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Synthesis and characterization of stable osmafuran starting from $HC\equiv CCH(OH)C\equiv CH$ and $OsHCl(CO)(PPh_3)_3$

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This paper presents a new convenient route to prepare osmafuran starting from readily accessible $HC\equiv CCH(OH)C\equiv CH$ and $OsHCl(CO)(PPh_3)_3$. Treatment of a solution of $OsHCl(CO)(PPh_3)_3$ in dichloromethane with $HC\equiv CCH(OH)C\equiv CH$, followed by the addition of acetic acid, produced osmafuran $[Os(CHC(PPh_3)CO(CH_2CH_3))Cl(CO)(PPh_3)_2]Cl$ (**2**). **2** has been isolated in good yield and fully characterized. ^1H and ^{13}C NMR spectra show the characteristic downfield chemical shifts of the ring hydrogen and carbon atoms. NMR and X-ray diffraction data provide strong evidence for the aromatic nature of **2**. Probably due to the effect of the phosphonium substituent, **2** exhibits remarkable thermal stability, air stability and lower reactivity.

osmafuran, metallaaromatics, phosphonium salt, synthesis, stability

1 Introduction

Metallacyclic compounds containing transition metals are of significant interest, because they are useful and versatile synthetic intermediates of many synthetically significant transition-metal-assisted reactions [1]. As a consequence, the preparation and reaction chemistry of metallacyclic compounds have continuously been one of the major research topics in organometallic chemistry [2–5].

As a special class of metallacyclic compounds, metallaaromatics have attracted considerable attention in recent years due to their aromatic properties and organometallic reactivities [6]. Among the five-membered representatives of metallaaromatics, metallafurans are the most extensively investigated compounds, which have also been referred to as chelated vinyl ketone complexes or oxametallacyclopentadiene complexes in previous reports [7]. A great variety of approaches have been developed to construct stable metallafuran rings, which have been classified and discussed by Wright *et al*. [8].

In an effort to construct metallaaromatics with different metals and substituents, we have prepared several metallafurans starting from the reactions between transition-metal-containing complexes and alkynes [9]. During an investigation of the reactivity of $OsHCl(CO)(PPh_3)_3$ with terminal alkynes, we found a new convenient route to prepare osmafurans starting from readily accessible $HC\equiv CCH(OH)C\equiv CH$. The investigation led us to isolate the phosphonium salt of metallafurans.

2 Experimental

All manipulations were carried out at room temperature under nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (diethyl ether) or calcium hydride (CH_2Cl_2). The starting materials $OsHCl(CO)(PPh_3)_3$ [10] and $HC\equiv CCH(OH)C\equiv CH$ [11] were synthesized by previously reported procedures. Infrared spectra were measured with a Nicolet Avatar 360 FT-IR

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spectrometer using film KBr pellet techniques. Column chromatography was performed on alumina gel (200–300 mesh). NMR experiments were performed on 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 a Thermo Quest Italia S.P.A. EA 1110 instrument.

2.1 Synthesis of [Os(CHC(PPh$_3$)CO(CH$_2$CH$_3$))Cl(CO)-(PPh$_3$)$_2$]Cl (2)

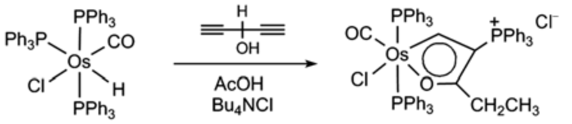
To a suspension of $OsHCl(CO)(PPh_3)_3$ (0.60 g, 0.58 mmol) and Bu_4NCl (0.40 g, 5.4 mmol) in CH_2Cl_2 (10 mL) was added a solution of HC≡CCH(OH)C≡CH (93 mg, 1.16 mmol) in CH_2Cl_2 (2 mL). After 2 min, acetic acid (0.2 mL) was added and the reaction mixture was stirred at room temperature for ca. 1 h to give a brownish-black suspension. The solid was removed by filtration, and the volume of the filtrate was reduced to ca. 1 mL under vacuum. The residue was purified by column chromatography (neutral alumina, eluent: acetone/methanol, 6:1) to give **2** as a green solid. Yield: 0.37 g, 55%. IR (film): v (C≡O) 1930, v(C≡O) 1435 cm^{-1}. ^{1}H NMR plus ^{1}H-^{1}H COSY NMR (300.1 MHz, $CDCl_3$): δ 12.8 (d, $^3J(PH) = 18.0$ Hz, 1 H, OsCH), 7.9–6.8 (m, 45H, PPh_3), 1.6 (q, $^3J(HH) = 6.0$ Hz, 2H, CH_2), 0.7 ppm (t, $^3J(HH) = 6.0$ Hz, 3H, CH_3). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 15.9 (s, CPPh$_3$), 12.5 ppm (s, OsPPh$_3$). ^{13}C{^{1}H} NMR plus ^{13}C DEPT NMR and ^{1}H-^{13}C COSY NMR (75.5 MHz, $CDCl_3$): δ 245.6 (br, OsCH), 207.5 (d, $^2J(PC) = 24.9$ Hz, OsOCEt), 183.1 (t, $^2J(PC) = 10.8$ Hz, OsCO), 133.5–125.7 (m, PPh_3), 114.0 (d, $^1J(PC) = 85.3$ Hz, OsCHC(PPh$_3$)), 32.9 (s, CH$_2$CH$_3$), 8.7 ppm (s, CH$_2$$CH_3$). Anal. calcd for $C_{60}H_{51}O_2P_3Cl_2Os$: C, 64.19; H, 4.58. Found: C, 64.26; H, 5.02.

2.2 X-ray crystallography

Crystal data for **2**·1.5CHCl$_3$·2H$_2$O: $2(C_{60}H_{51}O_2P_3Cl_2Os)\cdot 1.5CHCl_3\cdot 2H_2O$, M_r = 2479.46, monoclinic, space group $P21/c$, $Z = 4$, $a = 23.308(4)$, $b = 25.040(4)$, c = 19.334(3) Å, $\alpha = 90$, $\beta = 95.023(3)$, $\gamma = 90°$, $V = 11241(3)$ Å^3, $\rho_{calcd} = 1.465$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 2.564$ mm^{-1}, $F(000) = 4988$, 79934 reflections, 19785 independent reflections ($R_{int} = 0.0586$); $R_1 = 0.0493$, $wR_2 = 0.1512$ for 1317 parameters and 16555 reflections with $[I > 2\sigma(I)]$. Crystals of **2** suitable for X-ray diffraction were grown from a solution in CH_2Cl_2 layered with diethyl ether. Intensity data were collected on a Bruker SMART CCD Area Detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 173 K. The structure was solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares methods on F^2 by using the Bruker SHELXTL (Version 6.10) program package. All non-hydrogen atoms were refined anisotropically. CCDC-767431 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3 Results and discussion

As indicated by *in situ* NMR spectroscopy, when a mixture of **1** and excess HC≡CCH(OH)C≡CH (in 1:2 molar ratio) in CH_2Cl_2 was stirred at room temperature for ca. 1 h, a brownish-black solution containing predominantly **2** along with some unidentified species was produced. When acetic acid and Bu_4NCl were added, the reaction was cleaner. As shown in eq. (1), in the presence of Bu_4NCl, treatment of a solution of $OsHCl(CO)(PPh_3)_3$ in dichloromethane with HC≡CCH(OH)C≡CH, followed by addition of acetic acid, produced osmafuran **2**. In this case, **2** can be isolated as a green solid in 55% yield. The structure of complex **2** can be inferred from its NMR spectroscopy. The presence of the metallacycle is clearly indicated by the ^{1}H and ^{13}C NMR data. The ^{1}H NMR spectrum shows the signal of OsCH at $\delta = 12.8$ ppm, the signal of C(PPh$_3$)CH_2CH$_3$ at $\delta = 1.6$ ppm, and the signal of C(PPh$_3$)CH$_2$$CH_3$ at $\delta = 0.7$ ppm. In the ^{13}C{^{1}H} NMR spectrum, the signals of the ethyl substituent of the metallacycle appear at $\delta = 32.9$ and 8.7 ppm, whereas the three carbon signals of the metallacycle appear at $\delta =$ 245.6, 207.5 and 114.0 ppm, respectively. In addition, the signal of CPPh$_3$ appears at $\delta = 15.9$ ppm, which is comparable with those related signals of our previous phosphonium-substituted metallacycles [9], and that of OsPPh$_3$ appears at 12.5 ppm in the ^{31}P{^{1}H} NMR spectrum.



1 2 (1)

The structure of **2** has also been determined by X-ray crystallography. The crystallographic asymmetric unit contains two independent molecules with the similar geometry, one of which is depicted in Figure 1. **2** is structurally related to our previously reported osmafurans [9], which belong to the rare examples of metallaaromatics bearing phosphonium groups. The X-ray structure of **2** shows the complex has an essentially planar five-membered metallacycle. The coplanarity is reflected by the small RMS deviation (0.131 Å) from the least-squares plane through the five atoms Os1, C1, C2, C3, and O1. The sum of angles in the six-membered ring is 539.98°, which is nearly equal to the ideal value of 540°. Within the metallacycle, the Os1–C1 and Os1–O1 distances are 1.993(5) and 2.136(4) Å, respectively, which are close to those of Esteruelas's osmafurans OsCl(CO)-(P^{i}Pr$_3$)$_2$(CHCHC(Ph)O) (Os1–C1 1.971(3) Å, Os1–O1 2.126(3) Å) [12a] and Os(SnPh$_2$Cl)(η^2-H$_2$)-(P^{i}Pr$_3$)$_2$(CHCHC-

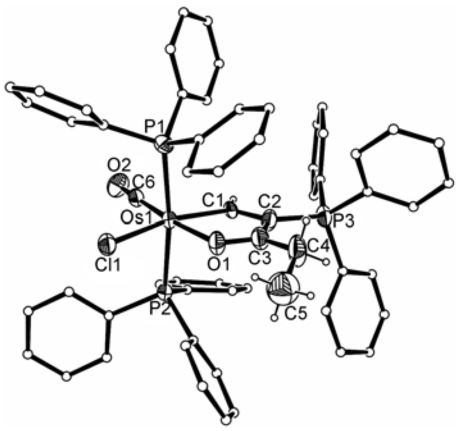
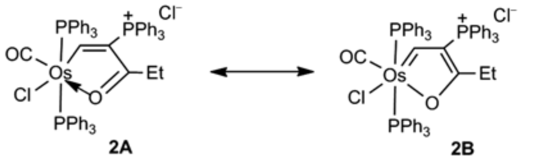


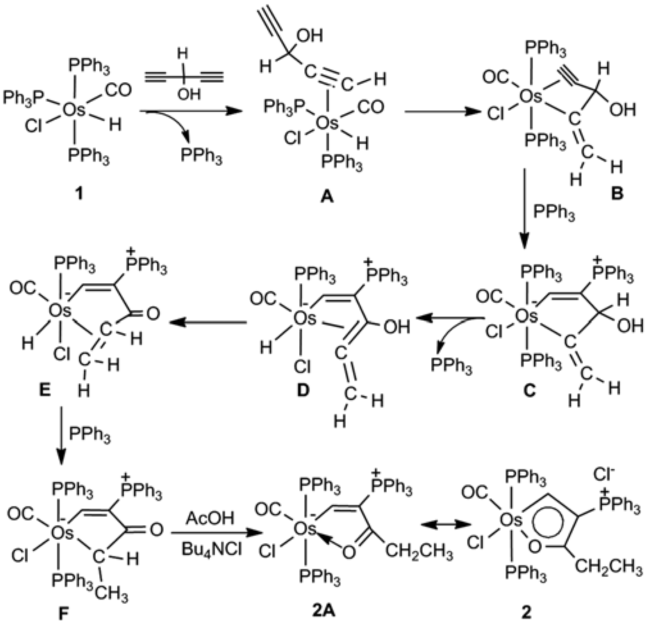
Figure 1 Molecular structure for the cation of complex **2** (ellipsoids at the 50% probability level). Counteranion and some of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1–P1 2.4040(15), Os1–P2 2.3750(15), Os1–C6 1.852(6), C6–O2 1.129(7), Os1–Cl1 2.4523(15), Os1–C1 1.993(5), Os1–O1 2.136(4), C1–C2 1.370(8), C2–C3 1.420(9), C3–O1 1.259(7), C3–C4 1.515(9), C4–C5 1.470(11), P3–C2 1.783(6); P1–Os1–P2 172.92(5), C6–Os1–Cl1 102.50(18), C1–Os1–O1 76.2(2), Os1–C1–C2 117.2(4), C1–C2–C3 114.5(5), C2–C3–O1 116.4(5), C3–O1–Os1 115.7(4).

$(CH_3)O)$ (Os1–C1 2.035(2) Å, Os1–O1 2.1657(15) Å) [12b], while are a little longer than our previously reported osmafuran $[OsCl(CO)(PPh_3)_2(CHC(PPh_3)C(CH_3)O)]Cl$ (Os1–C1 1.966(9) Å, Os1–O1 2.127(4) Å) [9d]. The C–C bond distances of the metallacycle are longer than typical C=C double bonds and shorter than typical C–C single bonds. The X-ray diffraction data as well as the characteristic downfield chemical shifts of the ring hydrogen and carbon atoms in the ^1H and ^{13}C NMR spectra indicate that the five-membered metallacycle of the complex cation of **2** has a delocalized structure with contribution of the two resonance structures **2A** and **2B** shown in eq. (2).



(2)

Scheme 1 shows a proposed plausible mechanism for the formation of the cationic complex **2** from the one-pot reaction of HC≡CCH(OH)C≡CH with **1**. Complex **1** could initially react with HC≡CCH(OH)C≡CH to give intermediate **A**, which may undergo an insertion reaction to give the vinyl-(π-alkyne) intermediate **B**. Insertion of alkynes into an Os–H bond is not surprising, which has been well documented [13]. Nucleophilic attack at the coordinated alkyne by external PPh_3 present in the solution could generate **C**. Then, the dissociation of PPh_3 and β-H elimination may produce hydrido-η^2-allene intermediate **D**. The transformation from **D** to **F** probably involves the keto-enol tautomerization of **D** to **E**, the insertion reaction and the recoordination of PPh_3. Finally, protolysis of the alkyl in **F** by the acetic acid, followed by the coordination of the carbonyl O atom to the osmium and subsequent aromatization would yield osmafuran **2**.



Scheme 1 Plausible mechanism for the formation of osmafuran **2**.

Consistent with our previous report [9], osmafuran **2** also exhibits remarkable thermal stability and air stability, which is probably related to the electronic effect of the phosphonium group and the protecting effect of the bulky PPh_3 substituents. A solution of **2** in chloroform remains nearly unchanged under refluxing for several days. In the solid state, **2** can be heated at 150 °C in air for five hours without appreciable decomposition.

It is noteworthy that complex **2** exhibits excellent acid- and alkali-resistant properties. As indicated by *in situ* NMR, no reaction occurred when the solution of **2** with strong acids or strong bases, such as HBF_4, HNO_3, $LiN(SiMe_3)_2$ or *t*-BuONa, was stirred at room temperature for several days. In addtion, complex **2** is not reactive to the reagents which were employed in the ligand substitution reactions of our metallaaromatics [14]. The lower reactivity of **2** is in accord with its higher stability.

4 Conclusions

An osmafuran bearing the phosphonium group was synthesized from readily accessible HC≡CCH(OH)C≡CH, which constituted an addition to the special class of metallaaromatics containing electron-withdrawing groups. The structural parameters associated with the metallacycle as well as the ^1H and ^{13}C NMR chemical shifts of the ring atoms provide strong evidence for the aromatic nature of osmafuran **2**. Its high stability would offer new opportunities for further development of the application of metallafuran.

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