

Carbon–Carbon Double Bond Formation from Two *o*-Methyl Groups in Osmium Phosphine Complexes

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The osmium complex [(NH₄)₂OsCl₆] reacts with PPh₂(2,6-Me₂C₆H₃) in a 2-propanol–water mixture at reflux to give quantitatively a cyclometalated osmium(II) complex containing a tridentate *trans*-stilbene-type ligand, which forms via a dehydrogenative carbon–carbon coupling of two phosphine *o*-methyl groups. The structure of this complex has been determined by an X-ray investigation. Carbon–carbon double bond formation has also been observed in the reaction of the osmium(II) precursor [OsCl₂(PPh₃)₃] with PPh₂(2,6-Me₂C₆H₃) in toluene, leading to a hydrido osmium(II) complex containing the same tridentate stilbene-type ligand.

Introduction

It has recently pointed out that the phosphine PPh₂(2,6-Me₂C₆H₃) (L) is a suitable ligand for the isolation of a rare example of the 14-electron ruthenium compound [RuCl₂L₂], stabilized by two agostic interactions of two *o*-methyl groups.¹ Bulky phosphines have been extensively employed to obtain coordinatively unsaturated complexes, which can be stabilized by agostic interactions,² or cyclometalated species that result from intramolecular C–H activation (i.e., oxidative addition),³ depending on the features of the metal center. The cleavage of a C–H bond by direct participation of a transition metal⁴ is a process of considerable interest for potential applications in catalytic hydrocarbon transformations.⁵ On the other hand, compounds containing agostic interactions have been proposed as intermediates in reactions involving C–H bond splitting.⁶

In continuation of our work on the chemistry of complexes having aryl phosphines with two methyl groups in ortho positions,¹ we report herein the results obtained with osmium. It can be anticipated that with osmium, which is more electron rich compared to ruthenium, cyclometalation is expected. Furthermore, it is well-known that haloosmium(II) derivatives bearing small phosphines are generally six-coordinate species of general formula [OsX₂(PR₃)₄] (X = halide),⁷ whereas with the bulky triphenylphosphine five-coordinate complexes such as [OsX₂(PPh₃)₃] are formed,⁸ similarly to the ruthenium analogues.⁹ We have now found that employment of PPh₂(2,6-Me₂C₆H₃) leads to formation in high yield of osmium complexes bearing the tridentate chelating ligand **BDPS** (Figure 1).

The latter contains an olefinic bond that is formed from two *o*-methyl groups of two phosphines, as result of activation of four C–H bonds. Coupling between *o*-methyl groups of aryl phosphines was previously observed by Bennett and Longstaff in the reaction of rhodium(III) halides with PPh_{*n*}(2-MeC₆H₄)_{3-*n*}, the products being isolated in only poor yields.¹⁰

Results and Discussion

Treatment of ammonium hexachloroosmate(IV) with PPh₂(2,6-Me₂C₆H₃) in a 2-propanol–water mixture un-

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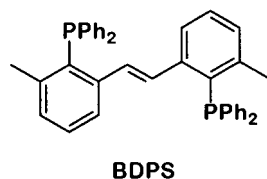
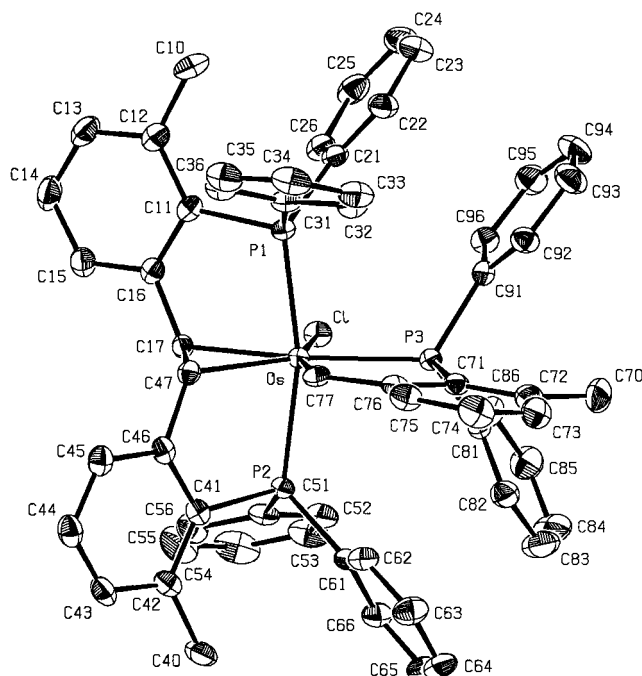
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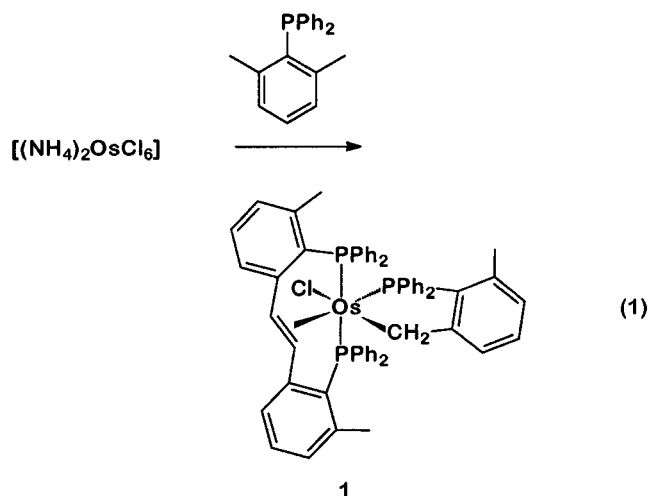
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**Figure 1.****Figure 2.** ORTEP^{22f} representation of compound **1** in the solid state. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

der reflux afforded quantitatively the light green product $[\text{OsCl}\{2\text{-CH}_2\text{-6-MeC}_6\text{H}_3\}\text{PPh}_2](\text{BDPS})$ (**1**) (eq 1).



It should be noted that no carbonyl abstraction from 2-propanol occurs and that addition of water is necessary to improve solubility of $[(\text{NH}_4)_2\text{OsCl}_6]$. The diamagnetic complex which was analyzed satisfactorily as **1** is thermally stable and slightly air sensitive in solid state and in solution. The X-ray analysis (Figure 2) shows that one phosphine group, $\text{PPh}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$, has undergone a cyclometalation of one methyl group,

Table 1. Selected Interatomic Distances (Å), Angles (deg), and Torsion Angles (deg) for $1 \cdot \text{CH}_2\text{Cl}_2$

Os–Cl	2.4819(6)	Os–C17	2.166(3)
Os–P1	2.3547(7)	Os–C47	2.152(3)
Os–P2	2.3597(7)	Os–C77	2.168(3)
Os–P3	2.3899(6)	C17–C47	1.437(4)
Cl–Os–P1	89.30(2)	P1–Os–C77	91.57(7)
Cl–Os–P2	92.06(2)	P2–Os–P3	96.35(2)
Cl–Os–P3	83.55(2)	P2–Os–C17	86.52(7)
Cl–Os–C17	82.90(7)	P2–Os–C47	80.01(7)
Cl–Os–C47	121.25(8)	P2–Os–C77	91.05(7)
Cl–Os–C77	163.31(7)	P3–Os–C17	166.24(7)
P1–Os–P2	166.25(3)	P3–Os–C47	154.88(8)
P1–Os–P3	97.40(2)	P3–Os–C77	79.81(7)
P1–Os–C17	80.06(7)	C17–Os–C47	38.88(10)
P1–Os–C47	87.59(7)		
		C16–C17–C47–C46	134.8(3)

whereas two other phosphines are converted into a tridentate *trans*-stilbene-type ligand by cleavage of four C–H bonds of two methyl groups.

The Os–P1 and Os–P2 distances are 2.3547(7) and 2.3597(7) Å, respectively, and are slightly shorter compared to the Os–P3 distance 2.3899(6) Å (Table 1) and to other six-coordinate osmium complexes with arylphosphines.¹¹

All the osmium–carbon distances are similar and are in agreement with those reported for alkyl¹² and olefinic¹³ osmium(II) complexes. The P1–Os–P2 angle is 166.25(3)°, and the P3–Os–C77 angle is 79.81(7)°, which probably reflects the geometrical constraints of the phosphine chelating ligand. The bound olefin has a C17–C47 distance of 1.437(4) Å, an expected lengthening on coordination, and the C17, C47, Os, C77, P3, and Cl atoms are almost coplanar (distance to the mean plane less than ±0.12 Å). Furthermore, the dihedral angle between the planes C46–C47–C17 and C47–C17–C16 is 134.8(3)°; the deviation from 180° is likely to be caused by the tridentate chelation.

In agreement with the solid-state structure of **1**, the ³¹P NMR spectrum of this complex in CDCl₃ shows a typical pattern for an ABC system. The ¹H{³¹P} NMR spectrum of **1** exhibits two doublets at δ 3.94 and 3.48 with a *J*(HH) value of 7.9 Hz for the *trans*-olefinic protons and two doublets at δ 3.50 and 2.62 with a *J*(HH) value of 19.1 Hz for the methylene protons.

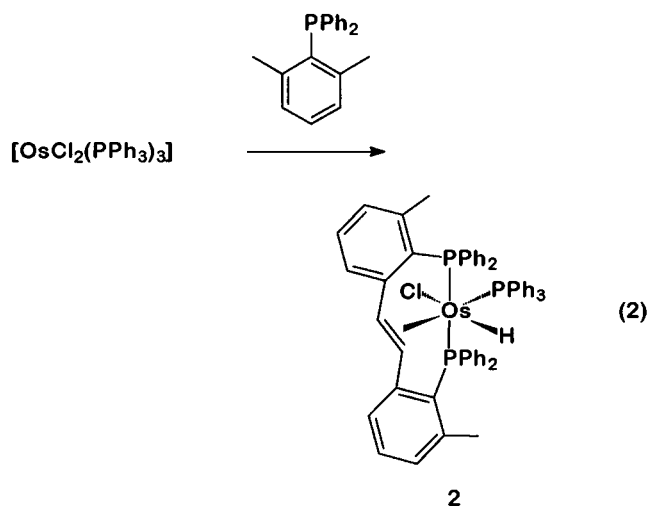
To obtain further insight into the mechanism of this type of carbon double bond formation, we have investigated the reaction between $\text{PPh}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ and the osmium(II) precursor $[\text{OsCl}_2(\text{PPh}_3)_3]$. The latter

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compound reacts with $\text{PPh}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ in toluene at reflux to give the complex $[\text{OsHCl}(\text{PPh}_3)(\text{BDPS})]$ (**2**), which was isolated in almost quantitative yield (eq 2).



The ^{31}P NMR spectrum of **2** reveals an ABX system with a $^2J(\text{PP})$ value of 297.5 for the trans phosphorus atoms and 14.5 and 13.2 Hz for the cis ones, which are values very close to those of **1**, thus suggesting a similar OsP_3 core. Furthermore, in the ^1H NMR spectrum of **2** a proton at $\delta -13.56$, attributable to a hydrido ligand, is coupled with one olefinic proton and three phosphorus atoms with $J(\text{HP})$ values of 12.4 and 30.3 Hz, suggesting that PPh_3 is cis to the hydride.¹⁴ The $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of the coordinated *trans*-olefin shows two signals at δ 3.98 and 3.39 with a $J(\text{HH})$ value of 7.4 Hz, similar to those of **1**, with the first proton coupled with the hydride ($J(\text{HH})$ value of 3.2 Hz). The comparison of the NMR data of **2** and **1** suggests that the two complexes are geometrically related, and **2** contains a *trans*-stilbene-type ligand with one PPh_3 trans to the coordinated olefin to minimize repulsion.

Apparently, the reactions for **1** and **2** are driven to the right because of the formation of final metal complexes containing a strong chelating tridentate ligand. However, the mechanism of the C–C coupling reaction is not obvious, and different routes can be tentatively suggested. In the formation of **2** from $[\text{OsCl}_2(\text{PPh}_3)_3]$ it is reasonable to assume that the primary step proceeds through displacement of PPh_3 with $\text{PPh}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$, affording a cyclometalated hydridometal intermediate. The presence of two methyl groups in the ortho position of $\text{PPh}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$, in addition to the two relatively bulky *gem*-phenyl groups, may facilitate the cyclometalation.¹⁵ According to the results of Bennett et al. on rhodium(I) complexes,¹⁶ one can assume that a second cyclometalation occurs, followed by a C–C coupling (reductive elimination) and dehydrogenation of the $\text{CH}_2\text{-CH}_2$ chain, giving complex **2**. Alternatively, the first cyclometalated intermediate can convert into a carbene complex, a process which was proposed by Werner in

osmium(II) phosphine complexes¹⁷ via α -hydride elimination.¹⁸ A subsequent cyclometalation of a second phosphine and a C–C coupling¹⁹ of the carbene with the alkyl carbon (a key step in the Fischer–Tropsch synthesis²⁰), followed by β -hydrogen elimination, can afford complex **2**. It is noteworthy that no formation of **1** was observed in the reaction of $[\text{OsCl}_2(\text{PPh}_3)_3]$ with an excess of $\text{PPh}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$, suggesting that the displacement of PPh_3 with the bulkier phosphine can occur only if a concomitant cyclometalation takes place. Furthermore, when the reaction of $[\text{OsCl}_2(\text{PPh}_3)_3]$ with $\text{PPh}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ is carried out under 1 atm of CO, no complexes containing the latter phosphine were detected. It is likely that the mechanism of the formation of **1** presents steps similar to those of **2** and may proceed via hydrido cyclometalated or cyclometalated-carbene species. The process here reported, together with that of Bennett,¹⁰ may represent an example of an intriguing mode for the functionalization of activated methyl groups. Work is in progress to extend this template synthesis to other metal systems.

Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Toluene, heptane, and diethyl ether were carefully dried by conventional methods and distilled under argon, while methanol and 2-propanol were previously degassed before use. Ammonium hexachloroosmate was purchased from Aldrich Chemical Co., and $[\text{OsCl}_2(\text{PPh}_3)_3]$ was prepared according to the literature.²¹ NMR measurements were carried out using a Bruker AC 200 spectrometer. Chemical shifts, in ppm, are relative to TMS for ^1H and ^{13}C and to external 85% H_3PO_4 for ^{31}P . The mass spectrum was recorded on a Finnigan MAT 90 spectrometer. Elemental analyses (C, H, N) were performed by the Microanalytical Laboratory of our department.

Preparation of $[\text{OsCl}(\{2\text{-CH}_2\text{-6-MeC}_6\text{H}_3\})\text{PPh}_2](\text{BDPS})$ (1**).** $[(\text{NH}_4)_2\text{OsCl}_6]$ (200 mg, 0.455 mmol) and $\text{PPh}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (600 mg, 2.07 mmol) were suspended in 10 mL of 2-propanol, and 4 mL of water was added. The mixture was refluxed for 3 h, affording a light green precipitate, which was collected by filtration. The product was suspended in methanol (10 mL) and the suspension stirred for 5 h, and after filtration the product was dried under reduced pressure. Yield: 430 mg (87%). Anal. Calcd for $\text{C}_{60}\text{H}_{52}\text{ClOsP}_3$: C, 66.0; H, 4.8. Found: C, 65.8; H, 4.7. ^1H NMR (200.1 MHz, CDCl_3 , 20 °C, TMS): δ 7.4–6.5 (m, 39H; aromatic protons), 3.94 (m, 1H; =CH), 3.50 (dt, $J(\text{HH}) = 19.1$ Hz, $J(\text{HP}) = 4.9$ Hz, 1H; CH_2), 3.48 (m, 1H; =CH), 2.62 (dt, $J(\text{HH}) = 19.1$ Hz, $J(\text{HP}) = 4.8$ Hz, 1H; CH_2), 1.53 (s, 3H; CH_3), 1.07 (s, 3H; CH_3), 0.96 (s, 3H; CH_3). ^{13}C NMR (50.3 MHz, CDCl_3 , 20 °C, TMS): δ 165.2 (d; $J(\text{CP}) = 40.3$ Hz;

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Table 2. Crystallographic Data for 1·CH₂Cl₂

chem formula	C ₆₀ H ₅₂ ClO ₅ P ₃ ·CH ₂ Cl ₂
fw	1176.58
color/shape	light green/fragment
cryst size (mm)	0.38 × 0.30 × 0.25
cryst syst	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	12.7810(1)
<i>b</i> (Å)	18.9967(2)
<i>c</i> (Å)	21.4222(2)
β (deg)	90.375(6)
<i>V</i> (Å ³)	5201.13(8)
<i>Z</i>	4
<i>T</i> (K)	163
ρ _{calcd} (g cm ⁻³)	1.503
μ (mm ⁻¹)	2.738
<i>F</i> ₀₀₀	2368
θ range (deg)	3.35–26.35
data collcd (<i>h, k, l</i>)	±15, ±23, ±26
no. of rflns collcd	57 109
no. of indep rflns/ <i>R</i> _{int}	10 557/0.032
no. of obsd rflns (<i>I</i> > 2σ(<i>I</i>))	9443
no. of params refined	828
<i>R</i> 1 (obsd/all)	0.0242/0.0279
<i>wR</i> 2 (obsd/all)	0.0658/0.0671
GOF (obsd/all)	1.118/1.074
max/min Δρ (e Å ⁻³)	+1.02/−1.24

CCH₂), 159.5–158.5 (m; CCH=), 143.9 (s; CMe), 143.1 (s; CMe), 142.3 (s; CMe), 137.3–124.6 (m; aromatic carbons), 74.9 (d, *J*(CP) = 16.9 Hz; =CH), 74.5 (d, *J*(CP) = 9.8 Hz; =CH), 24.5 (s; CH₃), 21.4 (s; CH₃), 21.0 (s; CH₃), 12.4 (s; CH₂). ³¹P NMR (81.0 MHz, CDCl₃, 20 °C, H₃PO₄): ABC spin system δ 11.6 (dd, *J*(PP) = 311.1 Hz, *J*(PP) = 14.8 Hz; P_A), 10.0 (dd, *J*(PP) = 311.1 Hz, *J*(PP) = 13.3 Hz; P_B), 9.4 (dd, *J*(PP) = 14.7 Hz, *J*(PP) = 13.3 Hz; P_C).

Preparation of [OsHCl(PPh₃)₂(BDPS)] (2). [OsCl₂(PPh₃)₃] (337 mg, 0.321 mmol) and PPh₂(2,6-Me₂C₆H₃) (200 mg, 0.689 mmol) were suspended in 5 mL of toluene, and the mixture was refluxed for 1 h. The solvent was evaporated, and the oily product was treated with heptane, affording a light brown precipitate. The product was washed with diethyl ether (0 °C), filtered off, and dried under reduced pressure. Yield: 250 mg (73%). Anal. Calcd for C₅₈H₅₀ClO₅P₃: C, 65.4; H, 4.7. Found: C, 65.3; H, 4.7. ¹H NMR (200.1 MHz, CDCl₃, 20 °C, TMS): δ 7.7–6.5 (m, 41H; aromatic protons), 3.98 (m, 1H; =CH), 3.39 (m, 1H; =CH), 1.24 (s, 3H; CH₃), 1.01 (s, 3H; CH₃), −13.56 (dtd, *J*(PH) = 30.3 Hz, *J*(PH) = 12.4 Hz, *J*(HH) = 3.2 Hz, 1H; OsH). ¹³C NMR (50.3 MHz, CDCl₃, 20 °C, TMS): δ 161.0–159.5 (m; CCH=), 142.9 (s; CMe), 142.5 (s; CMe), 136.0–124.5 (m; aromatic carbons), 65.2 (d, *J*(CP) = 22.9 Hz; =CH), 62.9 (s broad; =CH), 21.4 (d, *J*(CP) = 2.9 Hz; CH₃), 21.0 (d, *J*(CP) = 2.4 Hz; CH₃). ³¹P NMR (81.0 MHz, CDCl₃, 20 °C, H₃PO₄): ABX spin system δ 21.7 (dd, *J*(PP) = 297.5, *J*(PP) = 14.5 Hz; P_A), 11.4 (dd, *J*(PP) = 297.5, *J*(PP) = 13.2 Hz; P_B), −5.7 (dd, *J*(PP) = 14.5 Hz, *J*(PP) = 13.2 Hz; P_C). MS (CI): *m/z* (%) 1065 (5) [M⁺ − H], 805 (8) [M⁺ − H − PPh₃], 262 (100) [PPh₃].

X-ray Structure Determination of the Complex 1·CH₂Cl₂. Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in Table 2.

Crystals of the complex 1·CH₂Cl₂ suitable for an X-ray structure determination were grown from a saturated solution of **1** in a 1:1 mixture of dichloromethane and heptane. Preliminary examination and data collection were carried out on a Kappa-CCD system (Nonius Mach3) equipped with a rotating anode (NONIUS FR591; 50 kV; 60 mA; 3.0 kW) and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data collection were performed at 163 K with an exposure time of 40 s per film (φ and Ω-scans, oscillation modus, Δφ/ΔΩ = 1.0°). A total of 57 109 reflections were collected.^{22a} After merging a sum of 10 557 independent reflections remained, which were used for all calculations. Data were corrected for Lorentz and polarization effects. Corrections for absorption and decay effects were not applied. The unit cell parameters were obtained by full-matrix least-squares refinements of 61 468 reflections with the program Scalepack.^{22b} The structure was solved by a combination of direct methods and difference Fourier syntheses.^{22c} All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms, except those of the solvent molecule, were found in the difference Fourier map and refined freely with individual isotropic thermal displacement parameters. The hydrogen atoms of the solvent were calculated in ideal positions riding on the parent carbon atom. Full-matrix least-squares refinements were carried out by minimizing Σw(*F*_o² − *F*_c²)² with the SHELXL-97 weighting scheme and stopped at a maximum shift/error of <0.001.^{22d} Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 22e. All other calculations (including ORTEP graphics) were done with the program PLATON.^{22f} Calculations were performed on a PC workstation (Intel Pentium II) running LINUX.

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Supporting Information Available: Tables of crystal and data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for 1·CH₂Cl₂ in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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