Supporting Information belonging to the Manuscript entitled:

Mono and Dinuclear Osmium *N,N'*-Di- and Tetraphenylbipyridyls and Extended Bipyridyls. Synthesis, Structure and Electrochemistry

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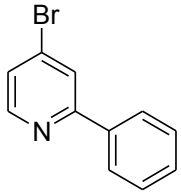
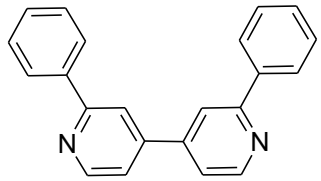
Experimental Section

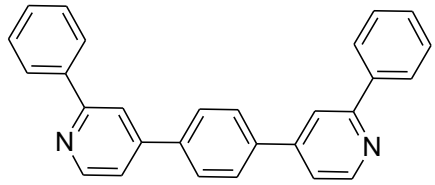
General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Flame-dried glassware was used for moisture-sensitive reactions. Solvents (toluene and chloroform that were dried and distilled under argon) were obtained oxygen- and water-free from an MBraun or Pure Solvent PS-MD-5 solvent purification apparatuses. Diisopropylamine was dried and distilled over CaH_2 under argon. Zinc powder was washed successively with 20% hydrochloric acid, water, ethanol, acetone and diethyl ether. Silica gel (Merck: 230-400 mesh) was used as stationary phase for purification of crude reaction mixtures by flash column chromatography. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Gemini 2000, Bruker ARX 300 MHz, Bruker Avance 300 MHz, Bruker Avance 400 MHz or Bruker Avance 500 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) or to external 85 % H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants *J* and *N* are given in hertz. Infrared spectra were recorded on a MIR (8000-400 cm^{-1}) or Perkin-Elmer Spectrum 100 spectrometer as solid films obtained by slow evaporation of the solvent or neat solids using the attenuated total reflectance (ATR) technique. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (BrukerDaltonics, Bremen, Germany). Commercially available reagents were used as received without further purification. 4-Bromo-2-phenylpyridine (**1**),[1] 4-chloro-2,6-diphenylpyridine (**7**)[2] and $OsH_6(P^iPr_3)_2$ (**9**)[3] were prepared as previously described.



4-Bromo-2-phenylpyridine (1). Colorless oil. IR ($CHCl_3$, cm^{-1}): ν(Carom-H) 3042; ν(C=C), ν(C=N) 1566, 1544. ^1H NMR (300MHz, $CDCl_3$, 293K): δ 8.52 (d, J_{H-H} = 5.3, 1H, C*H*-arom), 7.98 (dd, J_{H-H} = 8.0, 1.6, 2H, C*H*-arom), 7.97 (d, J_{H-H} = 1.6, 1H, C*H*-arom), 7.53-7.40 (m, 4H, C*H*-arom). $^{13}C\{^1H\}$ NMR (75.56 MHz, $CDCl_3$, 293K): δ 158.9, 138.0, 133.5 (all s, C_{ipso}), 150.3, 129.6, 128.8, 127.0, 125.2, 123.9 (all s, *C*H-arom).

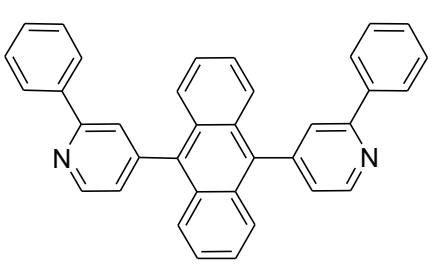


2,2´-diphenyl-4,4´-bipyridine (2). To a solution of $NiBr_2(PPh_3)_2$ (689 mg, 0.93 mmol) in 20 mL of dry tetrahydrofuran was added zinc powder (303 mg, 4.63 mmol) and Et_4NI (795 mg, 3.09 mmol). The mixture was stirred at room temperature for 30 min under argon. A solution of 4-bromo-2-phenylpyridine (**1**) (723 mg, 3.09 mmol) in 7 mL of dry tetrahydrofuran was added dropwise, and the resulting mixture was heated at 50ºC for 36 h. The reaction mixture was poured into 100 mL of 2M aqueous ammonia and diethyl ether (50 mL), and 50 mL of benzene were added. The precipitates were filtered and the organic layer separated. The aqueous layer was extracted with ethyl acetate/benzene (1:1). The combined organic layers were washed successively with water and brine, dried with anhydrous $MgSO_4$, and evaporated in vacuo. After purification by flash column chromatography (dichloromethane) 2,2´-diphenyl-4,4´-bipyridine (**2**) was obtained as white solid. Yield 409 mg (43%); mp 115.5-116.5ºC. HRMS-ESI$^+$ $(M+Na)^+$ calcd. for $C_{22}H_{16}N_2Na$: 331.1211. Found: 331.1207. IR ($CHCl_3$, cm^{-1}): ν(Carom-H) 3030; ν(C=C), ν(C=N) 1591, 1533. ^1H NMR (300MHz, $CDCl_3$, 293K): δ 8.85 (dd, J_{H-H} = 5.1, 0.7, 2H, C*H*-arom), 8.10-8.07 (m, 4H, C*H*-arom), 8.00 (dd, J_{H-H} = 1.6, 0.8, 2H, C*H*-arom), 7.57-7.48 (m, 8H, C*H*-arom). $^{13}C\{^1H\}$ NMR (75.56 MHz, $CDCl_3$, 293K): δ 158.5, 146.8, 138.9 (all s, C_{ipso}), 150.4, 129.3, 128.8, 127.0, 119.9, 118.4 (all s, *C*H-arom).

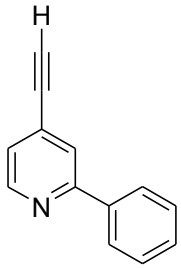


2-phenyl-4-(4-(2-phenylpyridin-4-yl)phenyl)pyridine (3). To a solution of 4-bromo-2-phenylpyridine (**1**) (200 mg, 0.82 mmol) and $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) in tetrahydrofuran (10 mL), was added a solution of 1,4-phenylboronic acid (68 mg, 0.41 mmol) and Na_2CO_3 (87 mg, 0.82 mmol) in ethanol (1mL) and distilled water (1mL). Both solutions were previously bubbled with argon for 15 minutes. The reaction mixture was stirred

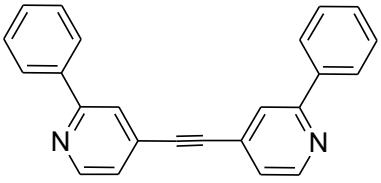
under argon at 80ºC and was monitored by ^{1}H NMR spectroscopy. After 23 h, the reaction mixture was cooled to room temperature, extracted with diethyl ether and washed with water and brine. The organic layer was dried with anhydrous $MgSO_4$ and the solvent was evaporated in vacuo. After purification by flash column chromatography (hexanes/chloroform, 1:5) compound **3** was obtained as a white solid. Yield 130 mg (82%); mp 181.6-184.2 ºC. Anal.Calcd. for $C_{28}H_{20}N_2 \cdot H_2O$: C, 83.56; H, 5.51; N, 6.96. Found: C, 83.93; H, 5.19; N, 6.93. HRMS-ESI^{+} $(M+2H)^{2+}$; Calcd. for $C_{14}H_{11}N$: 193.0891. Found: 193.0884. IR ($CHCl_3$, cm^{-1}): ν(Carom-H) 3028, 2924, 2856; ν(C=C), ν(C=N) 1597, 1546. ^{1}H NMR (300MHz, $CDCl_3$, 293K): δ 8.79 (d, J_{H-H} = 5.1, 2H, C*H*-arom), 8.09 (dd, J_{H-H} = 8.2, 1.3, 4H, C*H*-arom), 7.98 (d, J_{H-H} = 0.7, 2H, C*H*-arom), 7.82 (s, 4H, C*H*-arom), 7.56-7.46 (m, 8H, C*H*-arom). ^{13}C{^{1}H} NMR (75.56 MHz, $CDCl_3$, 293K): δ 158.2, 148.2, 139.3, 139.0 (all s, C_{ipso}), 150.2, 129.1, 128.7, 127.7, 126.9, 120.0, 118.5 (all s, *C*H-arom).



9,10-bis(2-phenylpyridin-4-yl)anthracene (4). A solution of 4-bromo-2-phenylpyridine (**1**) (406 mg, 1.74 mmol), anthracene-9,10-diboronic acid bis(pinacol) ester (300 mg, 0.70 mmol), $Pd(PPh_3)_4$ (96 mg, 0.08 mmol) and K_2CO_3 (192 mg, mmol) in 10 mL of tetrahydrofuran and 4 mL of distilled water, was bubbled with argon for 20 minutes and then was stirred under argon at 120ºC. After 42 h, the reaction was cooled to room temperature, extracted with diethyl ether and washed with brine. The organic layer was dried with anhydrous $MgSO_4$, and the solvent was evaporated in vacuo. After purification by flash column chromatography (hexanes/ethyl acetate, 20:1) compound **4** was obtained as pale yellow solid. Yield 120 mg (35%); the product decomposes over 315ºC. HRMS-ESI^{+} $(M+H)^{+}$ Calcd. for $C_{36}H_{24}N_2$: 485.2012. Found: 485.2016. IR ($CHCl_3$, cm^{-1}): ν(Carom-H) 3058, 2926, 2854; ν(C=C), ν(C=N) 1595, 1540. ^{1}H NMR (300MHz, $CDCl_3$, 293K): δ 9.00 (d, J_{H-H} = 4.9, 2H, C*H*-arom), 8.13 (dd, J_{H-H} = 7.9, 1.3, 4H, C*H*-arom), 7.96-7.93 (m, 2H, C*H*-arom), 7.73 (dd, J_{H-H} = 6.8, 3.3, 4H, C*H*-arom), 7.56-7.43 (m, 12H, C*H*-arom). ^{13}C{^{1}H} NMR (75.56 MHz, $CDCl_3$, 293K): δ 157.7, 148.3, 138.9, 135.0, 129.1 (all s, C_{ipso}), 149.9, 129.3, 128.9, 127.1, 126.4, 126.0, 124.8, 123.2 (all s, *C*H-arom).

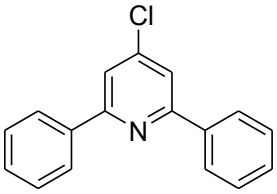


4-ethynyl-2-phenylpyridine (6). A solution of 4-bromo-2-phenylpyridine (**1**) (660 mg, 2.71 mmol), trimethylsilylacethylene (533 mg, 5.43 mmol), $Pd(PPh_3)_4$ (188 mg, 0.16 mmol) in dry diisopropylamine (25 mL) and dry toluene (64 mL) was stirred at 80ºC overnight. The reaction mixture was cooled to room temperature, filtered through Celite and the solvent was evaporated in vacuo. After purification by flash column chromatography (hexanes) 2-phenyl-4((trimethylsilyl)ethynyl)pyridine was obtained as pale yellow oil. Yield: 490 mg (71%). IR ($CHCl_3$, cm^{-1}): ν(Carom-H) 3047, 2962, 2901; ν(C≡C) 2162; ν(C=C), (C=N) 1594, 1539. ^1H NMR (300 MHz, $CDCl_3$, 293K): δ 8.65 (dd, J_{H-H} = 5.1, 0.7, 1H, CH-arom), 8.00 (dd, J_{H-H} = 8.1, 1.5, 2H, CH-arom), 7.78 (s, 1H, CH-arom), 7.52-7.44 (m, 3H, CH-arom), 7.26 (dd, J_{H-H} = 5.0, 1.3, 1H, CH-arom), 0.30 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (75.56 MHz, $CDCl_3$, 293K): δ 157.5, 138.6, 131.9 (all s, C_{ipso}), 149.5, 129.2, 128.7, 126.9, 124.0, 122.8 (all s, CH-arom), 102.3 (C≡C), 99.6 (C≡C), 0.3 (s, $Si(CH_3)_3$). To remove the TMS group, a solution of 2-phenyl-4((trimethylsilyl)ethynyl)pyridine (340 mg, 1.33 mmol) and K_2CO_3 (460 mg, 3.33 mmol) in dry tetrahydrofuran (2 mL) and methanol (4 mL) was stirred at room temperature for 24 h under argon. Then, the mixture was extracted with dichloromethane and water. The organic layer was dried with anhydrous $MgSO_4$, and evaporated in vacuo. After purification by flash column chromatography (hexanes) 4-ethynyl-2-phenylpyridine **6** was obtained as pale yellow oil. Yield: 210 mg (88%). IR ($CHCl_3$, cm^{-1}): ν(≡C-H) 3288; ν(Carom-H) 3059, 2923, 2851; ν(C≡C), 2108; ν(C=C), (C=N) 1594, 1538. ^1H NMR (300MHz, $CDCl_3$, 293K): δ 8.68 (dd, J_{H-H} = 5.0, 0.7, 1H, CH-arom), 8.00 (dd, J_{H-H} = 8.1, 1.5, 2H, CH-arom), 7.81 (s, 1H, CH-arom), 7.53-7.44 (m, 3H, CH-arom), 7.30 (dd, J_{H-H} = 5.0, 1.4, 1H, CH-arom), 3.32 (s, 1H, C≡C*H*). $^{13}C\{^1H\}$ NMR (75.56 MHz, $CDCl_3$, 293K): δ 157.6, 138.5, 131.0 (all s, C_{ipso}), 149.6, 129.3, 128.8, 126.9, 124.2, 122.9 (all s, CH-arom), 81.5 (H*C*≡C), 81.3 (CH≡*C*).

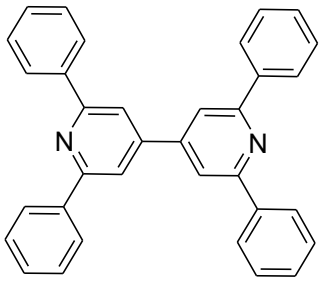


2-phenyl-4-(2-(2-phenylpyridin-4-yl)ethynyl)pyridine (5). A solution of 4-ethynyl-2-phenylpyridine (**6**) (210 mg, 1.17 mmol), 4-bromo-2-phenylpyridine (**1**) (248 mg, 1.17 mmol) and $Pd(PPh_3)_4$ (81 mg, 0.07 mmol) in 20 mL of dry toluene and 8 mL of freshly distilled diisopropylamine, was stirred under argon at 150ºC overnight. The reaction mixture was cooled to room temperature and filtered through Celite and the solvent was evaporated in vacuo. The residue was

recristalized in chloroform/hexanes to obtain **5** as a white solid. Yield 267 mg (68%); mp 202.8-204.5 ºC. HRMS-ESI^{+} $(M+2H)^{2+}$; Calcd. for $C_{12}H_9N$: 167.0735. Found: 167.0732. IR ($CHCl_3$, cm^{-1}): ν(Carom-H) 3028; ν(C≡C) 1937; ν(C=C), ν(C=N) 1595, 1538. ^{1}H NMR (300MHz, $CDCl_3$, 293K): δ 8.75 (dd, J_{H-H} = 5.1, 2H, C*H*-arom), 8.04 (dd, J_{H-H} = 8.1, 1.5, 4H, C*H*-arom), 7.91 (s, 2H, C*H*-arom), 7.60-7.46 (m, 6H, C*H*-arom), 7.39 (dd, J_{H-H} = 5.0, 1.4, 2H, C*H*-arom). ^{13}C{^{1}H} NMR (75.56 MHz, $CDCl_3$, 293K): δ 157.7, 138.3, 131.1 (all C_{ipso}), 149.7, 129.5, 128.9, 126.9, 123.8, 122.6 (all *C*H-arom), 90.9 (*C*≡C).

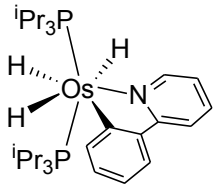


4-chloro-2,6-diphenylpyridine (7). White solid. mp 82.6-83.8ºC. IR ($CHCl_3$, cm^{-1}): ν(Carom-H) 3063, 3037; ν(C=C), ν(C=N) 1563, 1553. ^{1}H NMR (300MHz, $CDCl_3$, 293K): δ 8.14 (dd, J_{H-H} = 8.1, 1.5, 4H, C*H*-arom), 7.71 (s, 2H, C*H*-arom), 7.56-7.47 (m, 6H, C*H*-arom). ^{13}C{^{1}H} NMR (75.56 MHz, $CDCl_3$, 293K): δ 158.2, 145.3, 138.2 (all s, C_{ipso}), 129.6, 128.8, 127.1, 118.7 (all s, *C*H-arom).

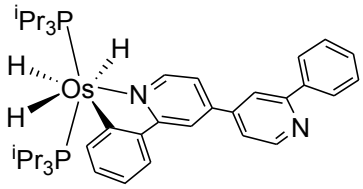


2,2´,6,6´-tetraphenyl-4,4´-bipyridine (8). To a solution of $NiBr_2(PPh_3)_2$ (1.19 g, 1.52 mmol) in 45 mL of dry tetrahydrofuran was added zinc powder (497 mg, 7.60 mmol) and Et_4NI (1.30 g, 5.65 mmol). The mixture was stirred at room temperature for 30 min under argon. A solution of 4-chloro-2,6-diphenylpyridine (**7**) (1.34 mg, 5.06 mmol) in 15 mL of dry tetrahydrofuran was added dropwise, the resulting mixture was heated at 50ºC for 36 h. The reaction mixture was poured into 200 mL of 2M aqueous ammonia, and diethyl ether (100 mL) and benzene (100 mL) were added. The precipitates were filtered and the organic layer was separated. The aqueous layer was extracted with ethyl acetate/benzene (1:1). The combined organic layers were washed successively with water and brine, dried with anhydrous $MgSO_4$, and evaporated in vacuo. After purification by flash column chromatography (hexanes/dichloromethane, 7:3) 2,2´,6,6´-tetraphenyl-4,4´-bipyridine (**8**) was obtained as a white solid. Yield 840 mg (36%); mp 245.8-247.0 ºC. Anal. Calcd. for $C_{34}H_{24}N_2$: C, 88.67; H, 5.25; N, 6.08. Found: C, 88.27; H, 5.37; N, 6.10. IR ($CHCl_3$, cm^{-1}): ν(Carom-H) 3061, 3037; ν(C=C), ν(C=N) 1585, 1539. ^{1}H NMR (300MHz, $CDCl_3$, 293K): δ 8.28-8.24 (m, 8H, C*H*-arom), 8.02 (s, 4H, C*H*-arom), 7.60-7.47 (m, 12H, C*H*-arom). ^{13}C{^{1}H} NMR (75.56 MHz,

$CDCl_3$, 293K): δ 158.0, 148.4, 139.1 (all s, C_{ipso}), 129.4, 128.8, 127.2, 116.9 (all s, *C*H-arom).

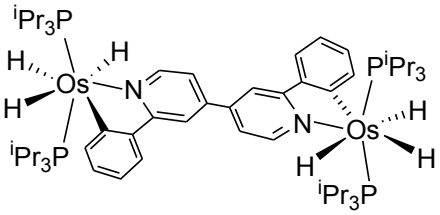


Reaction of $OsH_6(P^iPr_3)_2$ with 2-phenylpyridine: **Synthesis of complex 10.** 2-phenylpyridine (55.31 μL, 0.39 mmol) was added to a solution of $OsH_6(P^iPr_3)_2$ (**9**) (200 mg, 0.39 mmol) in toluene (10 mL) and heated under reflux for 18 hours, changing the color from pale yellow to dark yellow. The resulting solution was dried in vacuo. Methanol was added to afford a dark yellow solid which was washed with further portions of methanol and dried in vacuo. Yield: 200 mg (77 %). Anal. Calcd. for $C_{29}H_{53}NOsP_2$: C, 52.15; H, 8.00; N 2.09. Found: C, 52.55; H, 7.55; N, 2.05. IR (neat compound, cm^{-1}): ν(Os-H) 2150 (w), 2016 (w); ν(C=N) 1598 (m), ν(C=C) 1463 (m). ^{1}H NMR (500 MHz, C_6D_6, 293 K): δ 9.67 (d, J_{H-H} = 7.2, 1H, C*H*-arom), 8.71 (d, J_{H-H} = 7.5, 1H, C*H*-arom), 7.77 (d, J_{H-H} = 7.5, 1H, C*H*-arom), 7.54 (d, J_{H-H} = 7.2, 1H, C*H*-arom), 7.13 (d, J_{H-H} = 7.5, 1H, C*H*-arom), 7.08 (t, J_{H-H} = 7.5, 1H, C*H*-arom), 6.89 (t, J_{H-H} = 7.2, 1H, C*H*-arom), 6.20 (t, J_{H-H} = 7.2, 1H, C*H*-arom), 1.86 (m, 6H, PC*H*$(CH_3)_2$), 0.98 (dvt, J_{H-H} = 6.7, *N* = 12.5, 18H, PCH(C*H*$_3)_2$), 0.94 (dvt, J_{H-H} = 7, *N* = 12, 18H, PCH(C*H*$_3)_2$), –8.54 (br, 2H, Os*H*), –11.95 (br, 1H, Os*H*). ^{1}H NMR (400 MHz, C_7D_8, 203 K, high field region): δ –6.24 (d, J_{H-H} = 38, 1H, Os-H), –10.93 (d, J_{H-H} = 38, 1H, Os-H), –11.87 (s, 1H, Os-H). ^{13}C{^{1}H} NMR (100.63 MHz, C_6D_6, 293 K): δ 187.5 (t, J_{P-C} = 6.6, Os-*C*), 167.9, 144.7 (all s, C_{ipso}), 158.8, 147.0, 133.0, 128.7, 125.1, 120.0, 118.8, 118.4 (all s, *C*H-arom), 27.5 (vt, *N* = 24, P*C*H$(CH_3)_2$), 20.1, 19.8 (both s, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 293 K): δ 20.3 (s).



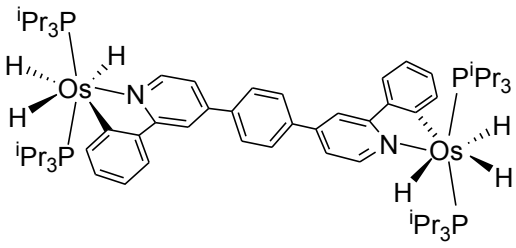
Reaction of $OsH_6(P^iPr_3)_2$ with 2,2´-diphenyl-4,4´-bipyridine (2): Synthesis of complex 11. 3 equiv of 2,2´-diphenyl-4,4´-bipyridine (**2**) (71 mg, 0.23 mmol) was added to a solution of $OsH_6(P^iPr_3)_2$ (**9**) (40 mg, 0.077 mmol) in toluene (5 mL) and heated under reflux for 0.5 hours, changing the color from pale yellow to dark red. The resulting solution was dried in vacuo. Methanol was added to afford a dark red solid which was washed with further portions of methanol and dried in vacuo. Yield: 32 mg (50 %). Anal. Calcd. for $C_{40}H_{61}N_2OsP_2$: C, 58.44; H, 7.48; N 3.41. Found: C, 58.10; H, 7.21; N, 3.51. IR (neat compound, cm^{-1}):

ν(Os-H) 2128 (w), 1980 (w); ν(C=N) ν(C=C) 1592 (m), 1459 (m). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 9.80 (d, J_{H-H} = 6, 1H, C*H*-arom), 8.76 (d, J_{H-H} = 7.2, 1H, C*H*-arom), 8.62 (d, J_{H-H} = 4.9, 1H, C*H*-arom), 8.12 (d, J_{H-H} = 7.3, 2H, C*H*-arom), 8.03 (s, 1H, C*H*-arom), 7.93 (d, J_{H-H} = 7.2, 1H, C*H*-arom), 7.74 (s, 1H, C*H*-arom), 7.28 (t, J_{H-H} = 7.3, 2H, C*H*-arom), 7.25 (t, J_{H-H} = 7.3, 1H, C*H*-arom), 7.17 (t, J_{H-H} = 7.2, 1H, C*H*-arom), 7.12 (t, J_{H-H} = 7.2, 1H, C*H*-arom), 6.87 (d, J_{H-H} = 4.9, 1H, C*H*-arom), 6.49 (d, J_{H-H} = 6, 1H, C*H*-arom), 1.91 (m, 6H, PC*H*$(CH_3)_2$), 1.01 (dvt, J_{H-H} = 6.5, N = 12, 18H, PCH(C*H*$_3)_2$), 0.98 (dvt, J_{H-H} = 6.5, N = 12, 18H, PCH(C*H*$_3)_2$), –8.36 (br, 2H, Os*H*), –11.65 (br, 1H, Os*H*). ^{1}H NMR (300 MHz, C_7D_8, 193 K, high field region): δ –6.40 (d, J_{H-H} = 48.3, 1H, Os-H), –10.87 (d, J_{H-H} = 48.3, 1H, Os-H), –11.82 (s, 1H, Os-H). ^{13}C{^{1}H} NMR (75.48 MHz, C_6D_6, 293 K): δ 188.4 (t, J_{P-C} = 6.6, Os-*C*), 168.5 (s, C_{ipso}), 159.4 (s, *C*H-arom), 158.6 (s, C_{ipso}), 150.8, 147.2 (both s, *C*H-arom), 146.0, 144.3, 142.5, 139.7 (all s, C_{ipso}), 129.4, 129.0, 128.4, 127.5, 125.5, 119.6, 118.9, 117.9, 117.6, 115.7 (all s, *C*H-arom), 27.7 (vt, N = 24, P*C*H$(CH_3)_2$), 20.2, 19.9 (both s, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 293 K): δ 20.7 (s).

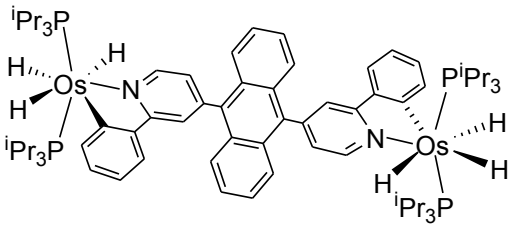


Reaction of $OsH_6(P^iPr_3)_2$ with 2,2´-diphenyl-4,4´-bipyridine (2): Synthesis of complex 12. 2,2´-diphenyl-4,4´-bipyridine (29 mg, 0.10 mmol) was added to a solution of $OsH_6(P^iPr_3)_2$ (**9**) (150 mg, 0.29 mmol) in toluene (8 mL) and heated under reflux for 24 hours, changing the color from pale yellow to dark red. The resulting solution was dried in vacuo. Methanol was added to afford a dark red solid which was washed with further portions of methanol and dried in vacuo. Yield: 117.6 mg (91 %). Anal. Calcd. for $C_{58}H_{106}N_2Os_2P_4$: C, 52.15; H, 8.00; N 2.10. Found: C, 51.8; H, 8.29; N, 1.62. IR (neat compound, cm^{-1}): ν(Os-H) 2098 (w), 1961 (w); ν(C=N) ν(C=C) 1578 (m), 1456 (m). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 9.77 (d, J_{H-H} = 6.0, 2H, C*H*-arom), 8.75 (d, J_{H-H} = 7.2, 2H, C*H*-arom), 8.21 (d, J_{H-H} = 1.4, 2H, C*H*-arom), 7.82 (d, J_{H-H} = 7.2, 2H, C*H*-arom), 7.16 (t, J_{H-H} = 7.2, 2H, C*H*-arom), 7.09 (t, J_{H-H} = 7.2, 2H, C*H*-arom), 6.64 (dd, J_{H-H} = 6.0, J_{H-H} = 1.4, 2H, C*H*-arom), 1.87 (m, 12H, PC*H*$(CH_3)_2$), 0.98 (dvt, J_{H-H} = 6.6, N = 13.3, 36H, PCH(C*H*$_3)_2$), 0.95 (dvt, J_{H-H} = 6.8, N = 13, 36H, PCH(C*H*$_3)_2$), –8.38 (br, 4H, Os*H*), –11.66 (br, 2H, Os*H*). ^{1}H NMR (300 MHz, C_7D_8, 213 K, high field region): δ –6.43 (d, J_{H-H} = 49.8, 2H, Os-H), –10.96 (d, J_{H-H} = 49.8, 2H, Os-H), –11.85 (br, 2H, Os-H). ^{13}C{^{1}H} NMR (100.63 MHz, C_6D_6, 293 K): δ 188.3 (t, J_{P-C} = 6.5, Os-*C*), 168.3,

144.3, 141.3 (all s, C_{ipso}), 159.3, 147.1, 128.3, 125.6, 118.8, 117.3, 114.8 (all s, *C*H-arom), 27.5 (vt, $N = 24.0$, P*C*H(CH_3)$_2$), 20.1, 19.9 (both s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6, 293 K): δ 20.8 (s).

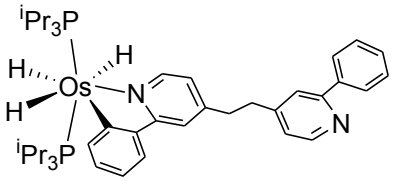


Reaction of $OsH_6(P^iPr_3)_2$ with 2-phenyl-4-(4-(2-phenylpyridin-4-yl)phenyl)pyridine: Synthesis of complex 13. 2-phenyl-4-(2-(2-phenylpyridin-4-yl)phenyl)pyridine (**3**) (248 mg, 0.06 mmol) was added to a solution of $OsH_6(P^iPr_3)_2$ (**9**) (100 mg, 0.19 mmol) in toluene (10 mL) and heated under reflux. The solution changed from pale yellow to dark red. After 6 h, the mixture was cooled to room temperature and the solvent was evaporated in vacuo. Addition of methanol (3 mL) caused the precipitation of a dark red solid, which was washed with methanol (2 x 2 mL) and dried in vacuo. Yield: 89 mg (99%). Anal. Calcd. for $C_{64}H_{108}N_2P_4Os_2$: C, 54.52; H, 7.72; N 1.99. Found: C, 54.15; H, 7.87; N, 2.13. IR (neat compound, cm^{-1}): ν(Os-H) 2134 (w), 1998 (w); ν(C=N) ν(C=C) 1609 (m), 1576 (m). ^1H NMR (400 MHz, C_6D_6, 293K): δ 9.81 (d, $J_{H-H} = 6.1$, 2H, C*H*-arom), 8.78 (d, $J_{H-H} = 6.8$, 2H, C*H*-arom), 8.17 (d, $J_{H-H} = 1.9$, 2H, C*H*-arom), 7.99 (dd, $J_{H-H} = 7.2, 1.4$, 2H, C*H*-arom), 7.49 (s, 4H, C*H*-arom), 7.21-7.10 (m, 4H, C*H*-arom), 6.69 (dd, $J_{H-H} = 7.7, 2.0$, 2H, C*H*-arom), 1.96-1.88 (m, 12H, PC*H*(CH_3)$_2$), 1.03 (dvt, $J_{H-H} = 6.9$, $N = 12.5$, 36H, PCHC*H*$_3$), 1.00 (dvt, $J_{H-H} = 6.8$, $N = 12.2$, 36H, PCHC*H*$_3$), –8.41 (br, 4H, Os-*H*), –11.71 (br, 2H, Os-*H*). ^1H NMR (300 MHz, C_7D_8, 203 K, high field region): δ –6.17 (d, $J_{H-H} = 42.4$, 1H, Os-H), –10.75 (d, $J_{H-H} = 42.4$, 1H, Os-H), –11.63 (s, 1H, Os-H). $^{13}C\{^1H\}$ NMR (100.63 MHz, C_7D_8, 293K): δ 188.0 (t, $J_{P-C} = 5.9$, Os-*C*), 168.6, 144.7, 144.3, 138.7 (all s, C_{ipso}), 159.4, 147.3, 128.9, 127.5, 125.3, 119.0, 118.0, 115.6 (all s, *C*H-arom), 27.8 (vt, $N = 24.0$, P*C*H(CH_3)$_2$), 20.2, 20.0 (both s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_7D_8, 293 K): δ 20.7 (s).



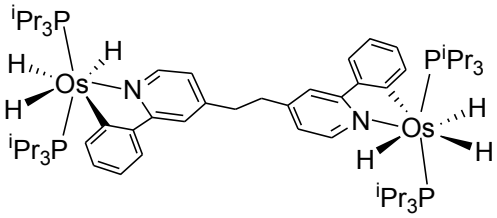
Reaction of $OsH_6(P^iPr_3)_2$ with 9,10-bis(2-phenylpyridin-4-yl)anthracene (4): Synthesis of complex 14. 9,10-bis(2-phenylpyridin-4-yl)anthracene (**4**) (55.0 mg, 0.11 mmol) was added to a solution of $OsH_6(P^iPr_3)_2$ (**9**) (250 mg, 0.48 mmol) in toluene (10 mL) and heated under reflux for

15 hours, changing the color from pale yellow to dark red. The resulting solution was dried in vacuo. Methanol was added to afford a dark red solid which was washed with further portions of methanol and ether and dried in vacuo. Yield: 150 mg (90 %). Anal. Calcd. for $C_{72}H_{112}N_2Os_2P_4$: C, 57.27; H, 7.48; N 1.86. Found: C, 56.88; H, 7.31; N, 1.92. IR (neat compound, cm^{-1}): ν(Os-H) 2122 (w), 1964 (w); ν(C=N) ν(C=C) 1604 (m), 1441 (m). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 9.87 (d, J_{H-H} = 5.5, 2H, C*H*-arom), 8.37 (d, J_{H-H} = 7.2, 2H, C*H*-arom), 7.96 (dd, J_{H-H} = 1.4, J_{H-H} = 5.5, 2H, C*H*-arom), 7.68 (dd, J_{H-H} = 3.2, J_{H-H} = 6.9, 4H, C*H*-arom), 7.64 (m, 2H), 7.39 (dd, J_{H-H} = 3.2, J_{H-H} = 6.9, 4H, C*H*-arom), 6.85 (t, J_{H-H} = 5.5, 2H, C*H*-arom), 6.84-6.70 (m, 4H, C*H*-arom), 1.96 (m, 12H, PC*H*$(CH_3)_2$), 1.03 (dvt, J_{H-H} = 6.8, N = 11.1, 36H, PCH(C*H*$_3)_2$), 1.02 (dvt, J_{H-H} = 6.8, N = 10.7, 36H, PCH(C*H*$_3)_2$), –8.62 (br, 4H, Os*H*), –12.04 (br, 2H, Os*H*). ^{1}H NMR (400 MHz, CD_2Cl_2, 193 K, high field region): δ –6.26 (d, J_{H-H} = 22.8, 2H, Os-H), –11.01 (d, J_{H-H} = 22.8, 2H, Os-H), –11.97 (s, 2H, Os-H). ^{13}C{^{1}H} NMR (100.63 MHz, CD_2Cl_2, 293 K): δ 188.6 (t, J_{P-C} = 6.0, Os-*C*), 167.8 (d, J_{P-C} = 2.5, C_{ipso}), 158.9, 147.0 (both s, *C*H-arom), 144.5, 144.3, 135.6, 129.7 (all s, C_{ipso}), 128.1, 126.6, 126.1, 125.0, 123.6 121.4, 118.0 (all s, *C*H-arom), 27.78 (vt, N = 24.2, P*C*H$(CH_3)_2$), 20.2, 19.9 (both s, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (161.99 MHz, C_6D_6, 293 K): δ 20.8 (s).



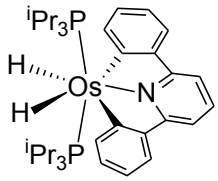
Reaction of $OsH_6(P^iPr_3)_2$ with 2-phenyl-4-(2-(2-phenylpyridin-4-yl)ethynyl)pyridine (5): Synthesis of complex 15. 2-phenyl-4-(2-(2-phenylpyridin-4-yl)ethynyl)pyridine (**5**) (109 mg, 0.33 mmol) was added to a solution of $OsH_6(P^iPr_3)_2$ (**9**) (56 mg, 0.11 mmol) in toluene (10 mL) and heated under reflux. The solution changed from pale yellow to dark green. After 10 min, the mixture was cooled to room temperature and the solvent was evaporated in vacuo. Addition of toluene (7 x 2 mL) caused the solution of the complex. This solution was separated and the solvent was evaporated in vacuo. Addition of diethyl ether (1 x 2 mL and 2 x 1 mL) caused the precipitation of the excess of ligand. The solution was separated and the solvent was evaporated in vacuo. The obtained residue was washed with methanol (2 x 2 mL) and dried in vacuo. Yield: 15 mg (16%). Anal. Calcd. for $C_{42}H_{64}N_2P_2Os$: C, 59.41; H, 7.60; N, 3.30. Found: C, 59.83; H, 7.85; N, 3.21. IR (neat compound, cm^{-1}): ν(Carom-H) 2960 (m), 2907 (m), 2857 (m); ν(Os-H) 2128 (w),

1999 (w); ν(C=N) ν(C=C) 1602 (m), 1576 (m). ^{1}H NMR (400MHz, C_6D_6, 293K): δ 9.57(d, J_{H-H} = 6.0, 1H, C*H*-arom), 8.73 (d, J_{H-H} = 7.3, 1H, C*H*-arom), 8.57 (d, J_{H-H} = 4.9, 1H, C*H*-arom), 8.23 (d, J_{H-H} = 7.2, 2H, C*H*-arom), 7.85 (d, J_{H-H} = 7.2, 1H, C*H*-arom), 7.52 (s, 1H, C*H*-arom), 7.30 (d, J_{H-H} = 7.7, 2H, C*H*-arom), 7.27 (s, 1H, C*H*-arom), 7.21-7.09 (m, 3H, C*H*-arom), 6.49 (dd, J_{H-H} = 4.9, 1.2, 1H, C*H*-arom), 6.05 (dd, J_{H-H} = 5.9, 1.7, 1H, C*H*-arom), 2.47 (m, 4H, CH_2), 1.91-1.84 (m, 6H, PC*H*$(CH_3)_2$), 1.00 (dvt, J_{H-H} = 6.8, *N* = 12.6, 18H, PCH(C$H_3)_2$), 0.95 (dvt, J_{H-H} = 6.7, *N* = 12.4, 18H, PCH(C$H_3)_2$), –8.56 (br, 2H, Os-*H*), –11.96 (br, 1H, Os-*H*). ^{1}H NMR (300 MHz, C_7D_8, 203 K, high field region): δ –6.51 (d, J_{H-H} = 30, 1H, Os-H), –11.21 (d, J_{H-H} = 30, 1H, Os-H), –12.16 (s, 1H, Os-H). ^{13}C{^{1}H} NMR (100.63 MHz, C_6D_6, 293K): δ 187.7 (t, J_{P-C} = 6.9, Os-*C*), 168.0 (s, C_{ipso}), 158.7 (s, *C*H-arom), 157.8, 150.0 (both s, C_{ipso}), 149.9, 147.1 (both s, *C*H-arom), 146.7, 144.5, 139.9 (all s, C_{ipso}), 130.2, 128.9, 128.8, 127.4, 124.9, 122.3, 120.6, 120.3, 118.7, 118.3 (all s, *C*H-arom), 35.6, 35.4 (both s, *C*H_2), 27.5 (vt, *N* = 23.8, P*C*H$(CH_3)_2$), 20.1, 19.8 (both s, PCH(*C*$H_3)_2$) .^{31}P{^{1}H} NMR (161.99 MHz, C_6D_6, 293 K): δ 20.2 (s).

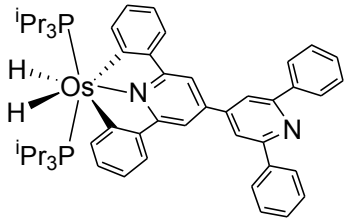


Reaction of $OsH_6(P^iPr_3)_2$ with 2-phenyl-4-(2-(2-phenylpyridin-4-yl)ethynyl) pyridine (5): Synthesis of complex 16. $OsH_6(P^iPr_3)_2$ (**9**) (100 mg, 0,19 mmol) was added to a solution of 2-phenyl-4-(2-(2-phenylpyridin-4-yl)ethynyl)pyridine (**5**) (32 mg, 0.10 mmol) in toluene (20 mL) and heated under reflux. The solution changed from pale yellow to dark green. After 4 h, the mixture was cooled to room temperature and the solvent was evaporated in vacuo. Addition of methanol (3 mL) caused the precipitation of a dark green solid, which was washed with methanol (2 x 3 mL) and dried in vacuo. Yield: 84 mg (63%). Anal. Calcd. for $C_{60}H_{108}N_2P_4Os_2$: C, 52.92; H, 7.99; N, 2.06. Found: C, 53.16; H, 8.23; N, 2.33. IR (neat compound, cm^{-1}): ν(Carom-H) 2957, 2923, 2868; ν(Os-H) 2121 (w), 1980 (w), 1946 (w); ν(C=N) ν(C=C) 1579 (m), 1531 (m). ^{1}H NMR (400 MHz, C_6D_6, 293K): δ 9.63 (d, J_{H-H} = 6.0, 2H, C*H*-arom), 8.75 (d, J_{H-H} = 7.0, 2H, C*H*-arom), 7.88 (d, J_{H-H} = 7.0, 2H, C*H*-arom), 7.53 (s, 2H, C*H*-arom), 7.25-7.07 (m, 4H, C*H*-arom), 6.09 (d, J_{H-H} = 6.0, 2H, C*H*-arom), 2.47 (s, 4H, CH_2), 1.94-1.89 (m, 12H, PC*H*$(CH_3)_2$), 1.03 (dvt, J_{H-H} = 6.8, *N* = 12.6, 36H, PCH(C$H_3)_2$), 0.99 (dvt, J_{H-H} = 6.8, *N* = 12.3, 36H, PCH(C$H_3)_2$), –8.54 (br, 4H, Os-*H*), –11.92 (br, 2H, Os-*H*). ^{1}H NMR (300 MHz, C_7D_8, 203 K, high field region): δ –6.49 (d, J_{H-H} = 26.1, 1H, Os-H), –11.20

(d, J_{H-H} = 26.1, 1H, Os-H), –12.12 (s, 1H, Os-H). $^{13}C\{^1H\}$ NMR (100.63 MHz, C_6D_6, 293K): δ 187.7 (t, J_{P-C} = 6.6, Os-*C*), 168.1, 147.1, 144.6 (all s, C_{ipso}), 158.6, 147.2, 128.8, 125.1, 120.8, 118.7, 118.4 (all s, *C*H-arom), 35.7 (*C*H$_2$), 27.5 (vt, *N* = 23.8, P*C*H(CH$_3$)$_2$), 20.2, 19.9 (both s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6, 293 K): δ 20.5 (s).

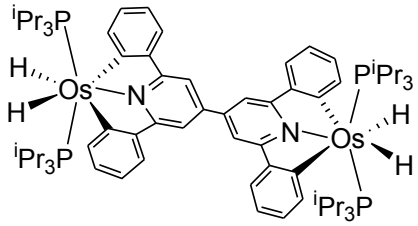


Reaction of OsH$_6$(P^{i}Pr$_3$)$_2$ with 2,6-diphenylpyridine: **Synthesis of complex 17.** 2,6-diphenylpyridine (44.76 mg, 0.19 mmol) was added to a solution of OsH$_6$(P^{i}Pr$_3$)$_2$ (**9**) (100 mg, 0.19 mmol) in toluene (5 mL) and heated under reflux for 15 hours, changing the color from pale yellow to dark orange. The resulting solution was dried in vacuo. Methanol was added to afford a dark orange solid which was washed with further portions of methanol and dried in vacuo. Yield: 90 mg (64 %). Anal. Calcd. for $C_{35}H_{55}NOsP_2$: C, 56.65; H, 7.47; N 1.89. Found: C, 56.98; H, 7.31; N, 1.94. IR (neat compound, cm^{-1}): ν(Os-H) 2146 (w); ν(C=N) 1575 (m), ν(C=C) 1471 (m). ^1H NMR (500 MHz, C_6D_6, 293 K): δ 8.35 (m, 2H, C*H*-arom), 7.70 (m, 2H, C*H*-arom), 7.32 (d, J_{H-H} = 8.6, 2H, C*H*-arom), 7.06 (m, 4H, C*H*-arom), 7.04 (t, J_{H-H} = 8.6, 1H, C*H*-arom), 2.02 (m, 6H, PC*H*(CH$_3$)$_2$), 0.815 (dvt, $J_{H–H}$ = 6.6, *N* = 13, 18 H, PCH(C*H*$_3$)$_2$), –8.05 (t, J_{H-H} = 15.4, 2H, Os*H*). $^{13}C\{^1H\}$ NMR (100.63 MHz, C_6D_6, 293 K): δ 177.7 (t, J_{P-C} = 7.1, Os-*C*), 167.5, 147.6 (all s, C_{ipso}), 146.3, 135.2, 129.4, 124.6, 120.0, 111.7 (all s, *C*H-arom), 26.9 (vt, *N* = 24, P*C*H(CH$_3$)$_2$), 19.2 (s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 293 K): δ 0.0 (s).



Reaction of OsH$_6$(P^{i}Pr$_3$)$_2$ with 2,2′,6,6′-tetraphenyl-4,4′-bipyridine (8): Synthesis of complex 18. OsH$_6$(P^{i}Pr$_3$)$_2$ (**9**) (100 mg, 0.19 mmol) was added to a solution of 2,2′,6,6′-tetraphenyl-4,4′-bipyridine (**8)** (267 mg, 0.58 mmol) in toluene (10 mL) and heated under reflux. The solution changed from pale yellow to red. After 14 h, the mixture was cooled to room temperature and a precipitate appeared. The precipitate was washed with toluene (3 x 5 mL) and dried in vacuo. Then, the residue was washed with diethyl ether (7 x 2 mL). ^1H NMR spectra of the final residue in C_6D_6 shows the presence of the complex **18** and 2,2′,6,6′-tetraphenyl-4,4′-bipyridine in a ratio 1:1. All attempts to separate complex **18** from 2,2′,6,6′-tetraphenyl-4,4′-bipyridine failed. IR (neat compound, cm^{-1}): ν(Carom-H) 2958, 2924, 2867; ν(Os-H), 2140 (w), 1998 (w), 1955

(w); ν(C=C), ν (C=N. 1576 (m), 1531 (m). ^{1}H NMR (400MHz, C_6D_6, 293K): δ 8.43 (d, J_{H-H} = 6.3, 2H, C*H*-arom), 8.22-8.19 (m, 4H, C*H*-arom), 7.96 (s, 2H, C*H*-arom), 7.93 (s, 2H, C*H*-arom), 7.91(dd, J_{H-H} = 7.3, 1.8, 2H, C*H*-arom), 7.42-7.24 (m, 6H, C*H*-arom), 7.13-7.11 (m, 4H, C*H*-arom), 2.17-1.89 (m, 6H, PC*H*$(CH_3)_2$), 0.81 (dvt, J_{H-H} = 6.8, *N* = 12.6, 36H, PCHC*H*$_3$), -7.75 (t, J_{H-P} = 15.6, 2H, Os-*H*). ^{31}P{^{1}H} NMR (161.99 MHz, C_7D_8, 293 K): δ 0.1 (s).



Reaction of $OsH_6(P^iPr_3)_2$ with 2,2´,6,6´-tetraphenyl-4,4´-bipyridine: Synthesis of complex 19. $OsH_6(P^iPr_3)_2$ (**9**) (250 mg, 0.48 mmol) was added to a solution of 2,2,6,6´-tetraphenyl-4,4´-bipyridine (**8**) (44 mg, 0.08mmol) in toluene (10 mL) and heated under reflux. The solution changed from pale yellow to dark red. After 120 h, the mixture was cooled to room temperature and the solvent was evaporated in vacuo. The obtained residue was washed with methanol (7 x 2 mL) and dried in vacuo. Yield: 112 mg (88%). Anal.Calcd. for $C_{70}H_{108}N_2P_4Os_2$: C, 56.73; H, 7.35; N, 1.89. Found: C, 57.01; H, 7.11; N, 2.02. IR (neat compound, cm^{-1}): ν(Carom-H) 3036, 2958, 2927; ν(Os-H) 2161 (w); ν(C=N), ν(C=C) 1578 (m), 1542 (m). ^{1}H NMR (400MHz, C_6D_6, 293K): δ 8.40 (d, J_{H-H} = 6.4, 4H, C*H*-arom), 8.31 (s, 4H, C*H*-arom), 7.78 (dd, J_{H-H} = 7.2, 1.9, 4H, C*H*-arom), 7.12-7.08 (m, 8H, C*H*-arom), 2.06-1.97 (m, 12H, PC*H*$(CH_3)_2$), 0.81 (dvt, J_{H-H} = 6.8, *N* = 12.6, 72H, PCH(C*H*$_3)_2$), -7.83 (t, J_{H-P} = 15.9, 4H, Os-*H*). ^{13}C{^{1}H} NMR (100.63 MHz, C_6D_6, 293K): δ 178.1 (t, J_{P-C} = 6.8, Os-*C*), 167.9, 147.3, 141.3 (all s, C_{ipso}), 145.4, 129.6, 125.3, 120.2, 109.6 (all s, *C*H-arom), 27.1 (vt, *N* = 24.6, P*C*H$(CH_3)_2$), 19.3 (s, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (161.99 MHz, C_6D_6, 293 K): δ 0.3 (s).

Electrochemical measurements. Cyclic voltammetry measurements were performed on a 263A of EG&PAR potentiostat/galvanostat controlled by a personal computer and driven by dedicated software. Cyclic voltammetry was performed with a conventional three-electrode configuration consisting on platinum working and auxiliary electrodes and a $Ag/AgCl_{(sat)}$ reference electrode. The experiments were carried out with a $5\cdot10^{-4}$ M solution of sample in the appropriate solvent containing 0.1 M $[(^{n}Bu)_4N]PF_6$ as supporting electrolyte. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min and the working electrode was cleaned after each run. The

cyclic voltammograms were recorded with a scan rate increasing from 0.05 to 1.00 Vs^{-1}. OSWV voltammograms were recorded in the adequate solvent: ΔEs = 4mV; ΔEp = 25mV and f = 15 Hz. Ferrocene was used as an internal reference both for potential calibration and for reversibility criteria in all the solvents used. Oxidations for the luminescence studies were performed by electrolysis (c = 2x10^{-6} M) in a three-electrode cell under nitrogen using dry solvents and 0.1 M [(^{n}Bu)$_4$N]PF_6 as supporting electrolyte. The progress of the oxidation was followed coulometrically (or chronoamperometrycally) by 263A of EG&PAR potenciostat-galvanostat. Analytical oxidations to obtain of the number of electrons of each process were carried out in the same conditions but with higher concentrations (c = 5x10^{-4} M). The reference electrode and the counter electrode were separately immersed in the solvent containing the supporting electrolyte and isolated from the bulk solution by a glass fit. The working electrode was a platinum grid. Fluorescence spectra were regularly recorded by transferring a small aliquot of the solution contained in the electrochemical cell into a quartz cell for different average number of removed electrons. λ_{exc} = 280 nm was chosen as the maximum of the band in the UV-vis spectrum. This wavelength coincides with the maximum emission of the complexes. Quantum yield values were measured with respect to anthracene as standard (Φ = 0.27 ± 0.01) (n_s^2/n_x^2),[4] using the equation $\Phi_x/\Phi_s = (S_x/S_s)[(1 - 10^{-As})/(1 - 10^{-Ax})]^2$, where x and s indicate the unknown and standard solution, respectively, Φ is the quantum yield, S is the area under the emission curve, A is the absorbance at the excitation wavelength, and n is the refractive index.

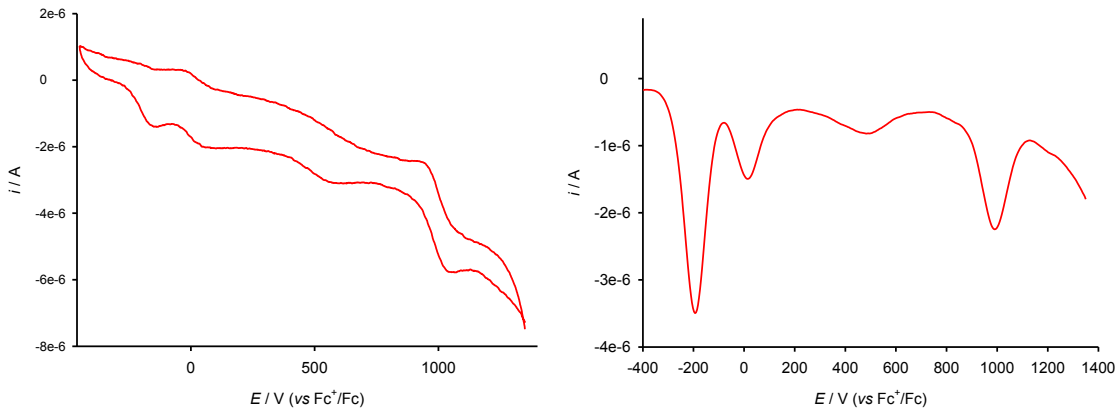


Figure S1. CV (left) and OSWV (right) of mononuclear complex **11** (c = 5·10^{-4} M) in CH_2Cl_2/CH_3CN (1:1) with 0.1 M of TBAHP as supporting electrolyte.

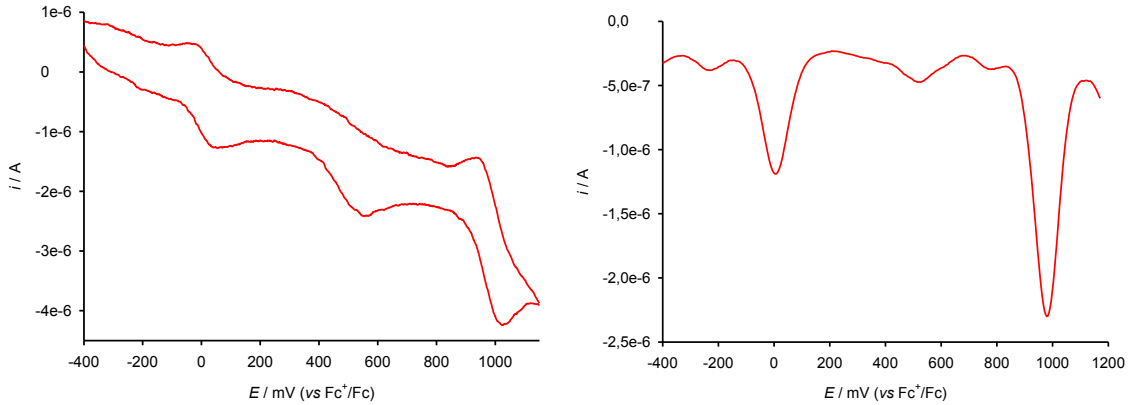


Figure S2. CV (left) and OSWV (right) of binuclear complex **19** (c = 5x10^{-4}M) in CH_2Cl_2/CH_3CN (1:1) with 0.1 M of TBAHP as supporting electrolyte.

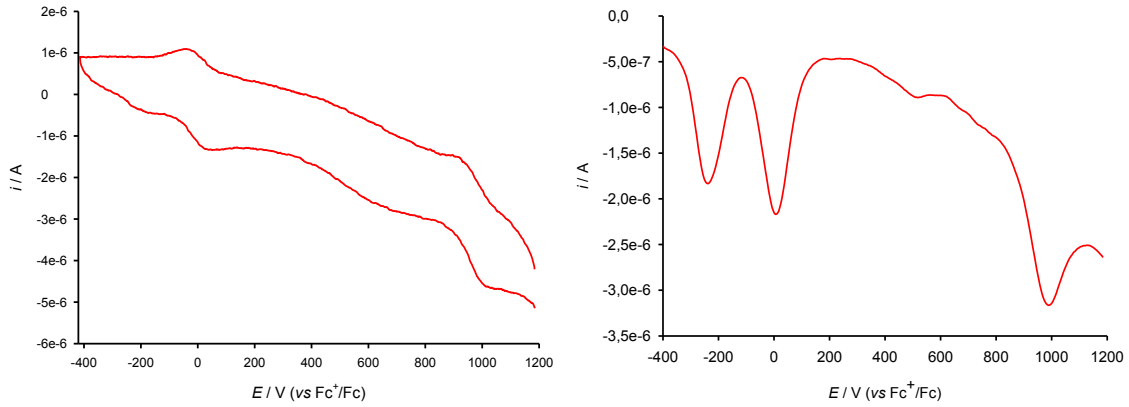


Figure S3. CV (left) and OSWV (right) of binuclear complex **13** (c = 5·10^{-4} M) in CH_2Cl_2/CH_3CN (1:1) with 0.1 M of TBAHP as supporting electrolyte.

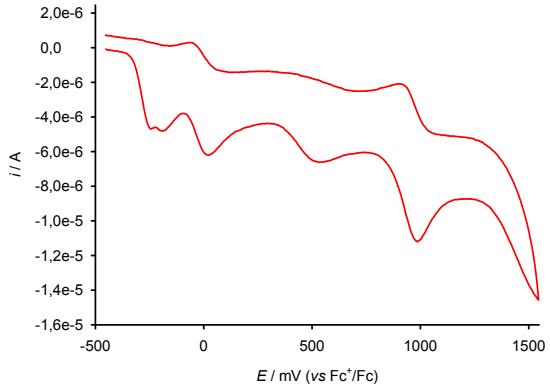


Figure S4. CV (left) of binuclear complex **12** (c = 5·10^{-4} M) in CH_2Cl_2/CH_3CN (1:1) with 0.1 M of TBAHP as supporting electrolyte.

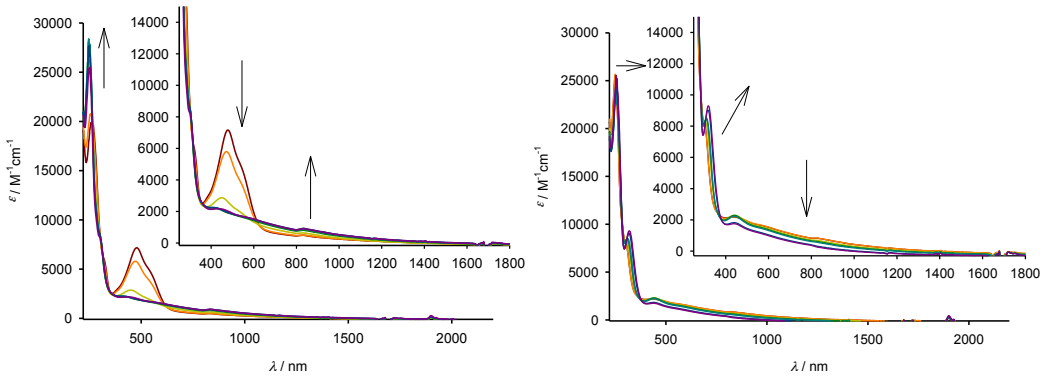


Figure S5. Evolution of UV-Vis-NIR spectra during the course of the oxidation of complex **12** (c = 5x10^{-4} M) in CH_2Cl_2/CH_3CN (1:1) with $[(nBu)_4N]PF_6$ (0.15 M) as supporting electrolyte when: a) 0<n<2 (left), or b) 2<n<4 (right) electrons are removed. Arrows indicate absorptions that increase or decrease during the experiment.

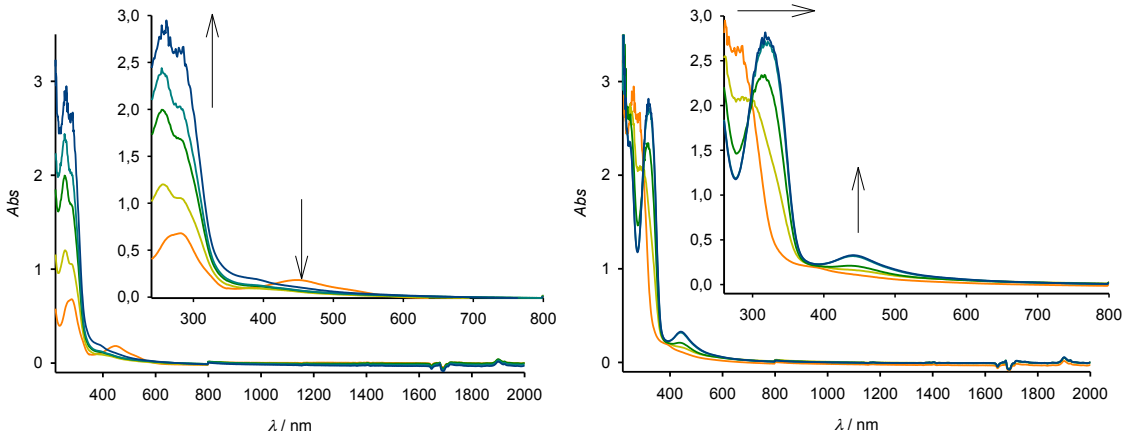


Figure S6. Evolution of UV-Vis-NIR spectra during the course of the oxidation of complex **13** (c = 5x10^{-4} M) in CH_2Cl_2/CH_3CN (1:1) with $[(nBu)_4N]PF_6$ (0.15 M) as supporting electrolyte when: a) 0<n<2 (left), or b) 2<n<4 (right) electrons are removed. Arrows indicate absorptions that increase or decrease during the experiment.

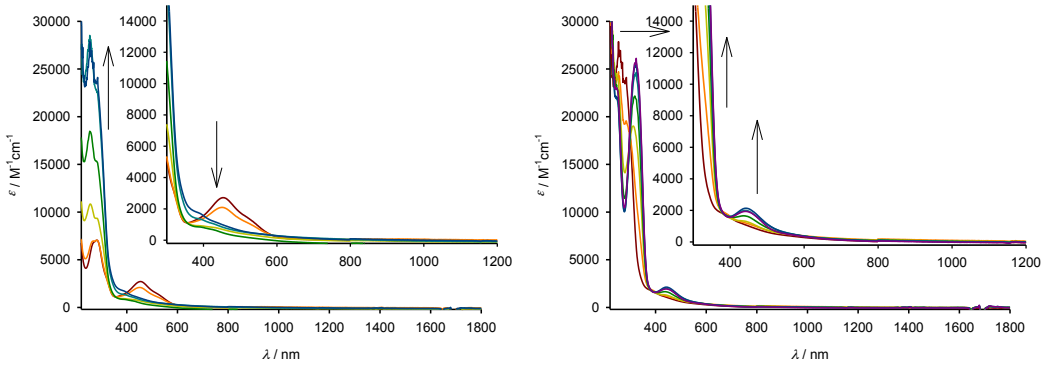


Figure S7. Evolution of UV-Vis-NIR spectra during the course of the oxidation of complex **19** (c = 5x10^{-4} M) in CH_2Cl_2/CH_3CN (1:1) with $[(nBu)_4N]PF_6$ (0.15 M) as supporting electrolyte when: a) 0<n<2 (left), or b) 2<n<4 (right) electrons are removed. Arrows indicate absorptions that increase or decrease during the experiment.

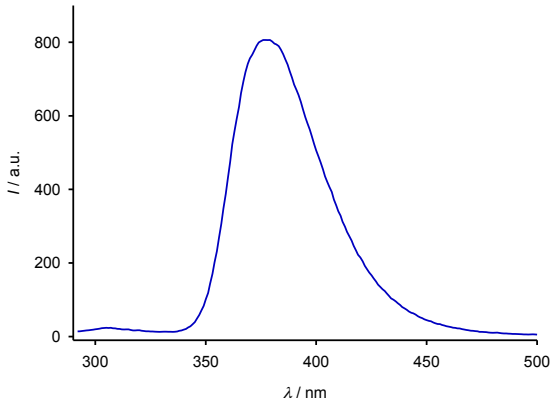


Figure S8. Emission spectrum of ligand **2** (c = 1 x 10^{-6} M) in dichloromethane/acetonitrile (1:1).

Computational Details:

Geometry optimizations without symmetry constraints were carried out using the Gaussian09 suite of programs[5] at the B3LYP[6]/def-SVP[7] and M06L[8]/def2-SVP levels of theory. Stationary points were characterized as minima by calculating the Hessian matrix analytically at this level. Nuclear independent chemical shift (NICS)[9] values have been computed using the gauge invariant atomic orbital (GIAO) method[10] at the GIAO-B3LYP/def2-SVP//B3LYP/def2-SVP level.

Donor-acceptor interactions have been computed using the natural bond orbital (NBO) method.[11] The energies associated with these two-electron interactions have been computed according to the following equation:

$$\Delta E^{(2)}_{\phi\phi^*} = -n_\phi \frac{\langle \phi^* | \hat{F} | \phi \rangle^2}{\varepsilon_{\phi^*} - \varepsilon_\phi}$$

where $\hat{F}$ is the DFT equivalent of the Fock operator and ϕ and ϕ^* are two filled and unfilled Natural Bond Orbitals having ε_ϕ y ε_{ϕ^*} and energies, respectively; n_ϕ stands for the occupation number of the filled orbital.

Cartesian coordinates (in Å) and total energies (in a. u., non corrected zero-point vibrational energies included) of all the stationary points discussed in the text. All calculations have been performed at the B3LYP/def2-SVP + ΔZPVE level of theory.

11M: E= -1970.104349

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C	-3.018531000	0.686538000	-0.134793000
C	-1.627326000	0.899805000	-0.137586000
H	-1.245337000	1.871374000	-0.447225000
C	-0.733271000	-0.113735000	0.215656000
C	-1.286068000	-1.358053000	0.576179000
H	-0.655937000	-2.191731000	0.888439000
C	-2.664376000	-1.513188000	0.571861000
H	-3.122749000	-2.459646000	0.859059000
C	-5.382050000	1.290637000	-0.430999000
C	-4.016310000	1.696017000	-0.506547000
C	-3.652314000	2.996026000	-0.918722000
H	-2.601357000	3.290820000	-0.973287000
C	-4.626646000	3.924905000	-1.265162000
H	-4.341409000	4.930144000	-1.584982000
C	-5.976880000	3.552230000	-1.198710000

H	-6.753367000	4.274596000	-1.468930000
C	-6.338407000	2.266766000	-0.790952000
H	-7.400875000	2.012921000	-0.751997000
Os	-5.732446000	-0.738142000	0.218232000
H	-5.370278000	-2.292321000	0.740757000
H	-6.935091000	-1.791525000	0.518792000
H	-7.269602000	-0.243225000	0.001213000
P	-5.791958000	-1.499000000	-1.994052000
H	-6.280245000	-0.645506000	-3.023414000
H	-4.592082000	-1.900037000	-2.653779000
H	-6.564652000	-2.647114000	-2.315167000
P	-5.949702000	-0.054560000	2.445507000
H	-6.761894000	-0.813796000	3.329985000
H	-4.803259000	0.037869000	3.289988000
H	-6.489469000	1.228497000	2.743909000
P	5.791911000	1.498892000	-1.994083000
H	4.592061000	1.900442000	-2.653545000
H	6.565037000	2.646650000	-2.315430000
H	6.279573000	0.645115000	-3.023505000
P	5.949762000	0.054472000	2.445484000
H	6.489530000	-1.228615000	2.743753000
H	6.762039000	0.813634000	3.329950000
H	4.803387000	-0.037992000	3.290055000

12M^{2+}: E= -2512.005346

Os	-5.717182000	-0.655909000	0.187759000
H	-5.461938000	-2.305058000	0.103157000
H	-7.132157000	-1.452030000	0.134544000
H	-7.246529000	-0.120252000	0.074033000
N	-3.519670000	-0.488669000	0.300361000
C	-3.002002000	0.718679000	-0.061104000
C	-1.612264000	0.923093000	-0.046883000
H	-1.218203000	1.886612000	-0.367521000
C	-0.736650000	-0.102789000	0.327276000
C	-1.306668000	-1.336630000	0.694484000
H	-0.692580000	-2.175999000	1.022709000
C	-2.687399000	-1.480943000	0.669791000
H	-3.154150000	-2.424619000	0.957611000
C	-5.357082000	1.300287000	-0.538499000
C	-3.994211000	1.723577000	-0.466409000

C	-3.658927000	3.059189000	-0.744353000
H	-2.628252000	3.407179000	-0.649412000
C	-4.641514000	3.969808000	-1.136129000
H	-4.368077000	5.004438000	-1.354206000
C	-5.972500000	3.552475000	-1.262255000
H	-6.741433000	4.262225000	-1.576773000
C	-6.318695000	2.226571000	-0.991299000
H	-7.359774000	1.918901000	-1.114877000
N	3.519672000	0.488654000	0.300369000
C	3.002002000	-0.718674000	-0.061162000
C	1.612263000	-0.923089000	-0.046945000
H	1.218201000	-1.886589000	-0.367636000
C	0.736652000	0.102772000	0.327277000
C	1.306672000	1.336593000	0.694551000
H	0.692587000	2.175943000	1.022827000
C	2.687403000	1.480907000	0.669858000
H	3.154155000	2.424567000	0.957729000
C	5.357081000	-1.300258000	-0.538592000
C	3.994209000	-1.723549000	-0.466528000
C	3.658923000	-3.059144000	-0.744555000
H	2.628246000	-3.407137000	-0.649637000
C	4.641507000	-3.969741000	-1.136386000
H	4.368069000	-5.004357000	-1.354528000
C	5.972495000	-3.552403000	-1.262483000
H	6.741427000	-4.262136000	-1.577043000
C	6.318692000	-2.226517000	-0.991446000
H	7.359772000	-1.918841000	-1.115002000
Os	5.717182000	0.655898000	0.187774000
H	5.461943000	2.305051000	0.103255000
H	7.132162000	1.452016000	0.134603000
H	7.246531000	0.120247000	0.074024000
P	5.728914000	1.146062000	-2.156837000
H	6.427802000	0.267966000	-3.018098000
H	4.475138000	1.202494000	-2.815714000
H	6.276310000	2.390785000	-2.541561000
P	5.974319000	0.782536000	2.583871000
H	6.956988000	1.680869000	3.060385000
H	4.867919000	1.168585000	3.382417000
H	6.364833000	-0.400981000	3.261301000
P	-5.728911000	-1.145951000	-2.156878000
H	-4.475134000	-1.202343000	-2.815757000

H	-6.276303000	-2.390655000	-2.541668000
H	-6.427802000	-0.267811000	-3.018094000
P	-5.974321000	-0.782675000	2.583848000
H	-6.364857000	0.400798000	3.261341000
H	-6.956974000	-1.681052000	3.060312000
H	-4.867915000	-1.168748000	3.382375000

12M^{4+}: E= -2511.110345

Os	5.688969000	0.571894000	0.191493000
H	5.587905000	1.442334000	1.553243000
H	7.366732000	0.903794000	0.467219000
H	7.355100000	0.314175000	-0.211164000
N	3.534280000	0.454667000	0.242978000
C	3.010112000	-0.673815000	-0.318577000
C	1.621981000	-0.874404000	-0.359468000
H	1.239016000	-1.782258000	-0.825840000
C	0.741378000	0.078324000	0.179051000
C	1.316225000	1.224056000	0.762130000
H	0.707854000	1.994641000	1.238040000
C	2.699511000	1.371480000	0.774602000
H	3.154596000	2.251224000	1.233602000
C	5.379450000	-1.365827000	-0.459934000
C	4.021590000	-1.609431000	-0.832806000
C	3.750407000	-2.655420000	-1.722865000
H	2.734841000	-2.826301000	-2.086704000
C	4.784907000	-3.478329000	-2.193517000
H	4.552751000	-4.297134000	-2.879184000
C	6.106448000	-3.264867000	-1.790110000
H	6.908871000	-3.909920000	-2.157146000
C	6.401293000	-2.232366000	-0.889457000
H	7.433645000	-2.112968000	-0.548179000
N	-3.534503000	-0.498478000	0.167168000
C	-3.013977000	0.746886000	-0.036985000
C	-1.625738000	0.951228000	-0.034359000
H	-1.245196000	1.955691000	-0.220693000
C	-0.741095000	-0.122770000	0.158816000
C	-1.311265000	-1.397737000	0.339099000
H	-0.698384000	-2.284284000	0.508749000
C	-2.695127000	-1.539853000	0.342919000
H	-3.147119000	-2.521362000	0.497846000

C	-5.370982000	1.350832000	-0.479941000
C	-4.028242000	1.788197000	-0.261089000
C	-3.778145000	3.163557000	-0.185647000
H	-2.777872000	3.534342000	0.047935000
C	-4.815411000	4.089493000	-0.373190000
H	-4.598798000	5.159501000	-0.322126000
C	-6.120049000	3.657408000	-0.630488000
H	-6.924874000	4.382138000	-0.777875000
C	-6.392948000	2.286238000	-0.725124000
H	-7.409740000	1.969717000	-0.974930000
Os	-5.691206000	-0.584727000	0.171737000
H	-5.546905000	-2.105651000	-0.365541000
H	-7.362156000	-1.033068000	0.080869000
H	-7.365676000	-0.147099000	0.233761000
P	-5.872503000	-0.669564000	-2.198008000
H	-6.712970000	0.274176000	-2.827769000
H	-4.647826000	-0.540385000	-2.890119000
H	-6.376734000	-1.908736000	-2.655097000
P	-5.899395000	-1.873186000	2.293383000
H	-7.001148000	-2.754957000	2.374030000
H	-4.818392000	-2.681179000	2.713794000
H	-6.101395000	-1.028613000	3.414158000
P	5.805866000	2.891878000	-0.704548000
H	4.731973000	3.777866000	-0.459926000
H	6.932770000	3.650190000	-0.313398000
H	5.899895000	2.913361000	-2.119085000
P	5.996154000	-0.808198000	2.103072000
H	6.860578000	-1.917640000	1.979759000
H	6.536429000	-0.095638000	3.198196000
H	4.810046000	-1.365234000	2.630239000

References

1. D. L. Comims, N. B. Mantlo, *J. Org. Chem*. 1985, **50**, 4410

2. L. L. Matz, D. O. Buchanan, *Proceedings of the International Technical Conference on Coal Utilization and Fuel Systems* 1997, **22**, 275

3. M. Aracama, M. A. Esteruelas, F. J. Lahoz, J. A. López, U. Meyer, L. A. Oro, H. Werner, *Inorg. Chem.* 1991, **30**, 288

4. W. R. Dawson; M. W. Windsor, *J. Phys. Chem.* 1968, **72**, 3251

5. Gaussian 09, Revision B.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

6. (a) A. D. Becke, *J. Chem. Phys*. 1993, **98**, 5648. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1998**, *37*, 785.

7. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297.

8. Y. Zhao, D. G. Truhlar, *Acc. Chem. Res*. **2008**, *41*, 157.

9. Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev*. 2005, **105**, 3842.

10. K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc*. 1990, **112**, 8251.

11. (a) J. P. Foster, F. Weinhold, *J. Am. Chem. Soc*. 1980, **102**, 7211; (b) A. E. Reed, F. J. Weinhold, *J. Chem. Phys*. 1985, **83**, 1736; (c) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys*. 1985, **83**, 735; (d) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev*. 1988, **88**, 899.