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Synthesis and Characterization of Osmium Polycyclic Aromatic Complexes via Nucleophilic Reactions of Osmapentalyne

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Treatment of osmapentalyne $[\mathrm{Os}\{\equiv\mathrm{C{-}C(COOMe){=}CH{-}C{=}CH{-}C(PPh_3){=}CH{-}}\}\mathrm{Cl(PPh_3)_2}]^+\ \mathrm{BF_4^-}$ with arylamines in the presence of Cs_2CO_3 produced osmium-bridged polycyclic aromatic complexes. In this reaction, metal carbyne of osmapentalyne was first attacked by nucleophiles, followed by a C−H oxidative addition. The UV-Vis spectra of these osmium-bridged polycyclic aromatic complexes were measured. The result shows that these osmium-bridged polycyclic aromatic complexes have broad absorption in the UV-Vis region up to 650 nm.

Keywords metallapentalyne, carbyne, aromaticity, nucleophilic, C−H activation

Introduction

In 1979, metallabenzene was proposed in theory by Thorn and Hoffmann as analogue of benzene, in which one of CH groups was replaced by anisolobal transition-metal fragment.[1] The first metallabenzene was isolated and characterized experimentally in 1982 by Roper and co-workers.[2] From then on, many metalla-aromatic complexes including metallabenzene,[3,4] metallabenzyne,[5] metallapyridine,[6] metallapyridyne,[7] metallapentalyne,[8] metallapentalene,[9] aza-metallapentalene,[10] and other metalla-aromatic complexes[11-13] were reported. Polycyclic aromatic compounds are very interesting molecules due to their highly conjugated system and being very useful in energy materials.[14] In contrast, the metal containing polycyclic aromatic complexes are still rare.[15]

Recently, we have reported that osmapentalyne **1** reacted with nucleophiles to give the first metal-bridged tricycle aromatic complexes, in which the metal center was shared by three aromatic five-membered rings.[15a] Herein, we further explore the reactivities of osmapentalyne **1** with other nucleophiles. A series of osmium-bridged polycyclic aromatic derivatives were synthesized and characterized *via* nucleophilic reaction and subsequent C−H activation reaction.

Results and Discussion

Reactions of osmapentalyne 1 with aniline and 1-aminopyrene

Recently, we have prepared osmapentalyne **1** with high strain in the five-membered ring due to the small angle (131.2°) of Os−C−C.[8] Therefore, the carbon of metal carbyne in osmapentalyne **1** is expected to be attacked easily by nucleophiles, which is a typical nucleophilic reaction for metal carbyne complexes. Keeping this in mind, we first tried to treat osmapentalyne **1** with a nucleophilic $PhNH^-$ generated *in situ* from aniline in the presence of Cs_2CO_3. Interestingly, an osmium-bridged polycyclic aromatic complex **2** was formed (Scheme 1) via the expected nucleophilic reaction, followed by an unexpected C−H oxidative addition on the osmium center.

Complex **2** has been characterized by X-ray diffraction analysis, multi-nuclear magnetic resonance (NMR) and high-resolution mass spectrometry (HRMS). As shown in Figure 1, complex **2** contains two axial PPh_3 bound to osmium center. The osmium center of complex **2** is seven-coordinated in pentagonal bipyramid geometry and is shared by three fused five-membered rings. Four rings (constituted by Os1, N1, and C1−C13) are almost coplanar, as reflected by the small

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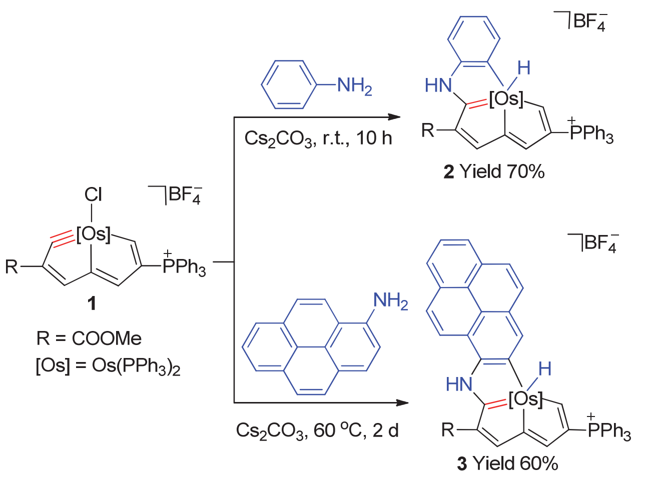
In Memory of Professor Enze Min.

Scheme 1 Preparation of complexes **2** and **3**



mean deviation from the least-squares plane (0.0422 Å). The sums of angles in the three osmium-bridged five-membered rings are 539.9°, 539.7°, and 539.8°, which are close to the ideal value of 540°. All of the lengths for the osmium-carbon bonds (1.999—2.175 Å) in **2** are within the range of Os—C single and double-bond lengths, which indicates complex **2** has a delocalized structure.

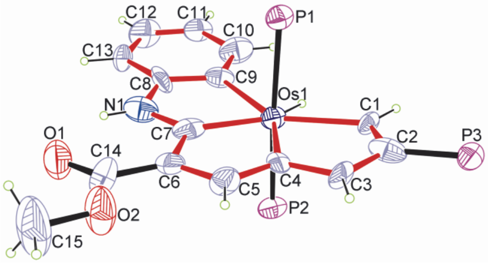


Figure 1 Molecular structure for the cation of **2** drawing with thermal ellipsoids at 50% probability level. The phenyl moieties in PPh$_3$ are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1—C1 2.175(8), Os1—C4 2.083(10), Os1—C7 1.999(12), Os1—C9 2.151(9), C1—C2 1.347(14), C2—C3 1.389(15), C3—C4 1.450(12), C4—C5 1.369(14), C5—C6 1.390(13), C6—C7 1.457(15), C7—N1 1.400(12), N1—C8 1.427(14), C8—C9 1.371(15); Os1—C1—C2 116.6(8), C3—C4—Os1 120.0(7), C4—Os1—C1 73.8(4), Os1—C4—C5 122.2(7), C6—C7—Os1 123.8(7), C7—Os1—C4 71.9(4), Os1—C7—N1 123.0(9), C8—C9—Os1 116.1(8).

Consistent with the solid state structure, the ^{1}H NMR spectrum of complex **2** shows characteristic Os—H and Os=C—H signals at δ –3.51 (td, J_{PH}=16.2, 6.4 Hz) and 11.63 (t, J_{PH}=15.4 Hz), respectively. In the ^{13}C{^{1}H} NMR spectrum, signals at δ 229.3, 196.9, 195.9 and 143.6 are assigned to C7, C1, C4 and C9, respectively. The ^{31}P{^{1}H} NMR spectrum shows two singlets at δ 12.43, which is assigned to the phosphorus of CPPh$_3$ phosphonium unit, and δ 2.35, which is assigned to the phosphorus directly coordinated to osmium center.

It is known that the nucleophilic reaction of metallabenzyne with HO$^-$ gives a metallabenzene intermediate following a migratory insertion to give η^5-complex with low valence metal center.[5e] Our example provides a new organometallic tandem reaction, which can be used to construct high valence polycyclic metalla-aromatic complex. Following this direction, we next attempt to prepare nanographene-like complex by using 1-aminopyrene as starting material.

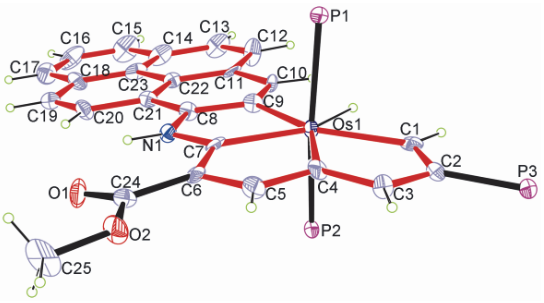


Figure 2 Molecular structure for the cation of **3** drawing with thermal ellipsoids at 50% probability level. The phenyl moieties in PPh$_3$ are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1—C1 2.084(5), Os1—C4 2.127(5), Os1—C7 2.048(5), Os1—C9 2.156(5), C1—C2 1.362(6), C2—C3 1.410(7), C3—C4 1.370(7), C4—C5 1.426(7), C5—C6 1.386(7), C6—C7 1.451(7), C7—N1 1.337(6), N1—C8 1.397(6), C8—C9 1.415(7); Os1—C1—C2 120.3(4), C3—C4—Os1 119.3(4), C4—Os1—C1 73.05(19), Os1—C4—C5 118.9(4), C6—C7—Os1 122.0(4), C7—Os1—C4 73.5(2), Os1—C7—N1 120.9(4), C8—C9—Os1 115.3(3), C9—Os1—C7 74.46(19).

Treatment of osmapentalyne **1** with 1-aminopyrene gives complex **3**, which contains up to seven fused aromatic rings (Scheme 1). Complex **3** has been also characterized by X-ray diffraction analysis, multinuclear NMR and HRMS. As shown in Figure 2, the coordination mode of osmium in **3** is similar to that in complex **2**. The ^{1}H NMR spectrum of complex **3** shows characteristic Os—H and Os=C—H signals at δ –2.90 (td, J_{PH}=16.9 Hz, J_{PH}=13.7 Hz) and 11.96 (t, J_{PH}=15.7 Hz) respectively, which are similar to those of complex **2**.

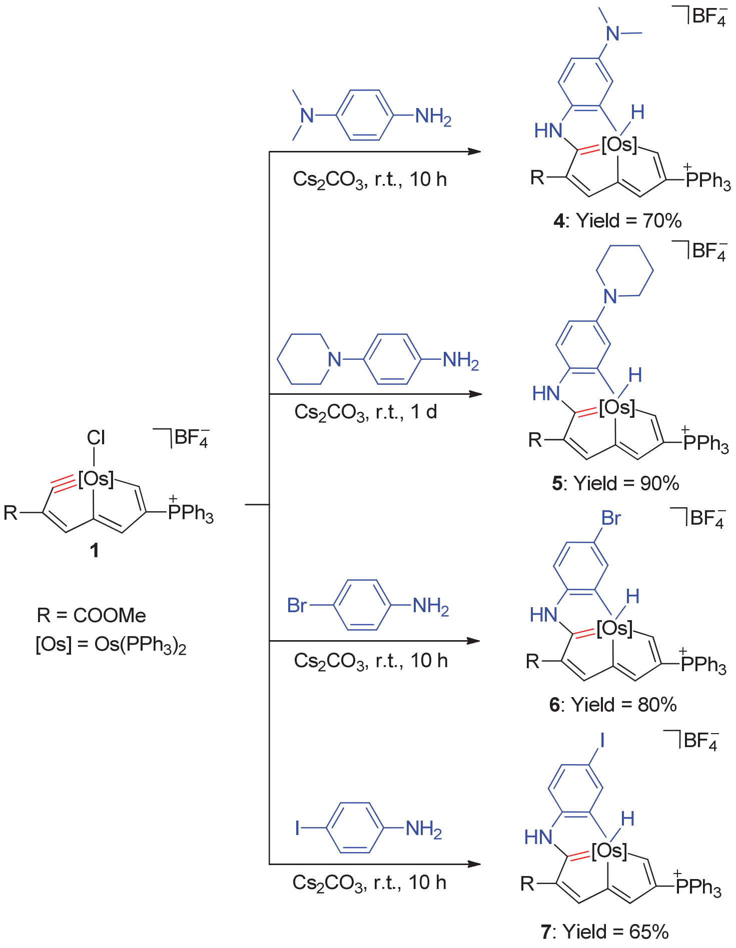
Complex **3** is interesting as its organic counterpart can be viewed as a small graphene-like compound, which is a useful energy material in recent years. The osmium and nitrogen doped complex **3** is also expected to be a useful material and applied in this area.

Reactions of osmapentalyne 1 with other arylamines

After the successful preparation of complex **3**, we then move to prepare other polycyclic metallaaromatic complexes with other arylamines. Treatment of osmapentalyne **1** with *N*,*N*-dimethylbenzene-1,4-diamine, 4-(1-piperidino)aniline, 4-bromoaniline and 4-iodoaniline in the presence of Cs$_2$CO$_3$ can also give corresponding complexes **4**—**7** in the yields of 65%—90% (Scheme 2).

For complex **4**, it has been also characterized by X-ray diffraction analysis, multinuclear NMR and

Scheme 2 Synthesis of complexes **4**—**7**



HRMS. The structure is similar to that of complex **2** except that it contains an electron donating group of NMe_2. As shown in Figure 3, the Os—C bond lengths [Os1—C1 (2.077 Å), Os1—C4 (2.105 Å), and Os1—C7 (2.085 Å)] are all in the range of those in osmapentalene (1.926—2.139 Å).[9c] The C—C bond lengths (1.354—1.433 Å) of the fused four rings are between C—C and C=C bond lengths. Thus, the structure is also delocalized.

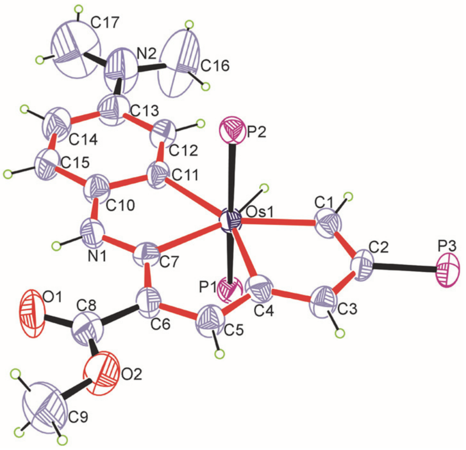


Figure 3 Molecular structure for the cation of **4** drawing with thermal ellipsoids at 50% probability level. The phenyl moieties in PPh_3 are omitted for clarity.

The structures of **4**—**7** can be readily assigned on the basis of the NMR data. In particular, the $^{31}P\{^1H\}$ NMR spectrum shows two singlets at δ 12.30 and 3.04 for complex **4**, at δ 12.63 and 2.83 for complex **5**, at δ 12.47 and 2.56 for complex **6**, at δ 12.53 and 2.49 for complex **7**. The characteristic Os—H and Os=C—H signals in the ^1H NMR spectrum are located at δ –3.53 and 11.69 for complex **4**, –3.53 and 11.73 for complex **5**, –3.40 and 11.87 for complex **6**, –3.43 and 11.86 for complex **7**.

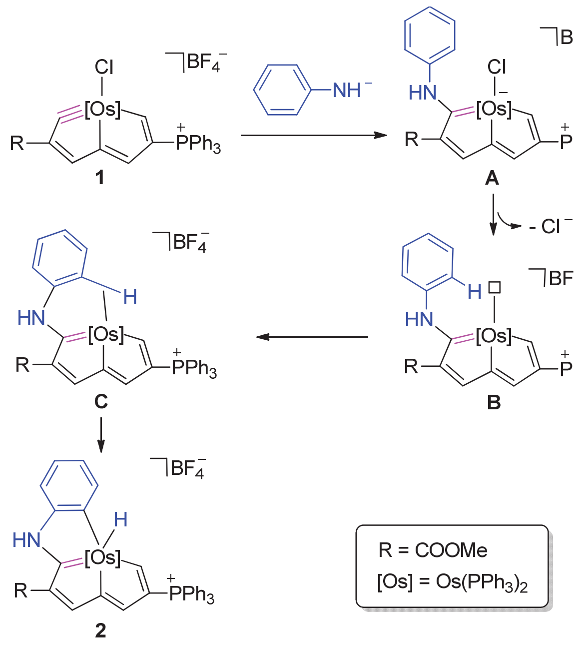
Proposed reaction mechanism

Scheme 3 shows a plausible mechanism for the formation of complex **2** from osmapentalyne **1**. In the presence of Cs_2CO_3, $PhNH^-$ can be generated *in situ* from aniline and attack the carbon of carbyne in osmapentalyne **1**, which can release the high strain in osmapentalyne **1** to give **A**. The Cl ligand of **A** dissociates to produce **B**. **B** contains a coordinate vacant site and undergoes the oxidative addition of C—H to give complex **2** eventually via the agostic intermediate **C**.

Spectroscopic properties

The UV-Vis absorption spectra of these interesting osmium-bridged polycyclic aromatics **2**—**7** are summa-

Scheme 3 A plausible mechanism for the formation of complex **2** from osmapentalyne **1**



rized in Figure 4. The absorption maxima of **2**—**7** in the visible region are 528 nm (complex **2**, log ε=3.81, ε: molar extinction coefficient in L•mol^{-1}•cm^{-1}), 557 nm (complex **3**, log ε=4.06), 556 nm (complex **4**, log ε=5.81), 542 nm (complex **5**, log ε=3.83), 520 nm (complex **6**, log ε=3.84), and 522 nm (complex **7**, log ε=3.69), respectively.

Obviously, the electron donating groups cause the red shift of absorption maximum in the visible region (*ca.* 28 nm, complex **4** *v.s.* complex **2**, Figure 4A), while the electron withdrawing groups cause the slight blue shift of absorption maximum in the visible region (*ca.* 8 nm, complex **6** *v.s.* complex **2**, Figure 4B). Thus, it makes our synthetic method to prepare osmium-bridged polycyclic aromatics as materials more designable. When the moiety of arylamine is pyrene, it causes the red-shift of absorption maximum in the visible region about 29 nm from complex **2** (Figure 4C), which indicates the metalla-nanographene complex is the most interesting complex.

Conclusions

We have investigate the nucleophilic reactions of osmapentalyne complex $[Os\{\equiv C-C(COOMe)=CH-C=CH-C(PPh_3)=CH-\}Cl(PPh_3)_2]^+ BF_4^-$ with arylamines in the presence of Cs_2CO_3. The nucleophilic reactions give osmium-bridged polycyclic aromatic complexes. We proposed that an arene C—H oxidative addition on the osmium metal center occurs after the attack of nucleophiles at carbon of metal carbyne. This synthetic strategy released here provides a possible route for the construction of large polycyclic metalla-aromatics or even metalla-nanographene.

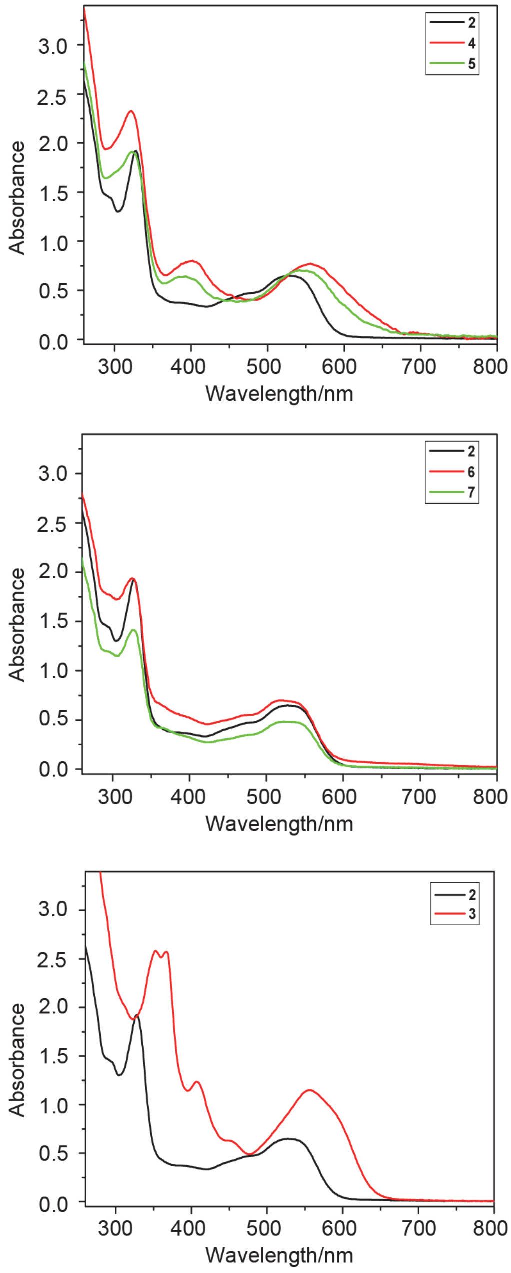


Figure 4 UV-Vis absorption spectra of **2**, **3**, **4**, **5**, **6** and **7** (1.0×10^{-4} mol•L^{-1}) measured in CH_2Cl_2 at room temperature.

Experimental

General comments

All syntheses were carried out under an inert atmosphere (N_2) by means of standard Schlenk techniques, unless otherwise stated. Solvents were distilled from sodium/benzophenone (hexane) or calcium hydride (dichloromethane and chloroform) under N_2 prior to use. The starting material, complex **1**, was synthesized according to the previously published procedure.[8a] Other reagents were used as received from commercial sources without further purification. Column chromatography was performed on alumina gel (200—300 mesh) in air. NMR spectroscopic experiments were performed on a Bruker AV-400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{31}P, 162.0 MHz) spectrometer, or a Bruker AV-500 (^{1}H, 500.2 MHz; ^{13}C, 125.8 MHz; ^{31}P, 202.5 MHz) spectrometer at room temperature. ^{1}H and ^{13}C NMR chemical shifts are relative to tetramethylsilane, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. The absolute values of the coupling constants are given in Hertz (Hz). High resolution mass spectra (HRMS) experiments were recorded on a Bruker En Apex Ultra 7.0T FT-MS.

Complex 2 A mixture of **1** (200 mg, 0.16 mmol), aniline (30 mg, 0.32 mmol) and Cs_2CO_3 (521 mg, 1.6 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature (r.t.) for 10 h and then the solid suspension was removed through a filter. The filtrate was concentrated to *ca.* 2 mL and then purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone=1：1) to give a red solution. The red solid of **2** (146 mg, 70%) was collected after the solvent was evaporated to dryness under vacuum. ^{1}H NMR plus ^{1}H-^{13}C HSQC (500 MHz, $CDCl_3$) δ: 11.63 (t, J_{PH}=15.4 Hz, 1H, H1), 11.26 (s, 1H, NH), 9.06 (s, 1H, H5), 8.19 (s, 1H, H3), 3.81 (s, 3H, $COOCH_3$), –3.51 (td, J_{PH}=16.2 Hz, J_{PH}=6.4 Hz, 1H, Os—H), 7.66—6.17 (m, 49H, other aromatic protons); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 12.43 (s, $CPPh_3$), 2.35 (s, $OsPPh_3$); ^{13}C NMR plus DEPT-135 and ^{1}H-^{13}C HSQC (126 MHz, $CDCl_3$) δ: 229.3 (t, J_{PC}=6.0 Hz, C7), 196.9 (t, J_{PC}=10.0 Hz, C1), 195.9 (dt, J_{PC}=28.7, 2.7 Hz, C4), 168.4 (s, C5), 166.1 (s, $COOCH_3$, confirmed by ^{1}H-^{13}C HMBC), 156.1 (s, C6), 148.0 (d, J_{PC}=24.6 Hz, C3), 143.6 (t, J_{PC}=10.8 Hz, C9), 136.3 (s, C8), 120.6 (d, J_{PC}=87.4 Hz, C2), 51.7 (s, $COOCH_3$), 148.9—114.6 (m, other aromatic carbon atoms); HRMS (ESI) calcd for $[C_{69}H_{57}NO_2OsP_3]^+$ 1216.3211; found 1216.3214.

Complex 3 A mixture of **1** (200 mg, 0.16 mmol), 1-aminopyrene (69 mg, 0.32 mmol) and Cs_2CO_3 (521 mg, 1.6 mmol) in CH_2Cl_2 (10 mL) was stirred at 60 ℃ for 2 d and then the solid suspension was removed through a filter. The filtrate was concentrated to *ca.* 2 mL and then purified by column chromatography (neutral alumina, eluent: acetone) to give a purple solution. The purple solid of **3** (137 mg, 60%) was collected after the solvent was evaporated to dryness under vacuum. ^{1}H NMR plus ^{1}H-^{13}C HSQC (500 MHz, $CDCl_3$) δ: 12.49 (s, 1H, NH), 11.96 (t, J_{PH}=15.7 Hz, 1H, H1), 9.28 (s, 1H, H5), 8.48 (s, 1H, H3), 3.98 (s, 3H, $COOCH_3$), –2.90 (td, J_{PH}=16.9, 13.7 Hz, 1H, Os—H), 8.16—6.77 (m, 53H, other aromatic protons); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 12.91 (s, $CPPh_3$), 1.91 (s, $OsPPh_3$); ^{13}C NMR plus DEPT-135 and ^{1}H-^{13}C HSQC (126 MHz, $CDCl_3$) δ: 228.7 (t, J_{PC}=6.1 Hz, C7), 197.6 (br, C1), 195.9 (d, J_{PC}=28.7 Hz, C4), 168.3 (s, C5), 166.6 (s, $COOCH_3$, confirmed by ^{1}H-^{13}C HMBC), 150.2 (s, C6), 149.0 (d, J_{PC}=24.3 Hz, C3), 143.7 (t, J_{PC}=10.1 Hz, C9), 136.7 (s, C8), 120.7 (d, J_{PC}=87.6 Hz, C2), 51.9 (s, $COOCH_3$), 146.1—117.8 (m, other aromatic carbon atoms). HRMS (ESI) *m*/*z*: calcd for $[C_{79}H_{61}NO_2OsP_3]^+$ 1340.3534; found 1340.3532.

Complex 4 A mixture of **1** (200 mg, 0.16 mmol), *N*,*N*-dimethylphenylene-1,4-diamine (44 mg, 0.32 mmol) and Cs_2CO_3 (521 mg, 1.6 mmol) in CH_2Cl_2 (10 mL) was stirred at r.t. for 10 h and then the solid suspension was removed through a filter. The filtrate was concentrated to *ca.* 2 mL and then purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone=5：1) to give a purple solution. The purple solid of **4** (150 mg, 70%) was collected after the solvent was evaporated to dryness under vacuum. ^{1}H NMR plus ^{1}H-^{13}C HMQC (500 MHz, $CDCl_3$) δ: 11.69 (t, J_{PH}=15.4 Hz, 1H, H1), 11.20 (s, 1H, NH), 9.12 (s, 1H, H5), 8.30 (s, 1H, H3), 3.92 (s, 3H, $COOCH_3$), 2.56 (s, 6H, $N(CH_3)_2$), –3.53 (td apparent q, J_{PH} = 13.5 Hz, Os-H), 7.75—6.29 (m, 48H, other aromatic protons). ^{31}P NMR (202 MHz, $CDCl_3$) δ: 12.30 (s, $CPPh_3$), 3.04 (s, $OsPPh_3$); ^{13}C NMR plus DEPT-135 and ^{1}H-^{13}C HSQC (126 MHz, $CDCl_3$) δ: 224.5 (m, C7), 196.5 (m, C1), 195.4 (d, J_{PC}=28.8 Hz, C4), 167.2 (s, C5), 166.1 (s, $COOCH_3$, confirmed by ^{1}H-^{13}C HMBC), 147.3 (d, J_{PC}=25.1 Hz, C3), 136.2 (s, C6), 120.9 (d, J_{PC}=86.9 Hz, C2), 52.2 (s, $COOCH_3$), 41.5 (s, $N(CH_3)_2$), 147.4—110.0 (m, other aromatic carbon atoms). HRMS (ESI) *m*/*z*: calcd for $[C_{71}H_{62}N_2O_2OsP_3]^+$ 1259.3639, found 1259.3637.

Complex 5 A mixture of **1** (200 mg, 0.16 mmol), 4-(1-piperidino)aniline (56 mg, 0.32 mmol) and Cs_2CO_3 (521 mg, 1.6 mmol) in CH_2Cl_2 (10 mL) was stirred at r.t. for 1 d and then the solid suspension was removed through a filter. The filtrate was concentrated to *ca.* 2 mL and then purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone=10：1) to give a purple solution. The purple solid of **5** (200 mg, 90%) was collected after the solvent was evaporated to dryness under vacuum. ^{1}H NMR plus ^{1}H-^{13}C HMQC (500 MHz, $CDCl_3$) δ: 11.73 (t, J_{PH}=15.9 Hz, 1H, H1), 11.20 (s, 1H, NH), 9.12 (s, 1H, H5), 8.35 (s, 1H, H3), 3.90 (s, 3H, $COOCH_3$), –3.53 (td apparent q, J_{PH}=13.8 Hz, Os-H), 7.75—6.35 (m, 48H, other aromatic protons). ^{31}P NMR (202 MHz, $CDCl_3$) δ: 12.63 (s, $CPPh_3$), 2.83 (s, $OsPPh_3$); ^{13}C NMR plus DEPT-135 and ^{1}H-^{13}C HSQC (126 MHz, $CDCl_3$) δ: 225.9 (m, C7), 196.5 (m, C1), 195.3 (dt, J_{PC}=28.8, 3.1 Hz, C4), 167.4 (s, C5), 166.1 (s, $COOCH_3$, confirmed by ^{1}H-^{13}C HMBC), 147.6 (d, J_{PC}=24.1 Hz, C3), 136.2 (s, C6), 120.8 (d, J_{PC}=87.2 Hz, C2), 51.6 (s, $COOCH_3$), 150.4—114.7 (m, other aromatic carbon atoms). HRMS (ESI) *m*/*z*: calcd for $[C_{74}H_{66}N_2O_2OsP_3]^+$ 1299.3952, found 1299.3949.

Complex 6 A mixture of **1** (200 mg, 0.16 mmol), 4-bromoaniline (55 mg, 0.32 mmol) and Cs_2CO_3 (521 mg, 1.6 mmol) in CH_2Cl_2 (10 mL) was stirred at r.t. for 10 h and then the solid suspension was removed through a filter. The filtrate was concentrated to *ca.* 2 mL and then purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone=6：1) to give a red solution. The red solid of **6** (170 mg, 80%) was collected after the solvent was evaporated to dryness under vacuum. ^{1}H NMR plus ^{1}H-^{13}C HMQC (400 MHz,

$CDCl_3$) δ: 11.87 (t, $J_{PH}=15.2$ Hz, 1H, H1), 11.70 (s, 1H, NH), 9.33 (s, 1H, H5), 8.59 (s, 1H, H3), 3.92 (s, 3H, $COOCH_3$), –3.40 (td apparent q, $J_{PH}=13.5$ Hz, Os—H), 7.94—6.47 (m, 48H, other aromatic protons); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 12.47 (s, $CPPh_3$), 2.56 (s, $OsPPh_3$); ^{13}C NMR plus DEPT-135 and ^{1}H-^{13}C HSQC (100 MHz, $CDCl_3$) δ: 230.1 (t, $J_{PC}=5.4$ Hz, C7), 197.5 (t, $J_{PC}=10.9$ Hz, C1), 196.1 (dt, $J_{PC}=27.9$ Hz, $J_{PC}=3.0$ Hz, C4), 169.2 (s, C5), 166.6 (s, $COOCH_3$, confirmed by ^{1}H-^{13}C HMBC), 155.1 (s, C6), 149.0 (d, $J_{PC}=10.6$ Hz, C9), 148.7 (d, $J_{PC}=24.6$ Hz, C3) 136.7 (s, C8), 120.7 (d, $J_{PC}=87.3$ Hz, C2), 51.6 (s, $COOCH_3$), 150.4—115.7 (m, other aromatic carbon atoms). HRMS (ESI) calcd for $[C_{69}H_{56}BrNO_2OsP_3]^+$ 1294.2322, found 1294.2334.

Complex 7 A mixture of **1** (200 mg, 0.16 mmol), 4-iodoaniline (70 mg, 0.32 mmol) and Cs_2CO_3 (521 mg, 1.6 mmol) in CH_2Cl_2 (10 mL) was stirred at r.t. for 10 h and then the solid suspension was removed through a filter. The filtrate was concentrated to *ca.* 2 mL and then purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone＝4：1) to give a red solution. The red solid of **7** (143 mg, 65%) was collected after the solvent was evaporated to dryness under vacuum. ^{1}H NMR plus ^{1}H-^{13}C HMQC (400 MHz, $CDCl_3$) δ: 11.86 (t, $J_{PH}=14.8$ Hz, 1H, H1), 11.67 (s, 1H, NH), 9.28 (s, 1H, H5), 8.56 (s, 1H, H3), 3.92 (s, 3H, $COOCH_3$), –3.43 (td apparent q, $J_{PH} = 12.6$ Hz, Os-H), 7.94—6.38 (m, 48H, other aromatic protons); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 12.53 (s, $CPPh_3$), 2.49 (s, $OsPPh_3$); ^{13}C NMR plus DEPT-135 and ^{1}H-^{13}C HSQC (100 MHz, $CDCl_3$) δ: 230.4 (m, C7), 197.6 (t, $J_{PC}=10.5$ Hz, C1), 196.8 (d, $J_{PC}=28.0$ Hz, C4), 168.9 (s, C5), 166.5 (s, $COOCH_3$, confirmed by ^{1}H-^{13}C HMBC), 155.6 (s, C6), 149.7 (t, $J_{PC}=9.5$ Hz), 148.4 (d, $J_{PC}=23.9$ Hz, C3), 136.7 (s, C8), 120.7 (d, $J_{PC}=87.6$ Hz, C2), 52.2 (s, $COOCH_3$), 155.5—116.3 (m, other aromatic carbon atoms). HRMS (ESI) calcd for $[C_{69}H_{56}INO_2OsP_3]^+$ 1342.2183; found 1342.2190.

X-ray crystallography

All single crystals suitable for X-ray diffraction were grown from chloroform solution layered with hexane. Diffraction data were collected on a Rigaku R-AXIS SPIDER IP CCD area detector for **2** and on an Oxford Gemini S Ultra CCD area detector for **3** and **4** using graphite-monochromated Mo Kα radiation ($\lambda=0.71073$ Å). Semi-empirical or multi-scan absorption corrections (SADABS) were applied.[18] All structures were solved by the Patterson function, completed by subsequent difference Fourier map calculations, and refined by full matrix least-squares on F^2 using the SHELXTL program package.[19] All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model. CCDC 982358 (**2**), CCDC 982359 (**3**), and CCDC 1416207 (**4**) contain 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.

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