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Reactions of osmapyridinium with terminal alkynes†

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We have synthesized a new type of ten-membered osmacycles by reaction of osmapyridinium with HC≡CCH(OH)R (R = Ph, Et). We propose that these reactions take place initially by coordination of the alkynes, [2 + 2] cycloaddition, subsequent 1,2-hydrogen migration and a final reductive elimination. The reactions with phenylacetylenes do not afford the corresponding derivatives but rather give η^4-coordinated cyclopentadiene complexes, which are proposed to derive from a [4 + 2] cycloaddition process. Related reactions of the η^4-coordinated cyclopentadiene complexes are also discussed.

Introduction

The chemistry of metalloaromatic compounds has made significant progress in the past decades.[1] The incorporation of a transition metal fragment into conventional aromatic hydrocarbons has recently attracted much attention from both theoretical and experimental chemists.[2,3] Whereas the synthesis of a variety of metallobenzene derivatives has been reported and allowed further insight into their reactivities,[2] reports on the isolation of analogues containing nitrogen atoms, *e.g.* metallopyridines, remain limited.[4] The first example of metallopyridines is tantalopyridine, which is significant in favoring the localized imido form.[4e,f] Another example of metallopyridines are osmapyridines with relatively delocalized structures.[4a,d] It is therefore not surprising that, so far, only the nucleophilic addition reactions[4d] and the ligand substitution reactions[4b] of delocalized metallopyridines have been reported.

As we were interested in the chemistry of metallacycles, we have studied the reactions of osmafuran with PhC≡CH and HC≡CCH(OH)Ph.[5] As shown in Chart 1, the reactions yielded nine-membered osmacycles, which might be formed through a [2 + 2] cycloaddition process relevant to olefin metathesis and alkyne polymerization. Another related approach is the investigation of the ruthenium vinyl carbene,[6] which can react with propargyl alcohols to produce a series of ten-membered η^2-olefine coordinated ruthenacycles (Chart 1(c)). The proposed mechanism for the reaction involves a regioselective [2 + 2] cycloaddition and 1,2-migration process.[6a] In this paper, we report the reactions of osmapyridinium with terminal alkynes to generate new osmacycles.

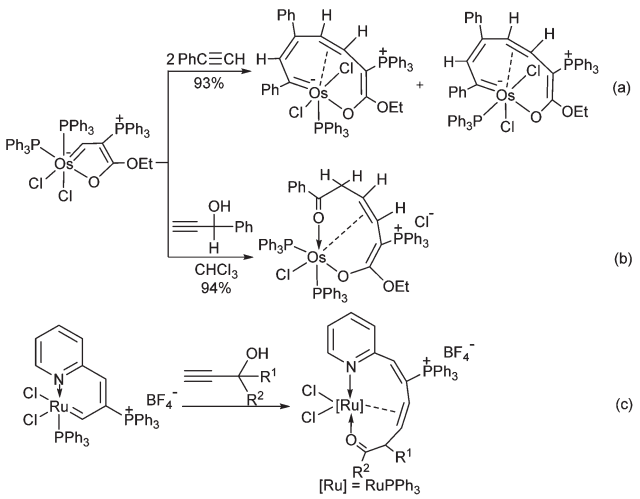

Chart 1 (a) Reaction of osmafuran with PhC≡CH; (b) reaction of osmafuran with HC≡CCH(OH)Ph; (c) reactions of ruthenium vinyl carbene with propargyl alcohols.

Results and discussion

Reactions of osmapyridinium with HC≡CCH(OH)R

Treatment of osmapyridinium **1**[4d] with excess HC≡CCH(OH)-Ph in dichloromethane under reflux led to the formation of

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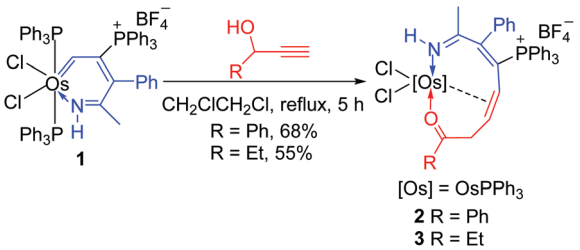
†Electronic supplementary information (ESI) available: Material including copies of ^{1}H and ^{13}C NMR spectra of all new products and crystallographic data for **2**, **5**, **6**, **8**. CCDC 1038534, 1038533, 1038537 and 1038535. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5qo00052a



Scheme 1 Reactions of **1** with HC≡CCH(OH)R.

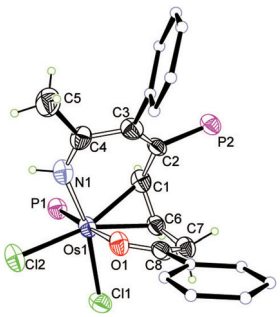


Fig. 1 X-ray structure of complex **2** (ellipsoids at the 50% probability level). Some of the hydrogen atoms, phenyl groups and the counter-anion are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–N1 2.012(7), Os1–O1 2.190(5), N1–C4 1.282(11), C3–C4 1.473(12), C2–C3 1.342(11), C1–C2 1.506(11), C1–C6 1.416(11), C6–C7 1.505(11), C7–C8 1.515(11), C8–O1 1.216(9), C4–C5 1.523(12); O1–Os1–N1 82.6(2), C4–N1–Os1 135.4(6), C3–C4–N1 121.8(7), C2–C3–C4 120.7(7), C1–C2–C3 125.8(7), C2–C1–C6 122.6(7), C1–C6–C7 124.7(7), C6–C7–C8 111.7(7), C7–C8–O1 119.2(7), C8–O1–Os1 116.4(5).

complex **2** (Scheme 1). **2** can be isolated as a purple solid in 68% yield, which was characterized by NMR spectroscopy and elemental analysis, and the structure was further confirmed by single-crystal X-ray diffraction.

The crystallographic details of complex **2** are given in Table 1. As shown in Fig. 1, **2** contains a distorted ten-membered metallacycle (N1, O1, C1, C2, C3, C4, C6, C7, C8, Os1). The osmium centre exhibits a somewhat irregular octahedral geometry, which may be attributed to the coordination of the double bond to the metal centre. The C–C distances within the osmacycle are similar to those in the ten-membered ruthenacycles (Chart 1(c)).[6a] Consistent with the X-ray structure, the ^{1}H NMR (CD_2Cl_2) spectrum shows the signals of the coordinated double bond at 5.9 (C1*H*) and 5.2 (C6*H*) ppm. The remaining ^{1}H signals of the metallacycle are observed at 10.6 (N*H*), 3.5 (C7*H*), and 0.9 ppm (C7*H*). With the aid of ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC and ^{13}C-dept 135 spectra, the seven carbon signals of the metallacycle are observed at δ = 219.8 (C8), 166.6 (C4), 156.5 (C3), 124.5 (C2), 61.9 (C6), 52.7 (C1), and 43.7 (C7) ppm in the ^{13}C{^{1}H} NMR spectrum. The ^{31}P NMR spectrum shows two signals at 19.7 and −9.5 ppm for C*P*Ph$_3$ and Os*P*Ph$_3$, respectively.

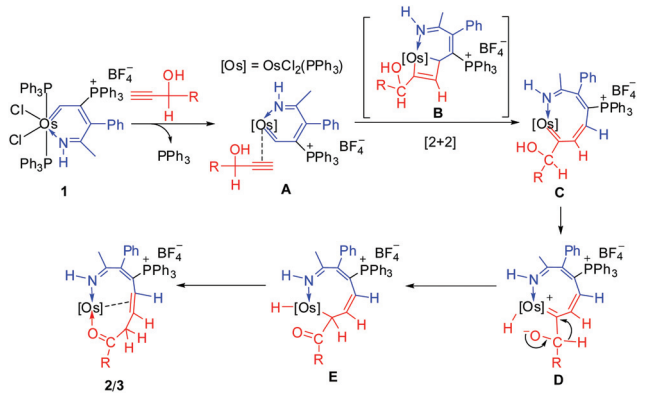
Reaction of osmapyridinium **1** with HC≡CCH(OH)Et was also investigated. As shown in Scheme 1, **1** reacted with HC≡CCH(OH)Et to produce insertion product **3**. **3** has been characterized by NMR spectroscopy and elemental analysis. The structure of **3** can be deduced easily, as its NMR data are similar to those of complex **2** (Table 2). The resonances of the osmacycle in the ^{1}H NMR spectrum (10.5 (N1*H*), 6.0 (C1*H*),

Table 1 Crystal data and structure refinement for **2**, **5**, **6** and **8**

	2·2H$_2$O·0.25CHCl$_3$	**5**·2CH$_2$Cl$_2$	**6**·CH$_2$Cl$_2$	**8**·2CH$_2$Cl$_2$
Formula	$C_{56.25}H_{52.25}BCl_{2.75}F_4NO_3OsP_2$	$C_{58}H_{52}BCl_6F_4NOOsP_2$	$C_{52}H_{55}BCl_4F_4N_3OsP$	$C_{50}H_{43}BCl_5F_4N_3OOsP$
M_r	1226.68	1330.65	1171.77	1187.10
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/n$	Cc	$P2_1/c$
a [Å]	11.9299(3)	16.5731(8)	19.3445(9)	12.0746(3)
b [Å]	14.1946(3)	19.6848(7)	16.8974(6)	18.8448(3)
c [Å]	33.0235(7)	18.1839(9)	16.1902(7)	20.9677(4)
α [°]	90	90	90	90
β [°]	98.5760(10)	112.182(2)	111.0040(10)	90.0230(10)
γ [°]	90	90	90	90
V [Å^3]	5529.7(2)	5493.2(4)	4940.5(4)	4771.06(17)
Z	4	4	4	4
ρ_{calcd} [g cm^{-3}]	1.473	1.609	1.574	1.653
μ [mm^{-1}]	2.553	2.727	2.884	3.044
F(000)	2458	2656	2352	2356
crystal size [mm^3]	0.18 × 0.12 × 0.10	0.30 × 0.10 × 0.10	1.00 × 0.60 × 0.40	0.80 × 0.50 × 0.30
θ Range [°]	3.08 to 25.00	3.02 to 27.48	3.25 to 24.99	3.11 to 27.48
Reflns collected	62 557	38 256	18 915	70 908
Independent reflns	9691	9642	7754	10 901
Observed reflns [$I \geq 2\sigma(I)$]	8011	7791	6954	8348
Data/restraints/params	9691/6/667	9642/0/669	7754/47/596	10 901/0/598
GOF on F^2	1.044	1.084	1.091	1.170
R_1/wR_2 [$I \geq 2\sigma(I)$]]	0.0566/0.1635	0.0643/0.1710	0.0344/0.0737	0.0526/0.1396
R_1/wR_2 (all data)	0.0694/0.1720	0.0779/0.1873	0.0439/0.0858	0.0723/0.1954
Largest peak/hole [e Å^{-3}]	2.14/−1.30	4.64/−2.06	1.43/−1.15	2.13/−2.64

Table 2 Selected NMR spectroscopic data for **2** and **3**

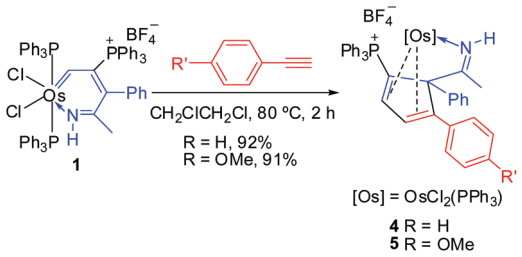
Compound		2	3
δ (^{1}H) (ppm)	NH	10.6	10.5
	H1	5.9	6.0
	H6	5.2	5.1
	H7	3.5	2.8
		0.9	0.7
δ (^{13}C) (ppm)	C4	166.6	167.4
	C3	156.5	158.1
	C2	124.5	124.7
	C1	52.7	53.1
	C6	61.9	62.0
	C7	43.7	48.8
	C8	219.8	236.5



Scheme 2 Proposed mechanism of the reaction of **1** with HC≡CCH-(OH)R.

5.1 (C6*H*), 2.8 (C7*H*), and 0.7 (C7*H*) ppm) and ^{13}C{^{1}H} NMR spectrum (236.5 (C8), 167.4 (C4), 158.1 (C3), 124.7 (C2), 62.0 (C6), 53.1 (C1), and 48.8 (C7) ppm) are very close to those observed for complex **2**.

Similar to our previous reported mechanism for the formation of ten-membered ruthenacycles from ruthenium vinyl carbene,[6a] the formation of osmacycles **2** and **3** may also involve a [2 + 2] cycloaddition and 1,2-migration process. As shown in Scheme 2, coordination of the terminal alkyne to the metal center in **1** accompanied by the dissociation of the PPh_3 ligand could generate π-alkyne intermediate **A**. Then, [2 + 2] cycloaddition of the alkyne with the Os=C in **A** may lead to



Scheme 3 Reactions of **1** with phenylacetylenes.

the formation of the metallacyclobutene intermediate **B**, which could undergo cycloreversion to form the nine-membered intermediate **C**. The following activation of hydroxyl in **C** could produce the hydride intermediate **D**. Subsequent 1,2-hydrogen migration, reductive elimination, and coordination of the carbonyl group to metal center could yield the final metallacycle **2**/**3**. It is also possible that the proton on the oxygen may transfer to the carbene carbon without the intermediacy of the Os center. The mechanism shown in Scheme 2 is similar to that for our ten-membered ruthenacycle synthesis from ruthenium vinyl carbene and propargyl alcohols as demonstrated by deuterium labeling experiments.[6a] In this context, it should be mentioned that similar [2 + 2] cycloadditions of alkynes with carbene complexes have been described in literature.[7]

Reactions of osmapyridinium with phenylacetylenes

To further study the reactions of osmapyridinium complex **1** with terminal alkynes, we also investigated its reactivity with phenylacetylenes. As shown in Scheme 3, **1** can react with phenylacetylene to produce complex **4** as a yellow solid in 92% yield. Similarly, complex **5** was obtained in 91% yield from the reaction of **1** with a substituted phenylacetylene, *i.e.* 1-ethynyl-4-methoxybenzene (Scheme 3).

These two complexes have been characterized by NMR spectroscopy and elemental analysis. As shown in Table 3, the complexes **4** and **5** must have similar structures as indicated by the similarity in their NMR spectroscopic data. Fortunately, we were able to obtain a single crystal for **5**, enabling determination of its solid-state structure. The crystallographic details for **5** are given in Table 1. As shown in Fig. 2, **5** contains a substituted cyclopentadiene unit, which is η^4-coordinated to the

Table 3 Selected NMR spectroscopic data for **4**, **5**, **6**, **7** and **8**

	δ (^{1}H) (ppm)			δ (^{13}C) (ppm)					
Compound	NH	H1	H6	C4	C3	C2	C1	C6	C7
4	8.3	6.8	6.9	191.0	88.3	78.6	118.2	83.4	102.9
5	8.3	6.8	6.7	190.7	88.3	77.6	117.4	82.1	105.6
6	11.1	8.2	6.5	180.3	81.9	105.3	170.4	59.2	96.7
7	11.1	8.2	6.5	180.2	82.0	104.9	170.6	59.5	97.1
8	12.2	6.1	4.7	179.6	80.3	76.3	135.4	68.9	133.8

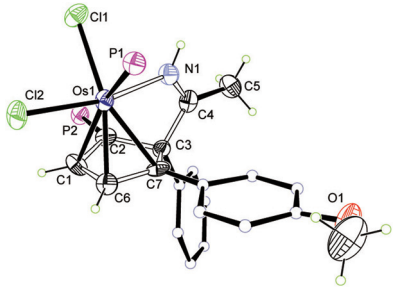
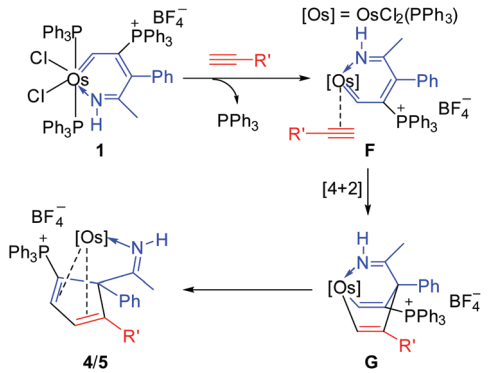


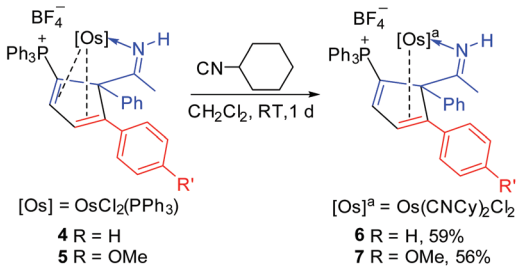
Fig. 2 X-ray structure of complex **5** (only the *R* enantiomer is shown, ellipsoids at the 50% probability level). Some of the hydrogen atoms, phenyl groups and the counteranion are omitted for clarity. Selected bond distances (Å) and angles (°): Os1–N1 2.054(7), Os1–C1 2.206(7), Os1–C2 2.264(7), Os1–C6 2.190(8), Os1–C7 2.307(7), C1–C2 1.395(10), C2–C3 1.595(11), C3–C7 1.577(10), C6–C7 1.419(10), C1–C6 1.424(11), N1–C4 1.258(10), C3–C4 1.520(11), C2–P2 1.805(8); C1–C2–C3 110.1(7), C2–C3–C7 95.4(5), C3–C7–C6 110.1(6), C7–C6–C1 109.1(6), C6–C1–C2 109.1(7), C4–N1–Os1 118.5(6), C3–C4–N1 108.2(7), C3–C4–C5 128.6(7), C2–C3–C4 107.3(6), C7–C3–C4 104.9(6).



Scheme 4 Proposed mechanism of the reactions of **1** with phenylacetylenes.

metal centre. The phenyl group and the imido group are located on the sp^3 carbon of the cyclopentadiene unit.

Based on the characterized structures, we postulate the reaction mechanism shown in Scheme 4 for the reaction of **1** with phenylacetylenes. The PPh_3 ligand in **1** could initially be displaced by phenylacetylene to give the π-alkyne complex **F**. Subsequent [4 + 2] cycloaddition of the osmium vinyl carbene fragment with the alkyne in **F** may lead to the formation of the metallacyclohexadiene intermediate **G**. Finally, **G** could undergo reductive elimination to generate complex **4**/**5** in which the cyclopentadiene is coordinated to the metal center as a ligand. It is interesting to note that, in our previous report, the osmafuran only underwent a head-to-tail double insertion of PhC≡CH to generate nine-membered osmacycles (Chart 1(a)).[5] We speculated that the difference may be attributed to the delocalized structure of the osmapyridinium **1**, which only shows a weak alternating double/single bond character around the metallacycle. A similar [4 + 2] cycloaddition process has been previously proposed in the reactions of



Scheme 5 Reactions of **4**/**5** with cyclohexyl isocyanide.

metallobenzenes with unsaturated substrates[8] and the reactions of alkenyl carbene complexes with alkynes or alkenes.[9] In the case of osmapyridinium **1** with HC≡CCH(OH)R, the [2 + 2] cycloaddition may be aided by the hydroxyl group, which helps stabilize the 16-electron intermediate.

Reactions of 4/5 with cyclohexyl isocyanide and 2,2′-bipyridine

The osmium complexes **4** and **5** are reactive towards strong ligands, such as isocyanides and bipyridines. As shown in Scheme 5, reactions of **4** and **5** with cyclohexyl isocyanide produce the ligand substitution products **6** and **7**, respectively. The structures of **6** and **7** can be assigned based on the NMR data. In particular, the NMR signals associated with the metallacycle are similar to those of the analogous cyclopentadiene complexes **4** and **5** (see Table 3). The different coordination mode of the substituted cyclopentadiene unit in **6** and **7** is supported by the chemical shifts of C1 and C2 in the ^{13}C NMR spectrum.

The structure of complex **6** was further confirmed by X-ray diffraction analysis (Fig. 3). As shown in Fig. 3 and Table 4, the structural parameters of complex **6** are similar to those of **5**. The two cyclohexyl isocyanide ligands are mutually *trans*, and the substituted cyclopentadiene fragment in **6** is η^2-coordinated to the metal centre. We think that the steric effect of the bulky phosphonium group would account for the observed regioselectivity.

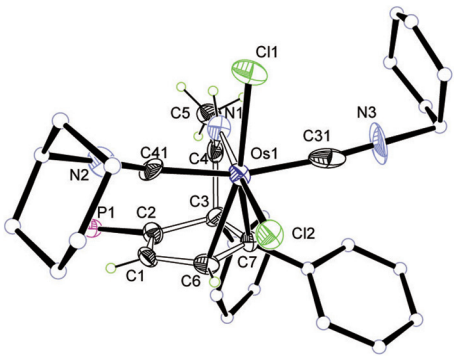
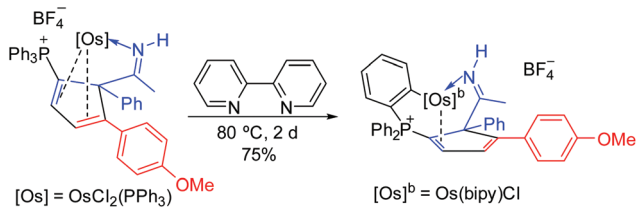


Fig. 3 X-ray structure of complex **6** (only the *R* enantiomer is shown, ellipsoids at the 50% probability level). Some of the hydrogen atoms, phenyl groups and the counteranion are omitted for clarity.

Table 4 Selected bond distances and angles for **6** and **8**

	6	8
Bond distances (Å)		
Os1–N1	2.020(6)	2.022(5)
N1–C4	1.280(9)	1.290(7)
C3–C4	1.546(10)	1.532(8)
C1–C2	1.360(10)	1.455(7)
C2–C3	1.552(10)	1.593(7)
C3–C7	1.602(9)	1.535(8)
C6–C7	1.412(10)	1.323(9)
C1–C6	1.454(9)	1.459(8)
Bond angles (°)		
Os1–N1–C4	125.6(5)	126.5(4)
N1–C4–C3	113.7(6)	113.1(5)
C4–C3–C2	103.4(5)	106.6(4)
C4–C3–C7	108.0(6)	103.4(5)
C1–C2–C3	109.9(6)	106.0(4)
C2–C3–C7	100.6(5)	101.5(4)
C3–C7–C6	108.2(6)	111.7(6)
C1–C6–C7	108.8(6)	111.9(5)
C2–C1–C6	112.3(6)	108.7(5)



Scheme 6 Reactions of **5** with 2,2′-bipyridine.

The reaction of **5** with 2,2′-bipyridine was also examined. Compound **8** could be readily obtained in 75% isolated yield by the reaction of **5** with 2,2′-bipyridine (Scheme 6). The complex has been characterized by NMR spectroscopy and elemental analysis. The structures of complexes **8** were assigned based on the fact that the NMR data associated with the complex are similar to those of **4**, **5**, **6** and **7**, as illustrated by the data shown in Table 3.

The structure of **8** has been confirmed by X-ray diffraction (Fig. 4). Like **6**, the cyclopentadiene ligand in **8** is also η^2-coordinated to osmium. The complex contains the 2,2′-bipyridine in the equatorial plane, and one of the phenyl groups of the phosphonium ligand bonded to the metal center which may derive from the C–H activation process. We have reported a similar oxidative addition of the phenyl C–H bond of PPh_3 which could give rise to tethered complexes.[10] In this case, the basicity of the 2,2′-bipyridine might facilitate the C–H activation of the phosphonium ligand. Thus, the reaction of **5** with pyridine under the above reaction conditions resulted in the formation of a similar tethered complex, as suggested by *in situ* NMR.

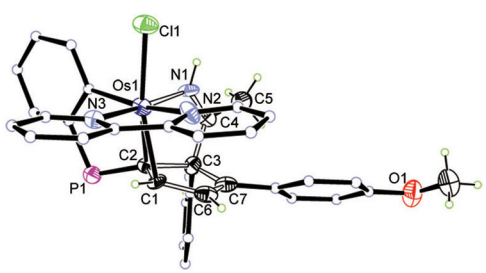


Fig. 4 X-ray structure of complex **8** (only the *R* enantiomer is shown, ellipsoids at the 50% probability level). Some of the hydrogen atoms, phenyl groups and the counteranion are omitted for clarity.

Conclusions

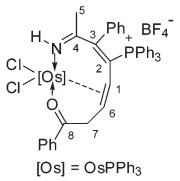
The reactions of osmapyridinium with terminal alkynes were studied, which led to the formation of new osmium complexes. For propargyl alcohols, the [2 + 2] cycloaddition and 1,2-hydrogen migration process was proposed for the formation of the final ten-membered osmacycles. For phenylacetylenes, η^4-coordinated cyclopentadiene complexes can be obtained, which may be attributed to a [4 + 2] cycloaddition process.

Experimental

General comments

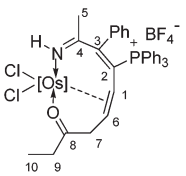
All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (diethyl ether) or calcium hydride (dichloromethane). Column chromatography was performed on neutral alumina gel (200–300 mesh) or silica gel (200–300 mesh). NMR experiments were performed on a Bruker AV-400 spectrometer (^{1}H 400.1 MHz; ^{13}C 101.6 MHz; ^{31}P 162.0 MHz) at room temperature unless otherwise stated. ^{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.

Preparation and characterization of complex 2. A solution of compound **1** (229 mg, 0.18 mmol) in CH_2ClCH_2Cl (30 mL) was heated under reflux for 5 h in the presence of 1-phenyl-2-propyn-1-ol (28 mg, 0.21 mmol). The solution was concentrated to about 3 mL. Subsequent addition of Et_2O (25 mL) gave a purple precipitate, which was washed with Et_2O (25 mL) and dried under vacuum. Yield: 140 mg, 68%.



^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 10.6 (s, 1 H, N*H*), 7.7–6.5 (39 H, other aromatic carbon atoms), 5.9 (dd, ^3J(P, H) = 9.6 Hz, ^3J(H, H) = 9.6 Hz, 1 H, H^1), 5.2 (m, 1 H, H^6), 3.5 (dd, ^2J(H, H) = 18.3 Hz, ^3J(H, H) = 6.0 Hz, 1 H, H^7), 1.8 (s, 3 H, H^5), 0.9 ppm (dd, ^2J(H, H) = 18.5 Hz, ^3J(H, H) = 8.2 Hz, 1 H, H^7). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ = 19.7 (s, C*P*Ph$_3$), −9.5 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (101.6 MHz, CD_2Cl_2, plus ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC and ^{13}C-dept 135): δ = 219.8 (s, C^8), 166.6 (d, ^3J(P, C) = 13.1 Hz, C^4), 156.5 (d, ^2J(P, C) = 14.9 Hz, C^3), 135.4–118.8 (other aromatic carbon atoms), 124.5 (d, ^1J(P, C) = 66.6 Hz, C^2), 61.9 (s, C^6), 52.7 (d, ^2J(P, C) = 10.0 Hz, C^1), 43.7 (s, C^7), 28.2 ppm (s, C^5). Elemental analysis calcd (%) for $C_{56}H_{48}Cl_2P_2BF_4NOOs$: C, 57.94; H, 4.17; N, 1.21. Found: C, 57.88; H, 4.08; N, 1.06.

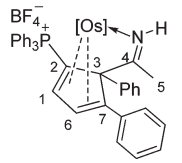
Preparation and characterization of complex 3. A solution of compound **1** (138 mg, 0.11 mmol) in CH_2ClCH_2Cl (30 mL) was heated under reflux for 5 h in the presence of 1-pentyn-3-ol (20 mg, 0.24 mmol). The solution was concentrated to about 3 mL. Subsequent addition of Et_2O (25 mL) gave a purple precipitate, which was washed with Et_2O (25 mL) and dried under vacuum. Yield: 65.4 mg, 55%.



3

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 10.5 (s,1 H, N*H*), 7.8–6.6 (35 H, other aromatic carbon atoms), 6.0 (dd, ^3J(P, H) = 10.0 Hz, ^3J(H, H) = 10.0 Hz, 1 H, H^1), 5.1 (m, 1 H, H^6), 2.8 (dd, ^2J(H, H) = 18.4 Hz, ^3J(H, H) = 4.1 Hz, 1 H, H^7), 2.5 (m, 2 H, H^9), 1.7 (s, 3 H, H^5), 1.0 (dd, ^3J(H, H) = 6.1 Hz, ^3J(H, H) = 6.1 Hz, 3 H, H^{10}), 0.7 ppm (dd, ^2J(H, H) = 18.6 Hz, ^3J(H, H) = 8.1 Hz, 1 H, H^7). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ = 19.0 (s, C*P*Ph$_3$), −10.7 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (101.6 MHz, $CDCl_3$, plus ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC and ^{13}C-dept 135): δ = 236.5 (s, C^8), 167.4 (d, ^3J(P, C) = 12.4 Hz, C^4), 158.1 (d, ^2J(P, C) = 15.0 Hz, C^3), 135.0–119.7 (other aromatic carbon atoms), 124.7 (d, ^1J(P, C) = 66.7 Hz, C^2), 62.0 (s, C^6), 53.1 (d, ^2J(P, C) = 10.2 Hz, C^1), 48.8 (s, C^7), 35.7 (s, C^9), 28.8 (s, C^5), 7.8 ppm (s, C^{10}). Elemental analysis calcd (%) for $C_{52}H_{48}Cl_2P_2BF_4NOOs$: C, 56.12; H, 4.35; N, 1.26. Found: C, 56.41; H, 4.65; N, 1.52.

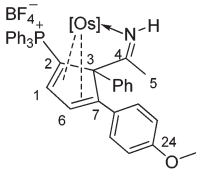
Preparation and characterization of complex 4. A solution of compound **1** (230 mg, 0.18 mmol) in CH_2ClCH_2Cl (30 mL) was heated under reflux for 2 h in the presence of phenylacetylene (200 mg, 1.9 mmol). The solution was concentrated to about 3 mL. Subsequent addition of Et_2O (25 mL) gave a yellow precipitate, which was washed with Et_2O (25 mL) and dried under vacuum. Yield: 186 mg, 92%.



4

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 8.3 (s,1 H, N*H*), 6. 9 (d, ^3J(H, H) = 2.8 Hz, 1 H, H^6), 6.8 (d, ^3J(H, H) = 2.8 Hz, 1 H, H^1), 7.8–7.1 and 6.8–6.3 (40 H, other aromatic carbon atoms), 1.5 ppm (s, 3 H, H^5). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ = 25.7 (s, C*P*Ph$_3$), −13.6 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (101.6 MHz, CD_2Cl_2, plus ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC and ^{13}C-dept 135): δ = 191.0 (s, C^4), 137.5–126.7 (other aromatic carbon atoms), 118.2 (dd, ^2J(P, C) = 12.6 Hz, ^2J(P, C) = 5.2 Hz, C^1), 102.9 (d, ^2J(P, C) = 10.0 Hz, C^7), 88.3 (d, ^2J(P, C) = 8.7 Hz, C^3), 83.4 (d, ^2J(P, C) = 9.6 Hz, C^6), 78.6 (dd, ^1J(P, C) = 71.6 Hz, ^2J(P, C) = 26.5 Hz, C^2), 26.0 ppm (s, C^5). Elemental analysis calcd (%) for $C_{55}H_{46}Cl_2P_2BF_4NOs$: C, 58.42; H, 4.10; N, 1.24. Found: C, 58.03; H, 4.53; N, 1.49.

Preparation and characterization of complex 5. A solution of compound **1** (500 mg, 0.39 mmol) in CH_2ClCH_2Cl (50 mL) was heated under reflux for 2 h in the presence of 4-ethynylanisole (510 mg, 3.9 mmol). The solution was concentrated to about 3 mL. Subsequent addition of Et_2O (30 mL) gave an orange precipitate, which was washed with Et_2O (30 mL) and dried under vacuum. Yield: 411 mg, 91%.

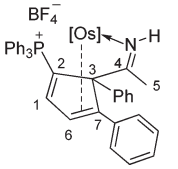


5

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 8.3 (s,1 H, N*H*), 6.8 (d, ^3J(H, H) = 2.6 Hz, 1 H, H^1), 6.7 (d, ^3J(H, H) = 2.6 Hz, 1 H, H^6), 7.7–7.0 and 6.6–6.3 (39 H, other aromatic carbon atoms), 3.7 (s, 3 H, OC*H*$_3$), 1.4 ppm (s, 3 H, H^5). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ = 25.9 (s, C*P*Ph$_3$), −13.1 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (101.6 MHz, CD_2Cl_2, plus ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC and ^{13}C-dept 135): δ = 190.7 (s, C^4), 159.3(s, C^{24}), 137.6–113.8 (other aromatic carbon atoms), 117.4 (dd, ^2J(P, C) = 13.9 Hz, ^2J(P, C) = 6.3 Hz, C^1), 105.6 (d, ^2J(P, C) = 10.1 Hz, C^7), 88.3 (d, ^2J(P, C) = 8.7 Hz, C^3), 82.1 (d, ^2J(P, C) = 9.9 Hz, C^6), 77.6 (dd, ^1J(P, C) = 71.9 Hz, ^2J(P, C) = 26.5 Hz, C^2), 54.7 (s, OCH_3), 26.1 ppm (s, C^5). Elemental analysis calcd (%) for $C_{56}H_{48}Cl_2P_2BF_4NOOs$: C, 57.94; H, 4.17; N, 1.21. Found: C, 58.04; H, 4.44; N, 1.25.

Preparation and characterization of complex 6. A solution of compound **4** (172 mg, 0.15 mmol) in DCM (30 mL) was stirred for 1 day in the presence of isocyanocyclohexane (80 mg, 0.73 mmol). The solution was concentrated to about 3 mL, Subsequent addition of Et_2O (25 mL) gave an orange precipi-

tate, which was washed with Et_2O (25 mL) and dried under vacuum. Yield: 97 mg, 59%.

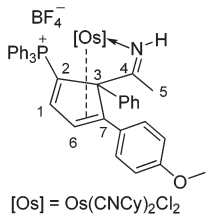


[Os] = $Os(CNCy)_2Cl_2$

6

^1H NMR (400.1 MHz, CD_2Cl_2): δ = 11.1 (s, 1 H, N*H*), 8.2 (dd, ^3J (H, H) = 10.1 Hz, ^3J(P, H) = 4.0 Hz, 1 H, H^1), 7.8–6.6 (20 H, other aromatic carbon atoms), 6.5 (br, 1 H, H^6), 3.8–3.4 (m, 2 H, C≡NC*H*), 2.0 (s, 3 H, H^5), 2.0–1.0 ppm (20 H, other alkyl carbon atoms). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): δ = 18.1 ppm (s, C*P*Ph_3). $^{13}C\{^1H\}$ NMR (101.6 MHz, CD_2Cl_2, plus ^1H–^{13}C HSQC and ^1H–^{13}C HMBC and ^{13}C-dept 135): δ = 180.3 (s, C^4), 170.4 (d, ^2J(P, C) = 11.3 Hz, C^1), 140.5–116.8 (other aromatic carbon atoms), 105.3 (d, ^1J(P, C) = 85.8 Hz, C^2), 96.7 (d, ^3J(P, C) = 6.9 Hz, C^7), 81.9 (d, ^2J(P, C) = 8.1 Hz, C^3), 59.2 (d, ^3J (P, C) = 16.2 Hz, C^6), 54.3 (s, CN*C*H), 52.8 (s, CN*C*H), 31.9–21.3 (other alkyl carbon atoms), 25.6 ppm (s, C^5). Elemental analysis calcd (%) for $C_{51}H_{52}Cl_2PBF_4N_3Os$: C, 56.41; H, 4.83; N, 3.87. Found: C, 56.80; H, 5.10; N, 3.76.

Preparation and characterization of complex 7. A solution of compound **5** (186 mg, 0.16 mmol) in DCM (30 mL) was stirred for 1 day in the presence of isocyanocyclohexane (88 mg, 0.81 mmol). The solution was concentrated to about 3 mL, subsequent addition of Et_2O (25 mL) gave an orange precipitate, which was washed with Et_2O (25 mL) and dried under vacuum. Yield: 100 mg, 56%.

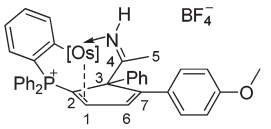


[Os] = $Os(CNCy)_2Cl_2$

7

^1H NMR (400.1 MHz, CD_2Cl_2): δ = 11.1 (s, 1 H, N*H*), 8.2 (dd, ^3J (H, H) = 10.2 Hz, ^3J(P, H) = 2.7 Hz, 1 H, H^1), 7.8–6.4 (19 H, other aromatic carbon atoms), 6.5 (br, 1 H, H^6), 3.8–3.5 (m, 2 H, C≡NC*H*), 3.6 (s, 3 H, OCH_3), 2.0 (s, 3 H, H^5), 1.9–1.1 ppm (20 H, other alkyl carbon atoms). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): δ = 18.0 ppm (s, C*P*Ph_3). $^{13}C\{^1H\}$ NMR (101.6 MHz, CD_2Cl_2, plus ^1H–^{13}C HSQC and ^1H–^{13}C HMBC and ^{13}C-dept 135): δ = 180.2 (s, C^4), 170.6 (d, ^2J(P, C) = 11.1 Hz, C^1), 157.2 (s, *C*N), 134.8–111.5 (other aromatic carbon atoms), 104.9 (d, ^1J(P, C) = 85.6 Hz, C^2), 97.1 (d, ^3J(P, C) = 7.5 Hz, C^7), 82.0 (d, ^2J(P, C) = 7.5 Hz, C^3), 59.5 (d, ^3J(P, C) = 16.2 Hz, C^6), 54.3 (s, OCH_3), 54.3 (s, CN*C*H), 31.9–21.3 (other alkyl carbon atoms), 25.6 ppm (s, C^5). Elemental analysis calcd (%) for $C_{52}H_{55}Cl_2PBF_4N_3OOs$: C, 55.92; H, 4.96; N, 3.76. Found: C, 55.99; H, 4.98; N, 3.48.

Preparation and characterization of complex 8. A solution of compound **5** (70 mg, 0.06 mmol) in CH_2ClCH_2Cl (30 mL) was heated under reflux for 2 day in the presence of 2,2′-dipyridyl (70 mg, 0.45 mmol). The solution was concentrated to about 3 mL, and then purified by column chromatography (silica gel, acetone) to give a red solution. The brown solid of **8** was collected after the solvent was evaporated to dryness under vacuum. Yield: 46 mg, 75%.



[Os] = Os(bipy)Cl

8

^1H NMR (400.1 MHz, DMSO-D6): δ = 12.2 (s,1 H, N*H*), 9.2–6.6 (31 H, other aromatic carbon atoms), 6.1 (s, 1 H, H^1), 4.7 (d, ^3J (H, H) = 8.2 Hz, 1 H, H^6), 3.7 (s, 3 H, OCH_3), 2.5 ppm (s, 3 H, H^5). $^{31}P\{^1H\}$ NMR (162.0 MHz, DMSO-D6): δ = 43.3 ppm (s, C*P*Ph_2). $^{13}C\{^1H\}$ NMR (101.6 MHz, DMSO-D6, plus ^1H–^{13}C HSQC and ^1H–^{13}C HMBC and ^{13}C-dept 135): δ = 179.6 (s, C^4), 171.4–114.4 (other aromatic carbon atoms), 135.4 (d, ^2J(P, C) = 4.4 Hz, C^1), 133.8 (s C^7), 80.3 (d, ^2J(P, C) = 12.3 Hz, C^3), 76.3 (d, ^1J(P, C) = 70.9 Hz, C^2), 68.9 (d, ^3J(P, C) = 3.8 Hz, C^6), 55.9 (s, O*C*H_3), 25.3 ppm (s, C^5). Elemental analysis calcd (%) for $C_{48}H_{40}ClPBF_4N_3OOs$: C, 56.61; H, 3.96; N, 4.13. Found: C, 56.84; H, 4.35; N, 3.88.

Crystallographic details

Single-crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD Area Detector or a Rigaku R-AXIS SPIDER IP CCD Area Detector with graphite-monochromated MoKa radiation (λ = 0.71073 Å). All of the data were corrected for absorption effects using the multi-scan technique. The structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F^2 using 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. For complexes **5**, **6** and **8**, the crystal suitable for X-ray diffraction was grown from a CH_2Cl_2 solution layered with hexane. For complex **2**, the crystal suitable for X-ray diffraction was grown from a $CHCl_3$ solution layered with hexane. Solvent molecules $CHCl_3$ in **2** are disordered and were refined with suitable restraints. Isocyanocyclohexane ligand molecules in **6** were refined isotropically using fixed C–C or C–N length. CCDC-1038534 (**2**), CCDC-1038533 (**5**), CCDC-1038537 (**6**), CCDC-1038535 (**8**), please see the supplementary crystallographic data for this paper.

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Notes and references

1 For recent reviews on the chemistry of metalloaromatics, see: (*a*) B. J. Frogley and L. J. Wright, *Coord. Chem. Rev.*, 2014, **270–271**, 151–166; (*b*) X.-Y. Cao, Q. Zhao, Z. Lin and H. Xia, *Acc. Chem. Res.*, 2014, **47**, 341–354; (*c*) C. Zhu, X. Cao and H. Xia, *Chin. J. Org. Chem.*, 2013, **33**, 657–662; (*d*) G. Jia, *Organometallics*, 2013, **32**, 6852–6866; (*e*) J. Chen and G. Jia, *Coord. Chem. Rev.*, 2013, **257**, 2491–2521; (*f*) J. Chen, G. He and G. Jia, *Chin. J. Org. Chem.*, 2013, **33**, 792–798; (*g*) A. F. Dalebrook and L. J. Wright, *Adv. Organomet. Chem.*, 2012, **60**, 93–177; (*h*) M. Paneque, M. L. Poveda and N. Rendón, *Eur. J. Inorg. Chem.*, 2011, 19–33; (*i*) A. T. Balaban, *Top. Heterocycl. Chem.*, 2009, **19**, 203–246; (*j*) G. Jia, *Coord. Chem. Rev.*, 2007, **251**, 2167–2187; (*k*) J. R. Bleeke, *Acc. Chem. Res.*, 2007, **40**, 1035–1047; (*l*) L. J. Wright, *Dalton Trans.*, 2006, 1821–1827; (*m*) C. W. Landorf and M. M. Haley, *Angew. Chem., Int. Ed.*, 2006, **45**, 3914–3936; (*n*) G. Jia, *Acc. Chem. Res.*, 2004, **37**, 479–486; (*o*) G. He, H. Xia and G. Jia, *Chin. Sci. Bull.*, 2004, **49**, 1543–1553; (*p*) J. R. Bleeke, *Chem. Rev.*, 2001, **101**, 1205–1227.

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