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Synthesis, Structure, and Reactivity of an Osmacyclopentene Complex

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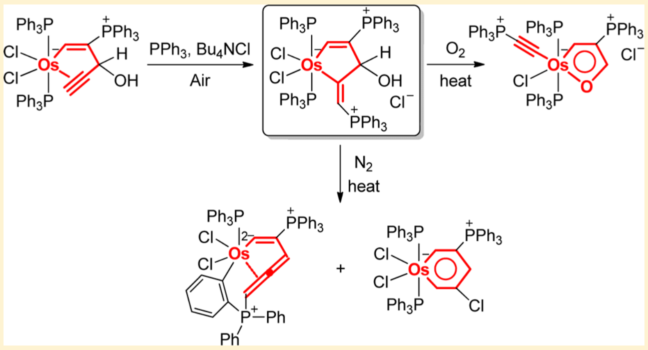
Supporting Information

ABSTRACT: Treatment of $OsCl_2(PPh_3)_2(CH{=}C(PPh_3)\text{-}CH(OH)\text{-}\eta^2\text{-}C{\equiv}CH)$ (**1**) with PPh_3 and Bu_4NCl in CH_2Cl_2 under air gave paramagnetic osmacyclopentene $[OsCl_2(PPh_3)_2(CH{=}C(PPh_3)CH(OH)C({=}CH(PPh_3)))]Cl$ (**5**). Heating the suspension of **5** in CH_2Cl_2 under a nitrogen atmosphere led to the formation of η^2-allene-coordinated osmacycle $OsCl_2(PPh_3)(CH{=}C(PPh_3)CH{=}C{=}CH(P(C_6H_4)Ph_2))$ (**6**) and chloro-osmabenzene $OsCl_2(PPh_3)_2(CHC(PPh_3)CHCClCH)$ (**7**) via disproportionation reaction. Oxidative transformation of **5** under an oxygen atmosphere yielded osmafuran $[OsCl(PPh_3)_2(CHC(PPh_3)CHO)(C{\equiv}C(PPh_3))]Cl$ (**10**). In addtion, complexes **6**, **7**, and **10** can also undergo ligand substitution reactions with NaSCN to afford more stable analogues.



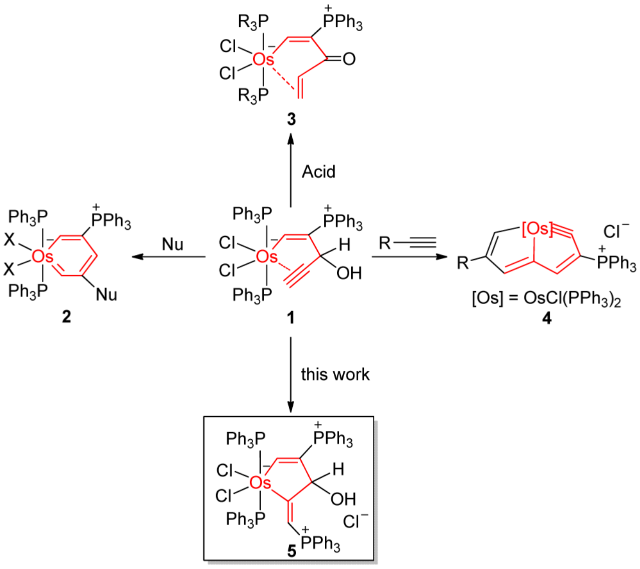
INTRODUCTION

Transition-metal-containing metallacycles are often regarded as key intermediates of transition-metal-catalyzed organic reactions, in which only a few of these species could be isolated and characterized. For example, metallacyclopentene is the key intermediate of metal-involved coupling reactions of olefin and alkyne.[1] Due to the high reactivities, there are only a few studies on the synthesis of metallacyclopentenes[2] to date.

In recent years, conjugated metallacycles are also an important class of transition-metal-containing metallacycles. In particular, aromatic metallacycles[3] have attracted most attention because they display special reactivity and properties compared with related cyclic organics. So far, the isolation and characterization of stable metallaaromatics represents one of the major issues of metallacycle chemistry.

Given our long-standing interests in metallacycle chemistry, our research group has successfully synthesized osmabenzene complexes **2**,[4−6] η^2-α,β-unsaturated ketone coordinated osmacycles **3**,[7] and osmapentalyne complexes **4**,[8] all starting from η^2-alkynol-coordinated osmacycle **1**.[4] Herein, we have obtained a paramagnetic osmacyclopentene complex by reacting complex **1** with PPh_3 and Bu_4NCl under air. The disproportionation of the osmacyclopentene complex promoted by heating yielded η^2-allene-coordinated osmacycle and chloro-osmabenzene complexes. In addition, oxidative transformation of osmacyclopentene into osmafuran complexes by using molecular oxygen as the sole oxidant is also studied.

Chart 1



RESULTS AND DISCUSSION

Preparation of an Osmacyclopentene Complex. Reaction of complex **1** with PPh_3 and Bu_4NCl in CH_2Cl_2

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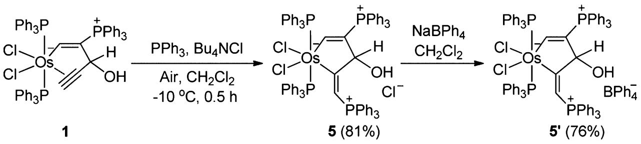
under air at −10 °C for 0.5 h afforded **5** as a yellow solid in a yield of 81% (Scheme 1). Complex **5** is insoluble in many organic solvents, such as chloroform, acetone, tetrahydrofuran, methanol, and diethyl ether. It is only slightly soluble in CH_2Cl_2.

Scheme 1. Formation of Complexes 5 and 5′



Due to the poor solubility of complex **5**, it is difficult to obtain a single crystal of **5** to determine its solid-state structure. Fortunately, the counteranion Cl^- in **5** could be easily replaced with BPh_4^- by treatment of **5** with $NaBPh_4$ to give complex **5′**. The structure of **5′** was confirmed unambiguously by X-ray diffraction. The crystallographic details are listed in Table S1. The single-crystal X-ray diffraction clearly revealed that complex **5′** (Figure 1) contained a five-membered metallacycle.

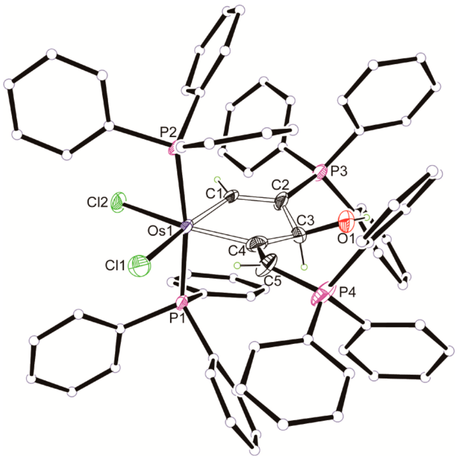


Figure 1. Molecular structure of the paramagnetic complex cation of **5′** (ellipsoids at the 50% probability level). Counteranion and some of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 2.007(7), Os1−C4 2.072(9), C1−C2 1.374(10), C2−C3 1.499(11), C3−C4 1.499(10), C3−O1 1.429(9), C4−C5 1.335(11), C2−P3 1.775(8), C5−P4 1.772(8), Os1−Cl1 2.4486(19), Os1−Cl2 2.445(2); C1−Os1−C4 78.4(3), C2−C1−Os1 121.0(6), C1−C2−C3 113.1(7), C2−C3−C4 109.7(6), C3−C4−Os1 114.6(6), C5−C4−Os1 124.6(6), C3−C4−C5 120.6(8).

The bond distances of Os1−C1 (2.007(7) Å) and Os1−C4 (2.072(9) Å) are within the range of typical Os−C single bonds. The C1−C2 and C4−C5 bond distances (1.374(10) and 1.335(11) Å, respectively) are typical for a C=C double bond, while the C2−C3 (1.499(11) Å) and C3−C4 (1.499(10) Å) bond distances are typical for a C−C single bond. The C3−O1 bond length (1.429(9) Å) indicates the existence of a hydroxyl group.[9] Both of osmacyclopentenes **5** and **5′** are the 17-electron paramagnetic metallacycles. As show in Figure 2, the EPR spectroscopy also suggests that osmacyclopentene **5** is paramagnetic.

A plausible mechanism for the formation of complex **5** is proposed in Scheme 2. Complex **1** may undergo metal-centered oxidation reaction under air in the presence of Bu_4NCl to generate the intermediate **A**. Then, the nucleophilic addition reaction of **A** with PPh_3 could afford complex **5**. In our early study, we found that the nucleophilic addition reactions of **1** with nucleophiles such as PPh_3, NaI, and NaSCN produced the osmabenzenes.[4,5] We think that the reaction atmosphere and the reaction temperature may play important roles in the formation of **5**.

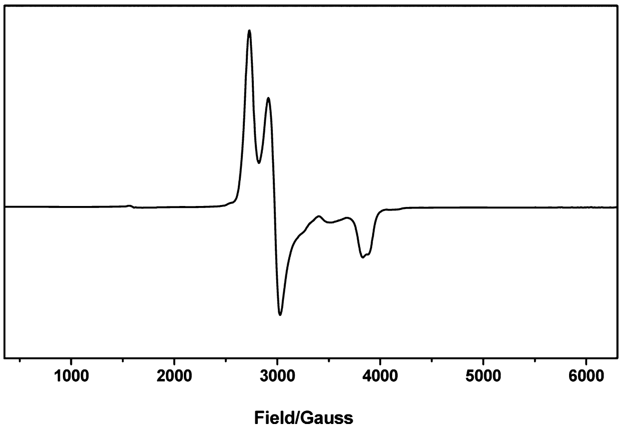
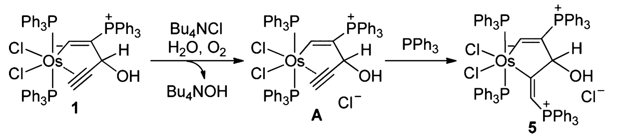


Figure 2. EPR spectroscopy (90 K) of the osmacyclopentene **5**.

Scheme 2. Proposed Mechanism for the Formation of 5



Disproportionation Reaction of Osmacyclopentene Complex under Heating Condition. We found that heating a suspension of **5** in dichloromethane at 65 °C under a nitrogen atmosphere in a sealed tube led to the formation of the two unexpected conjugated osmacycles **6** and **7** in a molar ratio of 1:1 (Scheme 3). Complex **6** could be isolated by column chromatography and characterized by X-ray single-crystal structural anaylsis, while complex **7** could not be isolated in pure form. However, the structure of complex **7** can be deduced easily, as its *in situ* ^1H NMR and $^{31}P\{^1H\}$ NMR spectroscopic data (Table 1) are absolutly the same as those of our previously reported chloro-osmabenzene.[5]

Scheme 3. Formation of Complexes 6 and 7

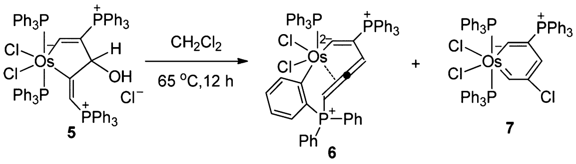


Table 1. Selected NMR Spectroscopic Data for Complexes 6, 7, 8, and 9

	δ (^1H) [ppm]			δ (^{31}P) [ppm]		
complex	H1	H3	H5	C^2PPh_3	C^5PPh_3	$OsPPh_3$
6	12.0	7.9	3.9	8.0	42.2	−8.3
8	11.3	7.6	3.8	9.1	42.3	−4.6
7	19.3	8.0	20.7	19.2		−13.0
9	17.3	7.7	18.8	19.4		−2.9

Complex **6** was isolated as a yellow solid. The structure of **6** (Figure 3) contains a conjugated osmacycle with a double bond of an allene coordinated to the metal center, which can also be viewed as a five-membered metallacycle with an exocyclic methylene group coordinated to the osmium center. The coordinated double bond C4═C5 is almost coplanar with the osmacycle consisting of Os1, C1, C2, C3, and C4. The coplanarity is reflected by the small deviation (0.0237 Å) from the rms (root-mean-square) planes of the best fit through the six atoms. The allene unit deviates slightly from linearity with a C3−C4−C5 angle of 152.2°.

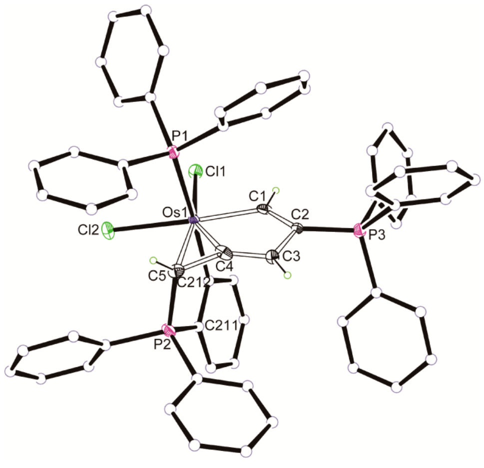
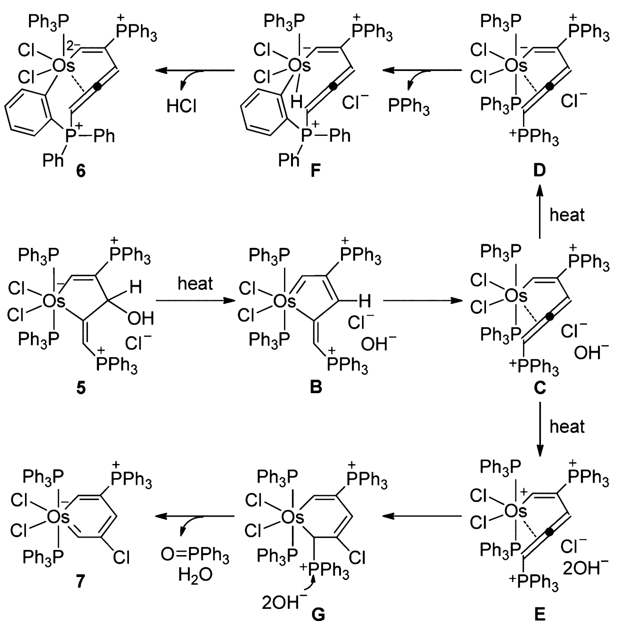


Figure 3. Molecular structure of the complex **6**. (ellipsoids at the 50% probability level). Some of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 2.007(4), Os1−C4 1.989(4), Os1−C5 2.156(4), C1−C2 1.370(6), C2−C3 1.468(5), C3−C4 1.343(6), C4−C5 1.397(5), Os1−C212 2.093(4), C2−P3 1.746(4), C5−P2 1.781(4), Os1−Cl1 2.4531(10), Os1−Cl2 2.5089(11); C1−Os1−C4 72.53(17), C2−C1−Os1 122.6(3), C1−C2−C3 110.6(4), C2−C3−C4 107.9(4), C3−C4−C5 152.2(4), C3−C4−Os1 126.1(3), C5−C4−Os1 76.9(3), C4−C5−Os1 64.0(2), C4−Os1−C5 39.15(15).

The solid-state structure of **6** is also fully supported by the solution NMR spectroscopic data and elemental analysis. In particular, the ^{1}H NMR spectrum showed the C^1*H* signal at 12.0 ppm and the signals attributed to C^3*H* and C^5*H* at 7.9 and 3.9 ppm, respectively. The ^{31}P{^{1}H} NMR spectrum displayed two sets of doublets and one singlet resonances with equal intensity at 42.2 (d, J(P,P) = 26.5 Hz), 8.0 (s), and −8.3 (d, J(P,P) = 26.5 Hz) ppm, indicating the presence of three inequivalent phosphorus nuclei of a structure devoid of symmetry. In the ^{13}C{^{1}H} NMR spectrum, the signals of C^1 and C^2 appeared at 217.2 and 110.3 ppm, respectively, while the three carbon signals of the coordinated allene backbone appeared at 191.2 (C^4), 140.4 (C^3), and 16.0 (C^5) ppm.

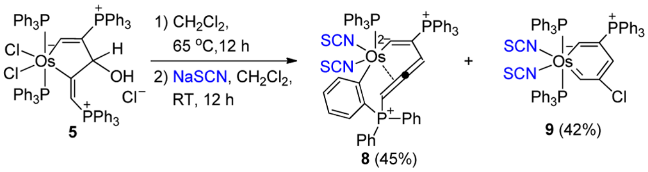
On the basis of our experimental observations,[10−12] we postulate the reaction mechanism shown in Scheme 4 for the formation of **6** and **7**. The process may involve the dissociation of OH$^-$ from **5** giving **B** followed by the intramolecular rearrangement to form **C**.[10] From structure **C**, there are two possible paths, which lead to the formation of **6** and **7**, respectively. **D** and **E** are generated from **C** via a disproportionation reaction. In path 1, dissociation of a PPh$_3$ ligand from **D** can provide a vacant site for the oxidative addition of the phenyl C−H bond of the PPh$_3$ to form the hydrido intermediate **F**.[11] Subsequent abstraction of the proton by counterion Cl$^-$ results in a η^2-allene-coordinated osmacycle **6**.[11] In the other path, the nucleophilic attack of counterion Cl$^-$ on **E** may form **G**. Then a P−C bond cleavage of **G** with the help of counterions OH$^-$ results in chloro-osmabenzene **7**.[12]

Scheme 4. Proposed Mechanism for the Formation of 6 and 7



Chloro-osmabenzene **7** is unstable in solution. From our previous work on metallacycle chemistry, we know that exchanging the ligands from Cl to SCN would make metallaorganic complexes more stable.[5,13] As expected, complex **8** and stable chloro-osmabenzene **9** can be isolated and characterized successfully by addition of NaSCN to the reaction mixture (see Scheme 5).

Scheme 5. Formation of Complexes 8 and 9



Complex **8** has been characterized by NMR spectroscopy and elemental analysis. The chemical shifts in the ^{1}H NMR spectrum (11.3 (C^1*H*), 7.6 (C^3*H*), and 3.8 (C^5*H*) ppm) (Table 1), ^{31}P{^{1}H} NMR spectrum (42.3 (C^5*P*Ph$_3$), 9.1 (C^2*P*Ph$_3$), and −4.6 (Os*P*Ph$_3$) ppm), and ^{13}C{^{1}H} NMR spectrum (212.1 (C^1), 114.8 (C^2), 140.6 (C^3), 194.2 (C^4), and 15.1 (C^5) ppm) are very close to those observed for complex **6**.

Complex **9** could be isolated as a green solid. The X-ray structure (Figure 4) indicates that **9** is a typical osmabenzene containing an essentially planar six-membered metallacycle. The mean rms deviation from the least-squares plane through Os1/C1/C2/C3/C4/C5 is 0.0486 Å. Within the metallacycle, the C−C bond distances are observed in the range 1.367(4)−1.419(4) Å, and the Os−C bond distances in the ring are approximately equal (1.958(3) and 1.943(3) Å). The lack of significant alternations in the C−C bond distances, together with the planarity of the ring, indicates that the metallacycle has a delocalized nature. The C−Cl bond (1.789(3) Å) is typical

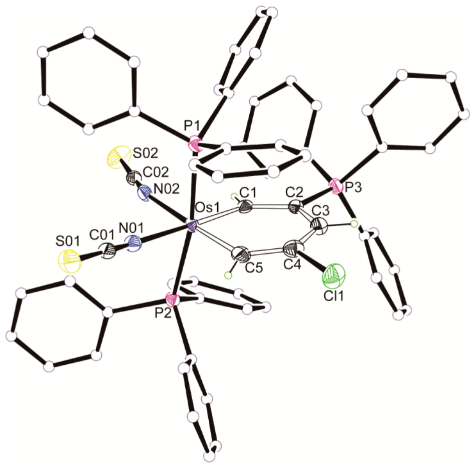


Figure 4. Molecular structure of complex **9** (ellipsoids at the 50% probability level). Some of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1–C1 1.958(3), Os1–C5 1.943(3), C1–C2 1.399(4), C2–C3 1.419(4), C3–C4 1.367(4), C4–C5 1.378(4), C4–Cl1 1.789(3), C2–P3 1.791(3), Os1–N01 2.141(3), N01–C01 1.164(3), C01–S01 1.632(3), Os1–N02 2.141(3), N02–C02 1.161(3), C02–S02 1.631(3); C1–Os1–C5 90.51(13), C2–C1–Os1 128.9(2), C1–C2–C3 121.4(3), C2–C3–C4 124.7(3), C3–C4–C5 126.4(3), C4–C5–Os1 126.7(2).

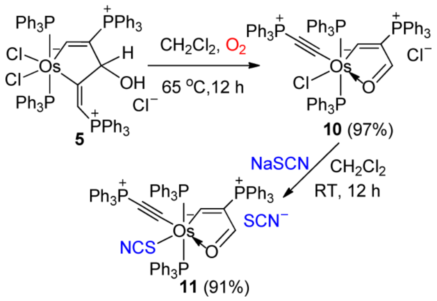
for a C–Cl single bond.[9] Complex **9** is a rare example of thermally stable metallabenzenes with a Cl group.

The solution NMR spectroscopic data of **9** are very close to *in situ* NMR (in CD_2Cl_2) for complex **7** (Table 1). The ^1H NMR spectrum (in $CDCl_3$) has three CH signals at 18.8 (C^5H), 17.3 (C^1H), and 7.7 ppm (C^3H). In the $^{31}P\{^1H\}$ NMR spectrum, the signal of $CPPh_3$ appears at 19.4 ppm and that of $OsPPh_3$ appears at −2.9 ppm.

Although metallabenzenes[4−6,14] act as the pioneer of metallaaromatics, the preparation routes of metallabenzenes are less frequently investigated, especially of the halo-metallabenzenes.[5,13b,14b] The reactions described here provide new available routes to prepare stable chloro-osmabenzene, which provide a new method for metallabenzenes.[14] It is worth noting that complex **9** shows remarkable air stability; it can even remain unchanged for a few months in solution.

Reactivity Study of the Osmacyclopentene Complex under Oxygen. To further study the reactivity of the paramagnetic osmacyclopentene **5**, we also investigated the reaction of **5** with molecular oxygen. On heating the suspension of **5** in dichloromethane under an oxygen atmosphere at 65 °C for 12 h in a sealed tube (Scheme 6), complex **10** could be isolated as the only product. However, it is difficult to obtain a single crystal of **10** to determine its solid-state structure.

Scheme 6. Formation of Complexes 10 and 11



Complex **10** underwent ligand and anion exchange reaction, affording complex **11**, which could be isolated as a dark green solid. The solid structures of complex **11** were unambiguously determined by X-ray crystallography.

Complex **11** has been also established by solution NMR spectroscopic data in addition to X-ray diffraction (Figure 5).

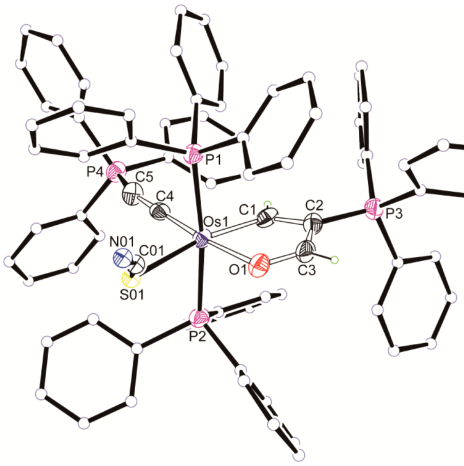


Figure 5. Molecular structure of the complex cation of **11** (ellipsoids at the 50% probability level). Counteranion and some of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1–C1 1.946(7), Os1–O1 2.163(4), C1–C2 1.419(9), C2–C3 1.408(9), C3–O1 1.266(8), Os1–C4 1.915(7), C4–C5 1.246(9), Os1–S01 2.481(2), S01–C01 1.497(12), C01–N01 1.311(13), C2–P3 1.756(7), C5–P4 1.677(7); C1–Os1–O1 77.5(2), C2–C1–Os1 117.5(5), C1–C2–C3 112.7(6), C2–C3–O1 118.9(6), C3–O1–Os1 112.8(4), C1–Os1–C4 96.4(3), C5–C4–Os1 178.4(6), C4–C5–P4 159.7(6).

The structure indicates that complex **11** is a typical osmafuran. The mean rms deviation from the least-squares plane through Os1/C1/C2/C3/O1 is 0.0338 Å. Within the metallacycle, the C–C bond distances are observed in the range 1.408(9)–1.419(9) Å, and the Os–C bond distances in the ring are approximately equal (1.946(7) Å). The lack of significant alternations in the C–C bond distances, together with the planarity of the ring, indicates that the metallacycle has a delocalized charater. The C4–C5 bond distance (1.246(9) Å) is typical for a carbon–carbon triple bond.

The NMR spectroscopic data of **11** are consistent with its solid-state structure. In particular, the ^1H NMR spectrum showed the characteristic C^1H signals at 13.8 ppm. The proton signal on C^3 can be observed at 8.2 ppm, which is close to those of organic aromatic rings. These data suggest that the metallacycle of **11** is delocalized. The ^{31}P NMR spectrum of **11** consists of three signals: δ = 14.0 and 11.0 ppm for two $CPPh_3$ groups and δ = −19.8 ppm for $OsPPh_3$. Two carbon signals of the alkynylphosphonium group are found at δ = 174.2 ppm for C^4 and δ = 80.7 ppm for C^5. The structure of complex **11** is close to that reported for the structure of osmacycle $[OsCl(PPh_3)_2(CHC(PPh_3)CHCH)(C{\equiv}C(PPh_3))]Cl$.[15]

Complex **10** has been characterized by NMR spectroscopy and elemental analysis as well. The chemical shifts in the ^1H NMR spectrum (14.0 (C^1H) and 8.3 (C^3H) ppm), $^{31}P\{^1H\}$ NMR spectrum (11.2 ($CPPh_3$), 10.0 ($CPPh_3$), and −22.2 ($OsPPh_3$) ppm), and $^{13}C\{^1H\}$ NMR spectrum (248.4 (C^1), 115.5 (C^2), 193.7 (C^3), 178.3 (C^4), and 80.5 (C^5) ppm) are very close to those observed for complex **11** (Table 2).

Table 2. Selected NMR Spectroscopic Data for Complexes 10 and 11

	δ (^{1}H) [ppm]		δ (^{31}P) [ppm]		
complex	H1	H3	C*P*Ph$_3$	C*P*Ph$_3$	Os*P*Ph$_3$
10	14.0	8.3	11.2	10.0	−22.2
11	13.8	8.2	14.0	11.0	−19.8

	δ (^{13}C) [ppm]				
complex	C1	C2	C3	C4	C5
10	248.4	115.5	193.7	178.3	80.5
11	253.5	117.0	194.5	174.2	80.7

Furthermore, complexes **10** and **11** show high stability. Although they contain an acetylide group at the osmium center, in contrast to most air-sensitive metal acetylide complexes, the solution of **10** and **11** can be stored in air for months without decomposition. This unexpected stability may be due to the stabilization effect and electron-withdrawing property of the phosphonium group.

■ CONCLUSION

In summary, we have reported the isolation, characterization, and reactions of a paramagnetic osmacyclopentene complex. The paramagnetic osmacyclopentene complex can be obtained from an η^2-alkynol-coordinated osmacycle via oxidation reaction. The three conjugated osmacycles, namely, η^2-allene-coordinated osmacycle, chloro-osmabenzene, and osmafuran complexes, could be isolated based on a disproportionation reaction and oxidation reaction of this osmacyclopentene complex. This new method allowed us to synthesize certain interesting stable complexes that contain phosphonium moieties in the metallacyclic rings.

■ EXPERIMENTAL SECTION

General Comments. All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (diethyl ether) or calcium hydride (dichloromethane). The starting material $OsCl_2(PPh_3)_2(CH{=}C(PPh_3)CH(OH)\text{-}\eta^2\text{-}C{\equiv}CH)$ (**1**) was synthesized by literature procedures.[4] Column chromatography was performed on neutral alumina gel (200−300 mesh) or acidic alumina gel (200−300 mesh). NMR experiments were performed on a Bruker AV-500 spectrometer (^{1}H 500.2 MHz; ^{13}C 125.8 MHz; ^{31}P 202.5 MHz) or a Bruker AV-300 spectrometer (^{1}H 300.1 MHz; ^{13}C 75.5 MHz; ^{31}P 121.5 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Elemental analysis data were obtained on an Elementar Analysensystem GmbH Vario EL III instrument. EPR spectroscopy was measured on a Bruker EMX-10/12 (X-band) spectrometer at 9.4 GHz, modulation frequency 100 kHz, modulation amplitude 2 G.

Preparation and Characterization of Complex 5. A mixture of complex **1** (1.08 g, 0.96 mmol), tetrabutylammonium chloride (0.80 g, 2.88 mmol), and PPh_3 (0.76 g, 2.90 mmol) in dichloromethane (25 mL) under air was stirred at −10 °C for 0.5 h to give a yellow solution. Then purification by column chromatography (neutral alumina, eluent: dichloromethane/acetone, 1:1) afforded complex **5** as a yellow solid. Yield: 1.10 g, 81%. Anal. Calcd (%) for $C_{77}H_{64}OOsP_4Cl_3$: C 64.86; H 4.52. Found: C 64.48; H 4.75.

Preparation and Characterization of Complex 5′. To a suspension of complex **5** (131 mg, 0.09 mmol) in dichloromethane (10 mL) was slowly added a solution of $NaBPh_4$ (387 mg, 1.13 mmol) in methanol (10 mL). The reaction mixture was stirred for 2 min to give a brown solution. The volume of the mixture was reduced to about 1 mL under vacuum. Addition of diethyl ether (10 mL) to the residue produced an orange solid, which was collected by filtration, washed with methanol and diethyl ether, and then dried under vacuum. Yield: 120 mg, 76%. Anal. Calcd (%) for $C_{101}H_{84}OOsP_4Cl_2B$: C 70.96; H 4.95. Found: C 70.73; H 5.19.

Preparation and Characterization of Complex 6. A suspension of **5** (512 mg, 0.36 mmol) in dichloromethane (20 mL) was heated to 65 °C for 12 h in a sealed tube. Then the reaction system was cooled to room temperature and depressurized to atmospheric pressure. A brown solution was collected. The volume of the mixture was reduced to about 2 mL under vacuum and was purified by column chromatography (acidic alumina, eluent: dichloromethane/acetone, 2:1) to give complex **6** as a yellow solid. Yield: 187 mg, 47%. ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ 12.0 (1H, d, J = 15.6 Hz, C^{1}*H*), 7.9 (1H, m, C^{3}*H*), 6.8−7.7 (44H, m, PPh$_3$), 3.9 (1H, d, J = 18.0 Hz, C^{5}*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 42.2 (d, J(P,P) = 26.5 Hz, C^{5}*P*Ph$_3$), 8.0 (s, C^{2}*P*Ph$_3$), −8.3 (d, J(P,P) = 26.5 Hz, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz, plus ^{1}H−^{13}C HMQC and ^{13}C-dept 135): δ 217.2 (br, C^{1}), 191.2 (d, J = 27.6 Hz, C^{4}), 175.1 (m, OsC^{212}), 140.4 (d, J = 16.2 Hz, C^{3}), 118.5−136.7 (m, Ph), 110.3 (d, J = 80.5 Hz, 1H, C^{2}), 16.0 (dd, J = 75.7 Hz, J = 4.0 Hz, C^{5}). Anal. Calcd (%) for $C_{59}H_{47}OsP_3Cl_2$: C 63.84; H 4.27. Found: C 64.11; H 4.44.

Preparation and Characterization of Complexes 8 and 9. A suspension of **5** (498 mg, 0.35 mmol) in dichloromethane (20 mL) was heated to 65 °C for 12 h in a sealed tube. Then the reaction system was cooled to room temperature and depressurized to atmospheric pressure to give a brown solution. The brown solution was transferred by filtration to a Schlenk bottle containing sodium thiocyanate (284 mg, 3.50 mmol). Then the mixture was stirred at room temperature for 12 h to give a brown suspension. The solid suspension was removed by filtration, and the volume of the filtrate was reduced to about 2 mL under vacuum. The volume of the mixture was purified by column chromatography (neutral alumina, eluent: dichloromethane and dichloromethane/acetone, 10:1) to give complex **8** as a yellow solid and complex **9** as a green solid, with complex **9** eluting first. Data for **8**: Yield: 181 mg, 45%. ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ 11.3 (1H, d, J = 15.8 Hz, C^{1}*H*), 7.6 (1H, C^{3}*H* obsured by the phenyl signals and confirmed by ^{1}H−^{13}C HMQC), 6.9−7.6 (44H, m, Ph), 3.8 (1H, d, J = 16.8 Hz, C^{5}*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 42.3 (d, J(P,P) = 29.9 Hz, C^{5}*P*Ph$_3$), 9.1 (s, C^{2}*P*Ph$_3$), −4.6 (d, J(P,P) = 29.8 Hz, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz, plus ^{1}H−^{13}C HMQC and ^{13}C-dept 135): δ 212.1 (br, C^{1}), 194.2 (d, J = 26.9 Hz, C^{4}), 168.6 (m, OsC^{212}), 140.6 (d, J = 16.3 Hz, C^{3}), 139.3 and 132.1 (s, SCN), 119.5−134.8 (m, Ph), 114.8 (d, J = 79.2 Hz, C^{2}), 15.1 (dd, J = 75.4 Hz, J = 3.9 Hz, C^{5}). Anal. Calcd (%) for $C_{61}H_{47}N_2OsP_3S_2$: C 63.42; H 4.10; N 2.42. Found: C 63.24; H 4.13; N 2.03. Data for **9**: Yield: 175 mg, 42%. ^{1}H NMR ($CDCl_3$, 500.2 MHz): δ 18.8 (1H, s, C^{5}*H*), 17.3 (1H, d, J = 22.3 Hz, C^{1}*H*), 6.8−7.7 (45H, m, PPh$_3$), 7.7 (1H, C^{3}*H* obsured by the phenyl signals and confirmed by ^{1}H−^{13}C HSQC). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.5 MHz): δ 19.4 (s, C*P*Ph$_3$), −2.9 (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz, plus ^{1}H−^{13}C HSQC): δ 254.1 (br, C^{5}), 228.3 (br, C^{1}), 147.6 and 143.1 (s, SCN), 144.9 (d, J = 21.9 Hz, C^{3}), 121.0−134.6 (m, Ph and C^{4}), 112.2 (d, J = 74.5 Hz, C^{2}). Anal. Calcd (%) for $C_{61}H_{48}N_2OsP_3S_2Cl$: C 61.48; H 4.06; N 2.35. Found: C 61.83; H 4.01; N 2.40.

Preparation and Characterization of Complex 10. A suspension of **5** (255 mg, 0.18 mmol) in dichloromethane (10 mL) under an oxygen atmosphere was heated to 65 °C for 12 h in a sealed tube. Then the reaction system was cooled to room temperature and depressurized to atmospheric pressure, and a dark green solution was collected. The volume of the mixture was reduced to about 1 mL under vacuum. Addition of diethyl ether (10 mL) to the residue produced a green solid as complex **10**, which was collected by filtration, washed with dichloromethane (1 mL) and diethyl ether (10 mL), and then dried under vacuum. Yield: 240 mg, 97%. ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ 14.0 (1H, d, J = 13.1 Hz, C^{1}*H*), 8.3 (1H, s, C^{3}*H*), 6.9−7.8 (60H, m, PPh$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 11.2 (s, C*P*Ph$_3$), 10.0 (s, C*P*Ph$_3$), −22.2 (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz, plus ^{1}H−^{13}C HMQC and ^{13}C-dept 135): δ 248.4

(br, C^1), 193.7 (d, J = 28.4 Hz, C^3), 178.3 (m, C^4), 120.2−135.6 (m, Ph), 115.5 (d, J = 85.3 Hz, C^2), 80.5 (d, J = 211.4 Hz, C^5). Anal. Calcd (%) for $C_{77}H_{62}Cl_2OOsP_4$: C 66.61; H 4.50. Found: C 66.40; H 4.43.

Preparation and Characterization of Complex 11. A suspension of complex **10** (205 mg, 0.15 mmol) and sodium thiocyanate (122 mg, 1.50 mmol) in dichloromethane (15 mL) was stirred at room temperature for about 12 h to give a dark green suspension. The solid suspension was removed by filtration, and the volume of the filtrate was reduced to about 2 mL under vacuum. Addition of diethyl ether (15 mL) to the residue produced a dark green solid, which was collected by filtration, washed with diethyl ether (3 × 5 mL), and dried under vacuum. Yield: 193 mg, 91%. ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ 13.8 (1H, d, J = 14.5 Hz, C^1H), 8.2 (1H, s, C^3H), 6.9−7.7 (60H, m, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 14.0 (s, $CPPh_3$), 11.0 (s, $CPPh_3$), −19.8 (s, $OsPPh_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, plus $^1H-^{13}C$ HMQC and ^{13}C-dept 135): δ 253.5 (br, C^1), 194.5 (d, J = 28.9 Hz, C^3), 174.2 (m, C^4), 144.0 (s, Os(SCN)), 119.9−135.2 (m, Ph and SCN^-), 117.0 (d, J = 85.2 Hz, C^2), 80.7 (d, J = 210.1 Hz, C^5). Anal. Calcd (%) for $C_{79}H_{62}N_2OOsP_4S_2$: C 66.18; H 4.36; N 1.95. Found: C 65.95; H 4.56; N 2.21.

Crystallographic Analysis. Single-crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All of the data were corrected for absorption effects using the multiscan technique. The structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full matrix least-squares on F^2 using the Bruker SHELXTL (version 6.10) program package. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. A crystal suitable for X-ray diffraction was grown from a CH_2Cl_2 solution layered with hexane for complexes **5′**, **6**, **8**, and **9**. A crystal suitable for X-ray diffraction was grown from a $ClCH_2-CH_2Cl$ solution layered with diethyl ether for complex **11**. The solvent molecules CH_2Cl_2 and the phenyl groups in **5′** are disordered and were refined with suitable restraints. One of phenyl groups in **6** is disordered and was refined with suitable restraints. The CH_2Cl_2 solvent molecules in **8** were refined isotropically using fixed C−Cl distances and Cl−C−Cl angles. The solvent molecules $ClCH_2-CH_2Cl$ in **11** are disordered and were refined with suitable restraints. CCDC-935885 (**5′**), CCDC-935886 (**6**), CCDC-935889 (**8**), CCDC-935887 (**9**), and CCDC-935888 (**11**) contain the supplementary crystallographic data for this paper. Further details on crystal data, data collection, and refinements are summarized in Table S1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF and pdf files giving crystallographic data of complexes **5′**, **6**, **8**, **9**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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