ORGANOMETALLICS

ARTICLE

pubs.acs.org/Organometallics

Preparation of Osmium η^5-Phospholide Complexes and Their Reactions with Acyl Electrophiles: C═O Bond Cleavage and C−C Bond Formation within the Metal Coordination Sphere

Masamichi Ogasawara,*[,†] Minoru Shintani,[†] Susumu Watanabe,[†] Takeshi Sakamoto,[†] Kiyohiko Nakajima,[‡] and Tamotsu Takahashi*[,†]

[†]Catalysis Research Center and Graduate School of Life Science, Hokkaido University, Kita-ku, Sapporo 001-0021, Japan

[‡]Department of Chemistry, Aichi University of Education, Igaya, Kariya, Aichi, 448-8542, Japan

Supporting Information

ABSTRACT: Two diphosphaosmocene species have been prepared in excellent yields by the reaction of a lithium 2,5-dialkylphospholide (alkyl = cyclohexyl, (−)-menthyl) and $[(\eta^6\text{-cymene})OsCl_2]_2$ in THF. These are the first examples of phosphametallocenes with an osmium core. For the success of the phosphaosmocene synthesis, the use of a sterically demanding phospholide is crucial. A treatment of the 2,2′,5,5′-Cy_4-diphosphaosmocene with an $AcCl/AlCl_3$ mixture in dichloromethane gives a novel (μ-vinylidene)osmium complex via activation of the acetyl C═O double bond. In the osmium complex, a μ-vinylidene moiety bridges between the osmium atom and a phosphorus of the η^4-(*P*-oxophospholide). In the presence of excess acetyl electrophile, the μ-vinylidene complex is subjected to further acetylation at the CH_2 terminus of the μ-vinylidene moiety to give a (μ-acetylvinylidene)osmium complex. A stepwise application of acetyl chloride and phenylacetyl chloride to this transformation enabled production of a [μ-(phenylacetyl)vinylidene]osmium species by C−C bond formation between the two different acyl chlorides.

INTRODUCTION

Since the discoveries of a series of phosphametallocenes in the late 1970s (phosphacymantrene in 1976;[1] mono-[2] and diphosphaferrecenes[3] in 1977 and 1978, respectively), it has been demonstrated that phospholide anions (phosphacyclopentadienides; phospholyls) are capable of coordinating to various metal cations, which include diverse transition metals as well as main-group elements, in an η^5 fashion.[4] Among such phosphametallocene species, those with a central iron(II) cation (phosphaferrocenes) have been the most extensively investigated by far. Heavier homologues of the group 8 triad, however, have received little attention. Phospharuthenocenes are relatively newer entries to this field: the first mono-[5] and diphospharuthenocenes[6] were reported in 1994 and 2002, respectively.[7] To the best of our knowledge, none of such complexes with an osmium core have been described to date.[8,9]

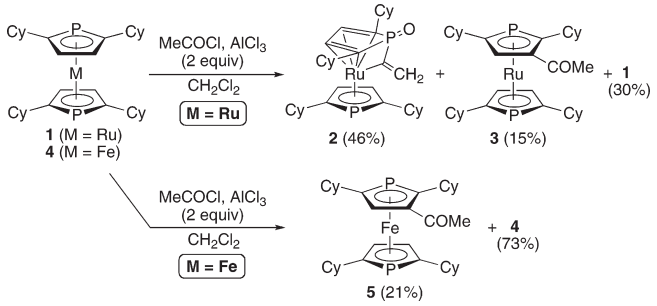
During our investigations of the diphospharuthenocene complexes, we disclosed an unprecedented reaction mode of phosphametallocenes.[10] A reaction between the Cy_4-diphospharuthenocene **1** and an acyl electrophile produced the μ-vinylidene species **2**, where the vinylidene moiety bridges the Ru center and the phosphorus atom, via activation of the acyl C═O double bond (Scheme 1, top). The homologous Cy_4-diphosphaferrocene **4** afforded the conventional Friedel−Crafts acylation product **5** under identical conditions (Scheme 1, bottom). Due to the striking differences between the iron(II) and the ruthenium(II) complexes in the reactions with acetyl electrophile, we became interested in the reactivity of osmium analogues. In this article, we report the preparation and characterization of the first (η^5-phospholyl)osmium(II) complexes and their reactions with acyl chlorides. The phosphaosmocene obtained in this study reacts with 2 equiv of acyl electrophiles in a stepwise fashion to give a μ-acylvinylidene complex via an initial C═O double-bond cleavage followed by C−C bond formation within the osmium coordination sphere.

RESULTS AND DISCUSSION

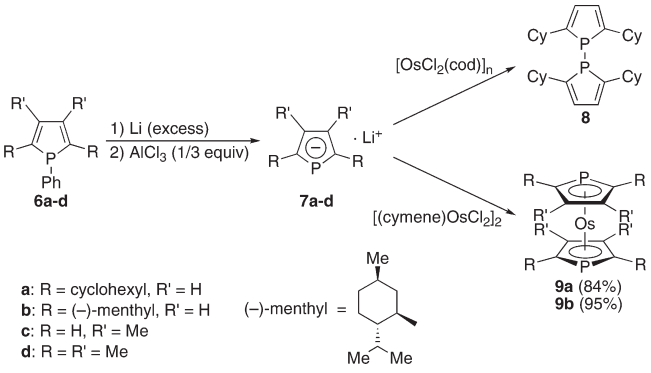
Preparation of Diphosphaosmocenes. Preparation of a yet unknown diphosphaosmocene complex is examined. As an initial trial, the conditions reported for preparation of the analogous diphospharuthenocenes[6] are studied. The reaction of polymeric $[OsCl_2(cod)]_n$[11] and lithium 2,5-dicyclohexylphospholide (**7a**; 2 equiv with respect to Os), which is generated in situ from the corresponding phosphole **6a** and lithium metal, in THF leads to formation of the 1,1′-biphospholyl **8** as a major product (∼60% determined by ^{31}P NMR) by oxidative homocoupling of the phospholide (Scheme 2, top).[12] The expected diphosphaosmocene is not detected in the ^1H and ^{31}P NMR spectra or by LRMS analysis. It is found that the use of the dimeric dichloroosmium complex $[(\eta^6\text{-cymene})OsCl_2]_2$,[13] which is soluble in THF, in the

Received: November 11, 2010
Published: February 21, 2011

Scheme 1. Reactions of Diphospharuthenocene 1 and Diphosphaferrocene 4 with Acetyl Electrophile



Scheme 2. Synthesis of Diphosphaosmocenes 9a,b



reaction with the phospholide **7a** affords the desired diphosphaosmocene **9a** cleanly in 84% isolated yield (Scheme 2, bottom). The diphosphaosmocene **9a** is a slightly air-sensitive colorless solid and can be purified by silica gel chromatography or sublimation under high vacuum. The method of diphosphaosmocene synthesis is highly sensitive to substituents on phospholide anions. While the diphosphaosmocenes **9a,b** are obtained in good yields using phospholides with bulky α substituents (**7a,b**), attempts to prepare analogous diphosphaosmocenes using sterically more compact phospholides, such as **7c,d**, were unsuccessful in giving complex mixtures. Apparently, steric protection of the nucleophilic phosphorus atoms in **7a,b** is the key to success in the preparation of **9a,b**.

Characterization of Diphosphaosmocenes. Prismatic crystals of **9a** suitable for X-ray analysis were grown by slow cooling of the hot octane solution. The crystal structure is shown in Figure 1 with selected bond lengths and angles, which confirms the η^5 coordination of the phospholyl ligand to the osmium(II) core (see the Supporting Information for details). The crystal structures of the homologous 2,2′,5,5′-tetracyclohexyl-1,1′-diphosphaferrocene **4** and -ruthenocene **1** were reported previously.[6] All three complexes are almost isostructural. The osmium atom in **9a** is located at the center of symmetry, and the two phospholyl rings are parallel and attain a staggered conformation. The nearly planar phospholyl ligands are slightly distorted, and the phosphorus atom lies out of the C(1)C(2)C(3)C(4) plane by 0.047 Å away from the central osmium atom. The distance between a least-squares plane of the phospholyl ligand

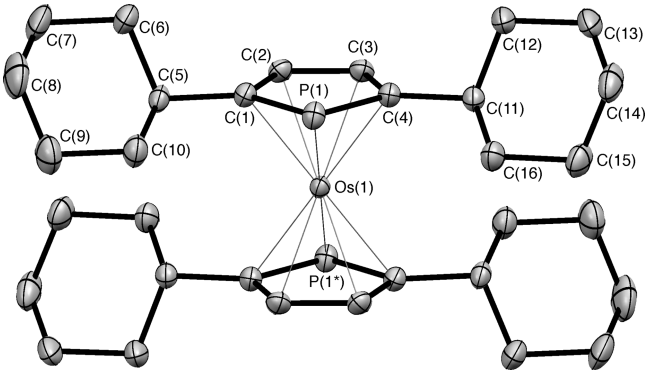


Figure 1. ORTEP drawing of **9a** with thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)−C(1) = 1.793(2), P(1)−C(4) = 1.784(3), C(1)−C(2) = 1.417(4), C(2)−C(3) = 1.429(4), C(3)−C(4) = 1.417(3), Os(1)−phospholyl = 1.819(4); C(1)−P(1)−C(4) = 90.2(1), P(1)−C(1)−C(2) = 111.9(2), C(1)−C(2)−C(3) = 112.6(2), C(2)−C(3)−C(4) = 113.3(2), P(1)−C(4)−C(3) = 111.9(2).

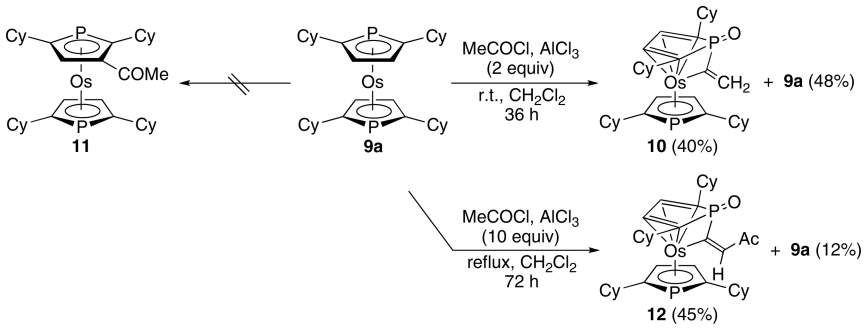
and the metal center is 1.819(4) Å in **9a**; this value is similar to that in **1** (1.811(2) Å) and is ca. 9% longer than that in **4** (1.671(3) Å).[6]

The ^{1}H and ^{13}C NMR characteristics of **9a** are similar to those of **1** and **4**. A resonance for the β-phospholyl hydrogens is detected at δ 5.28 as a doublet with a small J_{PH} value (4.7 Hz) in the ^{1}H NMR spectrum. The α-phospholyl and the β-phospholyl carbons show doublets at δ 101.6 (J_{PC} = 65.3 Hz) and 75.2 (J_{PC} = 5.8 Hz), respectively, in the ^{13}C{^{1}H} NMR spectrum. The ^{31}P{^{1}H} NMR spectrum shows a sharp singlet at δ −70.0, which is at higher field compared to those of **1** and **4**.[6]

Although the diphosphaosmocene **9b** is not crystalline, the η^5 coordination (not η^1 coordination) of the 2,5-bis[(−)-menthyl]phospholides in **9b** is confirmed by its NMR spectra. The C_2 symmetry of the free phospholide, which has two chiral (−)-menthyl substituents, is broken by the η^5 coordination to the Os(II) center. Thus, the two β-hydrogens of an η^5-phospholyl in **9b** are inequivalent with each other and give two resonances at δ 5.30 and 5.58 in the ^{1}H NMR spectrum. Likewise, the ^{13}C NMR spectrum of **9b** shows two C_α signals with large $^1J_{PC}$ couplings at δ 100.1 (J_{PC} = 66.1 Hz) and 103.0 (J_{PC} = 66.9 Hz) as well as two C_β signals with small $^1J_{PC}$

dx.doi.org/10.1021/om101060n |*Organometallics* 2011, 30, 1487–1492

Scheme 3. Reactions of Diphosphaosmocene 9a with Acetyl Electrophile



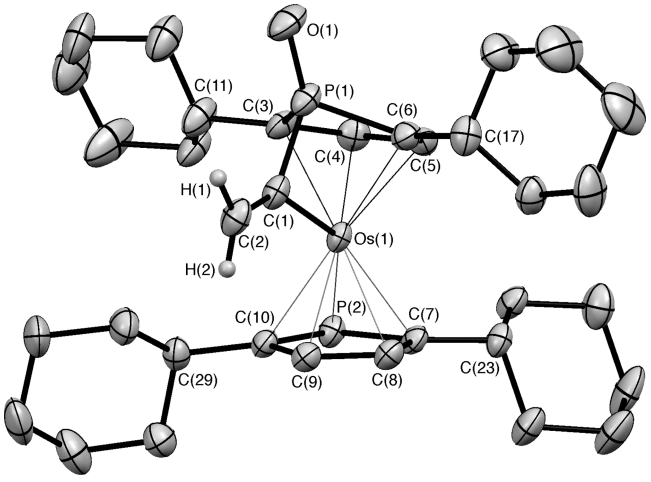


Figure 2. ORTEP drawing of **10** with thermal ellipsoids at the 30% probability level. All hydrogen atoms, except H(1) and H(2), are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os(1)−P(1) (nonbonding) = 2.654(2), Os(1)−P(2) = 2.440(2), Os(1)−C(1) = 2.159(6), P(1)−C(1) = 1.738(4), P(1)−O(1) = 1.480(5), C(1)−C(2) = 1.317(9); Os(1)−C(1)−P(1) = 85.1(2), C(3)−P(1)−C(6) = 90.1(2), Os(1)−C(1)−C(2) = 140.6(4), P(1)−C(1)−C(2) = 134.3(5).

couplings at δ 74.6 (J_{PC} = 4.8 Hz) and 79.9 (J_{PC} = 5.3 Hz). The ^{31}P NMR spectrum of **9b** shows a broad signal at 23 °C, which is sharpened at higher temperature. The variable-temperature NMR behavior of **9b** can be attributed to restricted rotation of the η^5-bis(menthyl)phospholides about the phospholyl−Os−phospholyl axis, as observed in the homologous tetrakis(menthyl)diphosphaferrocene and tetrakis(menthyl)diphospharuthenocene.[7b]

Reactions of Diphosphaosmocene 9a with Acetyl Chloride/AlCl$_3$. Treatment of the diphosphaosmocene **9a** with 2 equiv of an acetyl electrophile, which is generated from equimolar CH_3COCl and $AlCl_3$, in dichloromethane at room temperature for 36 h gave the off-white crystalline product **10** in 40% yield together with recovered **1** in 48% yield (Scheme 3). The product **10** is air and moisture stable and was easily purified by conventional silica gel column chromatography. Prismatic crystals of **10** were grown from the hot ethyl acetate solution, and X-ray crystallography reveals the identity of **10** as being a μ-vinylidene complex, as for the ruthenium analogue **2** (Figure 2).[10] One of the two phospholyl ligands in **10** coordinates to Os(1) in an η^4 fashion at the C(3)C(4)C(5)C(6) core, and the nonbonding distance between Os(1) and the oxidized phosphorus P(1) is 2.654(2) Å. The dihedral angle between the P(1)C(3)C(6) plane and the C(3)C(4)C(5)C(6) plane is 18.17°, and P(1) lies out of the C(3)C(4)C(5)C(6) plane by 0.400 Å away from Os(1). The vinylidene moiety C(1)═C(2)H(1)H(2) bridges between Os(1) and P(1). The C(2)C(1)P(1)Os(1) plane is nearly perpendicular to the η^4-C(3)C(4)C(5)C(6) plane (89.08°), which makes the two hydrogens at the vinylidene terminus inequivalent with each other. The C(1)−C(2) bond length is 1.317(9) Å, which is within the normal range for typical C═C double bonds. Analogous η^4 coordination of a *P*-oxophospholide was described in an iron complex.[14]

With free rotation of the η^5-phospholyl ligand about the Os(1)−phospholyl axis, the complex **10** is C_s symmetric in solution and the ^{1}H, ^{13}C, and ^{31}P NMR spectra are consistent with the solid-state structure. The complex **10** shows two signals of equal intensities at δ −53.6 and −17.9 in the ^{31}P NMR spectrum. The two hydrogen nuclei of the μ-vinylidene moiety in **10** are detected as two doublets at δ 5.66 (J_{PH} = 65.8 Hz) and 6.70 (J_{PH} = 37.7 Hz) in the ^{1}H NMR spectrum. The former, with the larger J_{PH} value, is assigned to a signal of H(2) that is trans to P(1) and the latter to that of H(1).

While a reaction of the diphospharuthenocene **1** with AcCl/$AlCl_3$ gives the Friedel−Crafts acetylation product **3** as a minor product together with **2** (Scheme 1, top), the reaction of **9a** does not afford the comparable acetyl compound **11**. These observations are consistent with the reported reactivity of Cp_2Ru and Cp_2Os: the parent osmocene is less reactive than the parent ruthenocene toward electrophilic substitutions and tends to give Friedel−Crafts acylation products in lower yields.[15] The relatively low yield of **10** is not improved, even with a large excess of acetyl electrophile and longer reaction time. The reaction of **9a** with AcCl/$AlCl_3$ (10 equiv to **9a**) for 72 h in refluxing dichloromethane affords the previously undetected osmium complex **12** in 45% yield together with several uncharacterized side products. Although the unreacted **9a** is recovered in 12% yield, the μ-vinylidene species **10** is not found among the minor products under these conditions (Scheme3).

The complex **12** is isolated as an off-white crystalline solid by silica gel chromatography, and its X-ray crystal structure is shown in Figure 3. The μ-vinylidene moiety is acetylated at C(2) in **12**, and the acetyl group takes a position trans to Os(1). Due to conjugation between the C(1)═C(2) and the C(3)═O(2) double bonds, the C(1)−C(2) bond length is slightly longer (1.335(7) Å) compared to that of the C═C vinylidene in **10**. The

dx.doi.org/10.1021/om101060n |*Organometallics* 2011, 30, 1487–1492

overall structure of **12** is, however, very similar to that of **10**. The complex **12** is insensitive to both oxygen and moisture and can be handled under air without appreciable decomposition. The ^{31}P NMR spectrum of **12** shows two signals of equal intensities at δ −44.8 and −18.3. The vinylidene hydrogen H(1) is detected at δ 6.77 in the ^{1}H NMR spectrum with a strong coupling with P(1) (J_{PH} = 58.0 Hz), which is consistent with the *E* configuration (with respect to the C(1)═C(2) double bond) shown by the X-ray structure analysis.

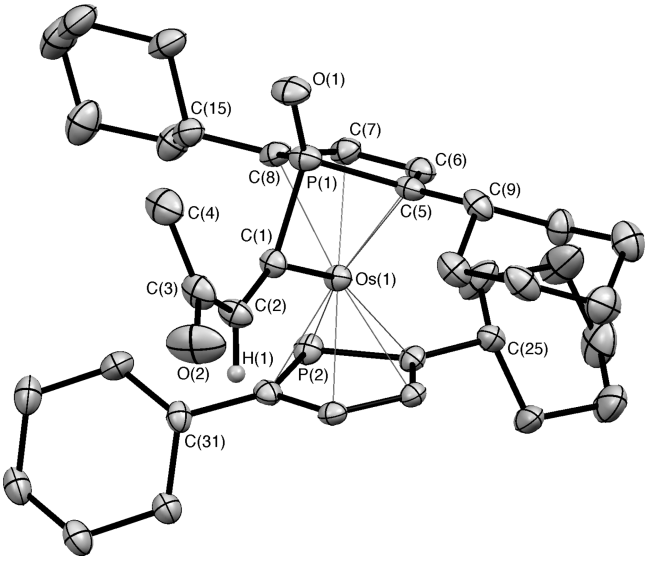
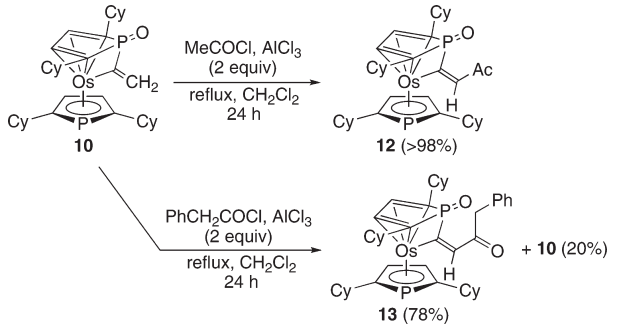


Figure 3. ORTEP drawing of **12** with 30% thermal ellipsoids. All hydrogen atoms except H(1) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os(1)−P(1) (nonbonding) = 2.660(1), Os(1)−P(2) = 2.450(1), Os(1)−C(1) = 2.125(5), P(1)−C(1) = 1.780(5), P(1)−O(1) = 1.484(4), C(1)−C(2) = 1.335(7), C(2)−C(3) = 1.490(8), C(3)−O(2) = 1.201(7); Os(1)−C(1)−P(1) = 85.4(2), C(5)−P(1)−C(8) = 90.0(2), Os(1)−C(1)−C(2) = 136.1(4), P(1)−C(1)−C(2) = 138.1(4), C(1)−C(2)−C(3) = 128.2(5).

Scheme 4. Reactions of μ-Vinylidene Osmium Complex 10 with Acyl Electrophiles

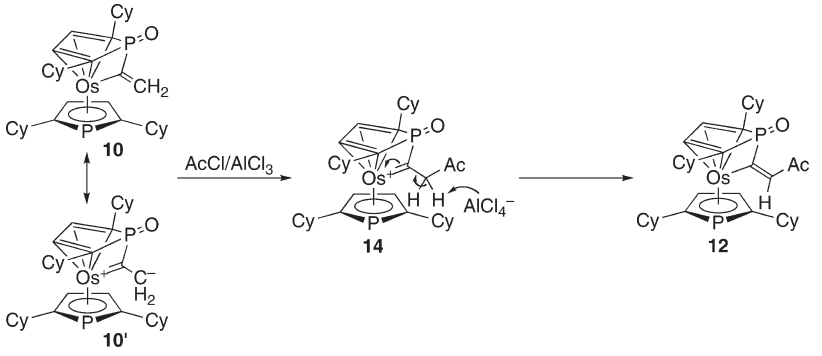


Reactions of the Os μ-Vinylidene Complex 10 with Acyl Chloride/$AlCl_3$. Whereas the formation of **12** is assumed to take place by way of **10**, a reaction between the isolated **10** and the acetyl electrophile ($AcCl/AlCl_3$) should be examined. As expected, treatment of **10** with $AcCl/AlCl_3$ (2 equiv with respect to **10**) in refluxing dichloromethane for 24 h cleanly converts **10** into **12**, and the Ac-vinylidene complex **12** is obtained in a nearly quantitative yield (Scheme 4, top). The vinylidene moiety in **10** can be acylated using acylium reagents other than $AcCl/AlCl_3$: i.e., the reaction of **10** with phenylacetyl chloride under conditions otherwise identical with those above provides the [μ-(phenylacetyl)vinylidene]osmium complex **13** in 78% yield. The reaction is somewhat slower in the latter case, and the unreacted **10** is recovered in 20% yield (Scheme 4, bottom). Complex **13** is obtained as a single isomer exclusively, and its configuration is determined as *E* on the basis of the large coupling constant between the bridged phosphorus and the alkenylidene hydrogen (J_{PH} = 57.7 Hz).

A possible mechanism for the formation of the μ-(acetylvinylidene) complex **12** is shown in Scheme 5. Because osmium tends to take a higher oxidation state compared to ruthenium, a resonance structure such as **10′**, in which the formal oxidation state of Os is +4, contributes to the reactivity of **10** to a certain extent. As a consequence, the terminal vinylidene carbon in **10** becomes nucleophilic. An electrophilic attack of the acetylium species at the vinylidene carbon followed by a nucleophilic abstraction of one of the hydrogens in the Ac−CH_2− moiety by the $AlCl_4^-$ anion affords the μ-(acetylvinylidene) complex **12**. The cationic charge in the intermediate **14** is stabilized by the Os^{4+} center. The overall process of converting **10** into **12** (or **13**) can be regarded as an olefinic electrophilic substitution (Friedel−Crafts-type acylation).[16] It was reported that electrophilic acylation of enamines[17] and ketene dithioacetals (and related compounds)[18] took place in a similar fashion, in which cationic intermediates were stabilized by the heteroatom substituents.

The transformation of **9a** into **12** involves C═O bond cleavage and C−C coupling within the osmium coordination sphere, and two molecules of acetyl electrophile play different roles during the transformation. When the first acetyl electrophile reacts with **9a** at the osmium center, the polarity of the C_2

Scheme 5. Possible Reaction Pathway of Formation of 12 from 10 and $AcCl/AlCl_3$



dx.doi.org/10.1021/om101060n |*Organometallics* 2011, 30, 1487–1492

moiety is reversed to nucleophilic via reductive C═O cleavage by the phospholyl ligand to give **10** in the same way as for the analogous ruthenium complex **1**.[10] Subsequently, the second acetyl electrophile attacks the vinylidene CH_2 terminus in **10** to furnish the β-acetylvinylidene complex **12**, as shown in Scheme 5.

CONCLUSIONS

Two novel diphosphaosmocenes have been prepared and characterized by X-ray crystallography and/or NMR spectroscopy. The 2,2′,5,5′-Cy_4-1,1′-diphosphaosmocene obtained in this study reacts with 2 equiv of acyl electrophiles in a stepwise fashion. The initial step is formation of a (μ-vinylidene)osmium complex via activation of the acetyl C═O double bond, in which a μ-vinylidene moiety bridges between the osmium core and a phosphorus of the η^4-(*P*-oxophospholide). The second step takes place in the presence of excess acetyl electrophile, and the μ-vinylidene complex is acetylated at the CH_2 terminus of the μ-vinylidene ligand to give a (μ-acetylvinylidene)osmium complex by C−C bond formation within the metal coordination sphere.

EXPERIMENTAL SECTION

General Considerations. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 101 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{31}P NMR (at 162 MHz) chemical shifts are externally referenced to 85% H_3PO_4. Tetrahydrofuran and benzene were distilled from benzophenone-ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. The phospholes (**6a**,[6] **6b**,[19] **6c**,[20] and **6d**[21]), $[OsCl_2(cod)]_n$,[11] and $[(\eta^6\text{-cymene})OsCl_2]_2$[13] were prepared as reported. All other chemicals were obtained from commercial sources.

Bis(η^5-2,5-dicyclohexyl-1-phosphacyclopentadienyl)-osmium(II) (9a). A THF (20 mL) solution of the phosphole **6a** (1.05 g, 3.24 mmol) was treated with lithium metal (300 mg, 43.2 mmol), and the mixture was stirred overnight at room temperature. The mixture was filtered through a glass filter, and to the filtrate was added anhydrous $AlCl_3$ (145 mg, 1.09 mmol) at 0 °C.[22] After the mixture was warmed to room temperature, a THF (5 mL) solution of $[(\eta^6\text{-cymene})OsCl_2]_2$ (600 mg, 1.52 mmol/Os) was added, and then the mixture was refluxed for 24 h. After the mixture was cooled, all the volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography (elution with hexane) to give the title compound in pure form. Alternatively, the compound could be recrystallized from hot octane. Yield: 873 mg (84%). ^{1}H NMR ($CDCl_3$): δ 1.06−1.26 (m, 20H), 1.60−1.63 (m, 4H), 1.68−1.84 (m, 20H), 5.28 (d, J_{PH} = 4.7 Hz, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.5 (s), 27.0 (s), 27.1 (s), 36.9 (d, J_{PC} = 8.8 Hz), 37.1 (d, J_{PC} = 4.4 Hz), 40.7 (d, J_{PC} = 13.7 Hz), 75.2 (d, J_{PC} = 5.8 Hz), 101.6 (d, J_{PC} = 65.3 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −70.0 (s). Anal. Calcd for $C_{32}H_{48}OsP_2$: C, 56.12; H, 7.06. Found: C, 55.98; H, 7.09. EI-HRMS: *m*/*z* calcd for $C_{32}H_{48}OsP_2$ 686.2846, found 686.2845.

Bis[η^5-2,5-bis((−)-menthyl)-1-phosphacyclopentadienyl]-osmium(II) (9b). The compound was prepared in the same way as described above and purified by silica gel chromatography (elution with hexane). Yield: 96%. ^{1}H NMR (toluene-d_8, 80 °C): δ 0.80−1.29 (m, 56H), 1.58−1.83 (m, 14H), 2.06−2.09 (m, 2H), 2.17−2.25 (m, 2H), 2.35−2.42 (m, 2H), 5.30 (dd, J_{PH} = 4.3 and 2.6 Hz, 2H), 5.58 (dd, J_{PH} = 4.9 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR (toluene-d_8, 80 °C): δ 16.4, 16.6 (d, J_{PC} = 7.4 Hz), 22.0, 22.1, 23.06, 23.07, 26.1, 26.3, 28.4 (2C), 34.68, 34.71, 36.1, 36.3, 41.7 (d, J_{PC} = 15.8 Hz), 44.3 (d, J_{PC} = 11.8 Hz), 46.4 (t, J_{PC} = 4.2 Hz), 48.5 (dd, J_{PC} = 6.6 and 5.5 Hz), 51.4, 53.7, 74.6 (d, J_{PC} = 4.8 Hz), 79.9 (d, J_{PC} = 5.3 Hz), 100.1 (d, J_{PC} = 66.1 Hz), 103.0 (d, J_{PC} = 66.9 Hz). ^{31}P{^{1}H} NMR (toluene-d_8, 80 °C): δ −59.3. $[\alpha]^{25.3}_D$ = −213° (*c* 1.65, $CHCl_3$). Anal. Calcd for $C_{48}H_{80}OsP_2$: C, 63.40; H, 8.87. Found: C, 63.45; H, 9.02. EI-HRMS: *m*/*z* calcd for $C_{48}H_{80}OsP_2$ 910.5350, found 910.5366.

Reactions of Phosphaosmocenes with Acyl Electrophiles. A typical procedure is given for the reaction of the diphosphaosmocene **9a** with 2 equiv of AcCl/$AlCl_3$. To a suspension of $AlCl_3$ (209 mg, 1.57 mmol) in dichloromethane (15 mL) was added acetyl chloride (127 mg, 1.62 mmol) at room temperature. The mixture was stirred at this temperature for 1 h and was then added to a dichloromethane (5 mL) solution of the diphosphaosmocene **9a** (561 mg, 819 μmol). The mixture was stirred for 36 h at room temperature. The reaction was quenched by the addition of water (0.5 mL) at 0 °C and then evaporated to dryness under vacuum. The residue was extracted with dichloromethane, and the extract was further purified by silica gel chromatography (eluents: chloroform then EtOAc). The μ-vinylidene complex **10** was obtained as a major product (238 mg, 327 μmol, 40%) together with the recovered **9a** (269 mg, 393 μmol, 48%). The characterization data of the products are given below.

(η^5-2,5-Dicyclohexyl-1-phosphacyclopentadienyl)(2,3,4,5-η^4-2,5-dicyclohexyl-1-oxo-1-phosphacyclopentadienyl)(μ-vinylidene-*Os*,*P*)osmium(II) (10). ^{1}H NMR ($CDCl_3$): δ 1.05−1.38 (m, 22H), 1.56−1.75 (m, 16H), 1.82−1.85 (m, 6H), 5.48 (d, J_{PH} = 14.0 Hz, 2H), 5.51 (d, J_{PH} = 4.0 Hz, 2H), 5.66 (d, J_{PH} = 65.8 Hz, 1H), 6.70 (d, J_{PH} = 37.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 25.88 (s), 25.92 (s), 26.3 (s), 26.55 (s), 26.57 (s), 26.8 (s), 33.6 (d, J_{PC} = 3.6 Hz), 34.3 (d, J_{PC} = 14.1 Hz), 35.3 (d, J_{PC} = 5.4 Hz), 38.4 (s), 39.0 (d, J_{PC} = 12.3 Hz), 40.3 (d, J_{PC} = 8.0 Hz), 78.5 (d, J_{PC} = 18.0 Hz), 84.9 (d, J_{PC} = 73.3 Hz), 93.2 (d, J_{PC} = 5.8 Hz), 110.6 (d, J_{PC} = 68.2 Hz), 118.5 (s), 127.9 (d, J_{PC} = 52.8 Hz). ^{31}P NMR ($CDCl_3$): δ −53.6, −17.9. Anal. Calcd for $C_{34}H_{50}OOsP_2$: C, 56.18; H, 6.93. Found: C, 55.92; H, 6.92. EI-HRMS: *m*/*z* calcd for $C_{34}H_{50}OOsP_2$ 728.2952, found 728.2929.

(η^5-2,5-Dicyclohexyl-1-phosphacyclopentadienyl)(2,3,4,5-η^4-2,5-dicyclohexyl-1-oxo-1-phosphacyclopentadienyl)-(μ-(*E*)-3-oxo-1-butenylidene-*Os*,*P*)osmium(II) (12). ^{1}H NMR ($CDCl_3$): δ 1.04−1.30 (m, 18H), 1.38−1.84 (m, 26H), 2.72 (s, 3H), 5.60 (d, J_{PH} = 3.9 Hz, 2H), 5.63 (d, J_{PH} = 15.0 Hz, 2H), 6.77 (d, J_{PH} = 58.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 25.7 (s), 25.8 (s), 26.2 (s), 26.4 (s), 26.5 (s), 26.8 (s), 28.7 (s), 32.6 (d, J_{PC} = 3.5 Hz), 34.3 (d, J_{PC} = 14.1 Hz), 36.2 (d, J_{PC} = 3.9 Hz), 38.3 (s), 39.0 (d, J_{PC} = 11.9 Hz), 40.9 (d, J_{PC} = 7.5 Hz), 78.2 (d, J_{PC} = 19.5 Hz), 81.5 (d, J_{PC} = 79.9 Hz), 94.6 (d, J_{PC} = 5.7 Hz), 115.3 (d, J_{PC} = 68.8 Hz), 138.8 (s), 153.3 (d, J_{PC} = 36.6 Hz), 196.7 (d, J_{PC} = 15.9 Hz). ^{31}P NMR ($CDCl_3$): δ −44.8, −18.3. Anal. Calcd for $C_{36}H_{52}O_2OsP_2$: C, 56.23; H, 6.82. Found: C, 56.19; H, 6.62. EI-HRMS: *m*/*z* calcd for $C_{36}H_{52}O_2OsP_2$ 770.3057, found 770.3047.

(η^5-2,5-Dicyclohexyl-1-phosphacyclopentadienyl)(2,3,4,5-η^4-2,5-dicyclohexyl-1-oxo-1-phosphacyclopentadienyl)-(μ-(*E*)-3-oxo-4-phenyl-1-butenylidene-*Os*,*P*)osmium(II) (13). ^{1}H NMR ($CDCl_3$): δ 1.01−1.80 (m, 44H), 4.54 (s, 2H), 5.58 (d, J_{PH} = 3.7 Hz, 2H), 5.62 (d, J_{PH} = 15.1 Hz, 2H), 6.83 (d, J_{PH} = 57.7 Hz, 1H), 7.16−7.20 (m, 1H), 7.25−7.30 (m, 2H), 7.35−7.37 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 25.6 (s), 25.7 (s), 26.2 (s), 26.4 (s), 26.5 (s), 26.7 (s), 32.9 (d, J_{PC} = 3.3 Hz), 34.3 (d, J_{PC} = 13.9 Hz), 35.9 (d, J_{PC} = 4.8 Hz), 38.2 (s), 39.0 (d, J_{PC} = 12.0 Hz), 40.5 (d, J_{PC} = 8.1 Hz), 45.4 (s), 78.2 (d, J_{PC} = 20.2 Hz), 81.7 (d, J_{PC} = 79.5 Hz), 94.4 (d, J_{PC} = 5.7 Hz), 115.2 (d, J_{PC} = 68.6 Hz), 126.1, (s), 128.1 (s), 129.7 (s), 136.2 (s), 138.2 (s), 152.9 (d, J_{PC} = 38.3 Hz), 195.2 (d, J_{PC} = 15.3 Hz). ^{31}P NMR ($CDCl_3$): δ −44.5, −17.7. Anal. Calcd for $C_{42}H_{56}O_2OsP_2$: C, 59.69; H, 6.68. Found: C, 58.99; H, 6.83. EI-HRMS: *m*/*z* calcd for $C_{42}H_{57}O_2OsP_2$ (M + H) 847.3449, found 847.3440.

■ ASSOCIATED CONTENT

Supporting Information. Figures giving ^{1}H, ^{13}C, and ^{31}P NMR spectra for all new compounds and CIF file giving crystallographic data for **9a**, **10**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*To whom correspondence should be addressed. E-mail: ogasawar@cat.hokudai.ac.jp (M.O.).

■ ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "Synergistic Effects for Creation of Functional Molecules" from the Ministry of Education, Culture, Sports, Science and Technology of Japan. S.W. has been a recipient of the JSPS Research Fellowship for the Young Scientists.

■ REFERENCES

(1) (a) Mathey, F. *Tetrahedron Lett.* **1976**, *17*, 4155. (b) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 5748.

(2) (a) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1977**, *99*, 3537. (b) Mathey, F. *J. Organomet. Chem.* **1977**, *139*, 77.

(3) (a) de Lauzon, G.; Mathey, F.; Simalty, M. *J. Organomet. Chem.* **1978**, *156*, C33. (b) de Lauzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 994. (c) de Lauzon, G.; Deschamps, B.; Mathey, F. *Nouv. J. Chim.* **1980**, *4*, 683.

(4) For reviews of phosphametallocenes, see:(a) Mathey, F.; Fischer, J.; Nelson, J. H. *Struct. Bonding (Berlin)* **1983**, *55*, 153. (b) Mathey, F. *Nouv. J. Chim.* **1987**, *11*, 585. (c) Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1. (d) Mathey, F. *J. Organomet. Chem.* **2002**, *646*, 15. (e) Carmichael, D.; Mathey, F. *Top. Curr. Chem.* **2002**, *220*, 27. (f) Mathey, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578. (g) Le Floch, P. *Coord. Chem. Rev.* **2006**, *250*, 627. (h) Fu, G. C. *Acc. Chem. Res.* **2006**, *39*, 853. (i) Ganter, C. In *Phosphorus Ligands in Asymmetric Catalysis*; Börner, A., Ed.; Wiley-VCH: Weinheim, Germany, 2008; Chapter 4.3, p 393.

(5) Carmichael, D.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1167.

(6) Ogasawara, M.; Nagano, T.; Yoshida, K.; Hayashi, T. *Organometallics* **2002**, *21*, 3062.

(7) For other reports on phospharuthenocenes, see:(a) Carmichael, D.; Mathey, F.; Ricard, L.; Seeboth, N. *Chem. Commun.* **2002**, 2976. (b) Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2003**, *22*, 1783. (c) Carmichael, D.; Klankermayer, J.; Ricard, L.; Seeboth, N. *Chem. Commun.* **2004**, 1144. (d) Carmichael, D.; Ricard, L.; Seeboth, N.; Brown, J. M.; Claridge, T. D. W.; Odell, B. *Dalton Trans.* **2005**, 2173. (e) Ogasawara, M.; Ito, A.; Yoshida, K.; Hayashi, T. *Organometallics* **2006**, *25*, 2715. (f) Carmichael, D.; Ricard, L.; Seeboth, N. *Organometallics* **2007**, *26*, 2964. (g) Loschen, R.; Loschen, C.; Frank, W.; Ganter, C. *Eur. J. Inorg. Chem.* **2007**, 553. (h) Carmichael, D.; Goldet, G.; Klankermayer, J.; Ricard, L.; Seeboth, N.; Stankevič, M. *Chem. Eur. J.* **2007**, *13*, 5492.

(8) For (η^5-P_5)Os complexes, see:(a) Rink, B.; Scherer, O. J.; Wolmershäuser, G. *Chem. Ber.* **1995**, *128*, 71. (b) Malar, E. J. P. *Eur. J. Inorg. Chem.* **2004**, 2723.

(9) For (μ-phospholide)osmium clusters, see:Deeming, A. J.; Powell, N. I.; Arce, A. J.; De Sanctis, Y.; Manzur, J. *J. Chem. Soc., Dalton Trans.* **1991**, 3381.

(10) Ogasawara, M.; Sakamoto, T.; Ito, A.; Ge, Y.; Nakajima, K.; Takahashi, T.; Hayashi, T. *Organometallics* **2007**, *26*, 6698.

(11) (a) Schrock, R. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 951. (b) Esteruelas, M. A.; García-Yebra, C.; Oñate, E. *Organometallics* **2008**, *27*, 3029.

(12) Analogous oxidative homocoupling of phospholide anions was reported using phosgene or iodine as an oxidizing agent; see: (a) Charrier, C.; Bonnard, H.; Mathey, F.; Neibecker, D. *J. Organomet. Chem.* **1982**, *231*, 361. (b) Holand, S.; Mathey, F.; Fischer, J.; Mitschler, A. *Organometallics* **1982**, *2*, 1234.

(13) (a) Werner, H.; Zenkert, K. *J. Organomet. Chem.* **1988**, *345*, 151. (b) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 4343.

(14) Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *Inorg. Chem.* **1981**, *20*, 3252.

(15) Rausch, M. D.; Fischer, E. O.; Grubert, H. *J. Am. Chem. Soc.* **1960**, *82*, 76.

(16) (a) Olah, G. A. *Friedel-Crafts and Related Reactions*; Wiley: New York, 1963. (b) Groves, J. K. *Chem. Soc. Rev.* **1972**, *1*, 73.

(17) (a) Metzger, H. *Tetrahedron Lett.* **1964**, *5*, 203.(b) Alt, G. H.; Cook, A. G. In *Enamines: Synthesis, Structure, and Reactions*; Cook, A. G., Ed.; Marcel Dekker: New York, 1988; Chapter 4, p 181. (c) Hickmott, P. W. In *Chemistry of Enamines*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 1994; p 727.

(18) (a) Hojo, M.; Masuda, R.; Kamitori, Y. *Tetrahedron Lett.* **1976**, *17*, 1009. (b) Hojo, M.; Masuda, R.; Kokuryo, Y.; Shioda, H.; Matsuo, S. *Chem. Lett.* **1976**, 499. (c) Hojo, M.; Masuda, R.; Okada, E. *Tetrahedron Lett.* **1986**, *27*, 353. (d) Hojo, M.; Masuda, R.; Sano, H.; Saegusa, M. *Synthesis* **1986**, 137.

(19) Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2001**, *20*, 1014.

(20) Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.

(21) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.

(22) Mathey, F.; de Lauzon, G. *Organomet. Synth.* **1986**, *3*, 259.