CH*$_3$), 2.17 (m, 2H, CH ^{i}Pr), 1.44 (m, 2H, CH ^{i}Pr), 1.03 (m, 6H, CH_3 ^{i}Pr), 0.81 (m, 6H, CH_3 ^{i}Pr), 0.74 (m, 12H, CH_3 ^{i}Pr), −12.09 (dt, $^2J_{PH}$ = 14.9 Hz, $^2J_{PH}$ = 13.0 Hz, 2H, Os(H)$_2$). ^{31}P-{^{1}H} NMR (162 MHz): δ 29.65 (d, $^2J_{PP}$ = 10.5 Hz, PCP), −7.33 (t, $^2J_{PP}$ = 10.5 Hz, PPh_3). ^{13}C{^{1}H} NMR (100 MHz): δ 143.25 (dt, $^2J_{PC}$ = 7.1 Hz, 1.0 Hz, C_{ipso} Ar), 140.70−127.37 (m, C Ar), 36.89 (dvt, $^vJ_{PC}$ = 16.8 Hz, $^3J_{PC}$ = 6.1 Hz, ArCH_2P), 25.40 (vt, $^vJ_{PC}$ = 13.5 Hz, CH ^{i}Pr), 24.43 (vt, J_{PC} = 10.8 Hz, CH ^{i}Pr), 22.74 (s, CH_3 Ar), 20.52 (CH_3 ^{i}Pr), 19.90 (CH_3 ^{i}Pr), 19.17 (CH_3 ^{i}Pr), 18.86 (CH_3 ^{i}Pr). MS (EI+): 855 ([M − H]$^+$).

Os{3,5-(CH$_3$)-2,6-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H}(Cl)(PPh$_3$) (8). A mixture of 20 mg of Os(H)(Cl)$(PPh_3)_3$ (0.020 mmol) and 7.5 mg of **6** (0.020 mmol) in 5 mL of THF was heated at 90 °C in a closed vessel for 16 h. A color change from brown to deep green was observed. Volatiles were evaporated from the green reaction mixture to yield a green solid, which contains **8** as the major species. Attempts to separate this product from excess PPh_3 were not successful due to the very similar solubility properties of these compounds in organic solvents such as pentane, diethyl ether, or ethanol. Chromatography attempts led to decomposition of **8**. Hydrogen bubbling through a C_6D_6 solution of this solid resulted in rapid conversion of **8** to **7**. ^{1}H NMR (250 MHz): δ 7.51 (m, 6H, PPh_3), 6.93 (m, 9H, PPh_3), 6.52 (s, 1H, H_{para} PCP), 2.86 (dvt, $^2J_{HH}$ = 17.0 Hz, $^vJ_{HP}$ =5.0 Hz, 2H, ArC*H*HP), 2.81 (m, 2H, CH ^{i}Pr), 2.24 (s, 6H, Ar*CH*$_3$), 1.73 (dvt, $^2J_{HH}$ = 17.0 Hz, J_{HP} = 3.5 Hz, 2H, ArCH*H*P), 1.43 (m, 6H, CH_3 ^{i}Pr), 1.27 (m, 8H, CH + CH_3 ^{i}Pr), 1.09 (m, 6H, CH_3 ^{i}Pr), 0.77 (m, 6H, CH_3 ^{i}Pr). ^{31}P{^{1}H} NMR (101 MHz): δ 37.60 (d, $^2J_{PP}$ = 11.3 Hz, 2P, PCP), 3.01 (t, $^2J_{PP}$ = 11.3 Hz, 1P, PPh_3).

Table 1. Crystal Data for 2 and 5

	2	**5**
formula	$C_{36}H_{50}ClOsP_3$	$C_{22}H_{36}O_2ClOsP_2$
fw	801.32	620.10
space group	$P\bar{1}$	*Pbca*
cryst syst	triclinic	orthorhombic
a, Å	10.430(2)	10.5700(3)
b, Å	10.944(2)	15.5690(4)
c, Å	17.643(4)	28.8730(7)
α, deg	72.55(3)	90
β, deg	81.04(3)	90
γ, deg	66.51(3)	90
V, Å^3	1760.5(6)	4751.5(2)
D_{calcd}, g cm^{-3}	1.512	1.734
Z	2	8
μ(Mo Kα), mm^{-1}	3.857	5.630
cryst size, mm^{-3}	0.3 × 0.1 × 0.1	0.1 × 0.07 × 0.03
T, K	120(2)	120(2)
no. of reflns collected	32 315	14 052
no. of indep reflns	11 563 [*R*(int) = 0.053]	3402 [*R*(int) = 0.092]
final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0318, wR_2 = 0.0632	R_1 = 0.0334, wR_2 = 0.0817
R indices (all data)	R_1 = 0.0435, wR_2 = 0.0662	R_1 = 0.0498, wR_2 = 0.0869

X-ray Crystal Structure Determination of 2. Red crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a THF solution. A crystal (0.3 × 0.1 × 0.1 mm^3) was mounted on a nylon loop and flash frozen in a cold nitrogen stream (at 120 K) on a Nonius KappaCCD diffractometer mounted on a FR590 generator equipped with a sealed tube with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The SHELX-97 program package was used for structure solution and refinement. The structure was solved using direct methods and refined by full-matrix least-squares techniques based on F^2. The final cycle of the least-squares refinement for **2** gave an agreement factor R = 0.032 (based on F^2) for data with $I > 2\sigma(I)$ and R = 0.044 for all data (11 563 reflections). Idealized hydrogens were placed and refined in a

riding mode. ORTEP views of the molecular structures and the adopted numbering are shown in Figure 1. Table 1 gives details of the crystal structure determination.

X-ray Crystal Structure Determination of 5. Colorless crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a pentane solution. A crystal ($0.1 \times 0.07 \times 0.03$ mm^3) was mounted on a nylon loop and flash frozen in a cold nitrogen stream (at 120 K) on a Nonius KappaCCD diffractometer mounted on a FR590 generator equipped with a sealed tube with Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The SHELX-97 program package was used for structure solution and refinement. The structure was solved using direct methods and refined by full-matrix least-squares techniques based on F^2. The final cycle of the least-squares refinement for **5** gave an agreement factor $R = 0.0334$ (based on F^2) for data with $I > 2\sigma(I)$ and $R = 0.0498$ for all data (3402 reflections). No constraints were used. During the structure solution, it appeared that a chlorine atom (denoted as Cl(5) in Supporting Information) was located between C(2) and O(2) with a 10% occupancy. The structure was refined with such dicrete disorder modeled; however the corresponding carbonyl that would have been located near Cl(4) could not be located. Idealized hydrogens were placed and refined in a riding mode. ORTEP views of the molecular structures and the adopted numbering are shown in Figure 2. Table 1 gives details of the crystal structure determination.

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Supporting Information Available: ^{1}H NMR spectra of **6** and **7** with PPh_3, tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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