Supporting Information for

Helicene-grafted vinyl- and carbene-osmium complexes: an example of acid-base chiroptical switching

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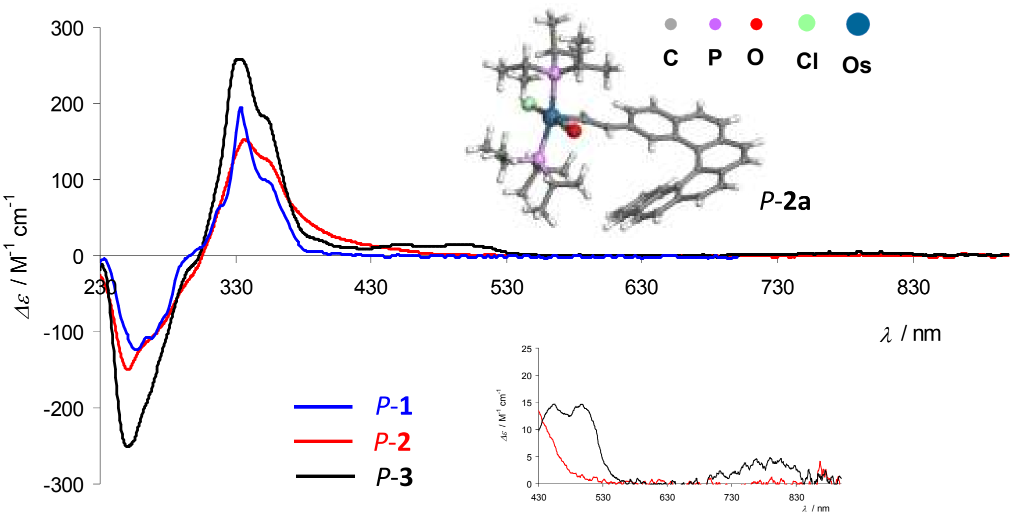

Figure 1. CD spectra of *P*-**1a** (blue) *vs.P*-**2** (red) and*P*-**3** (black) in CH_2Cl_2 (*C* 1-5 10^{-5} M^{-1}). Inserts: low-energy CD spectra of *P*-**2**,**3**. X-ray structure of complex **2** (one enantiomer shown).

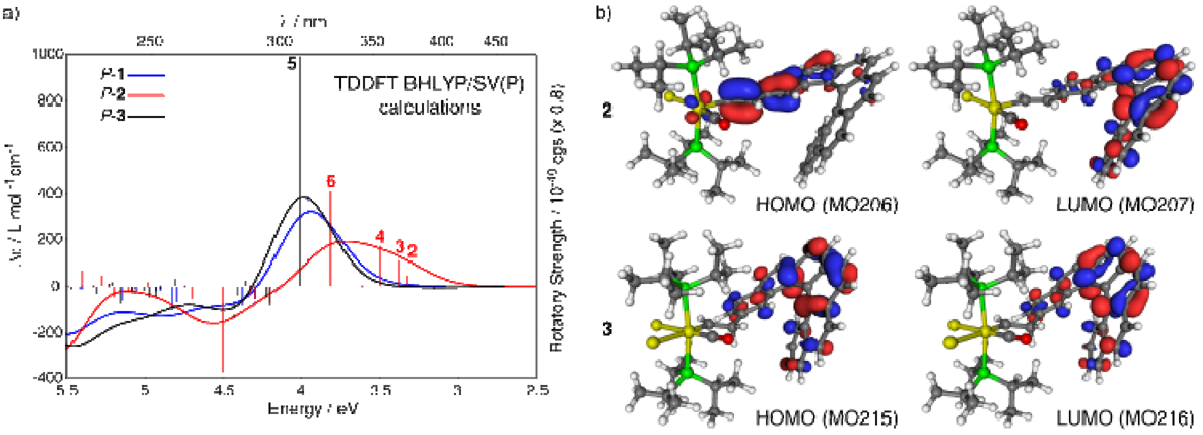

Figure 2. a) Calculated CD spectra of *P*-**1** (blue), *P*-**2** (red), and *P*-**3** (black)BHLYP/SV(P). b) Isosurfaces (0.04 au) of frontier MOs of **2** and **3**.

Computational details

All calculations were performed for the *P*-(+) isomers without imposing symmetry.DFT geometry optimizations were carried out with the Turbomole package version 5.7.1.[1,2] employing the BP functional[3-5] and the SV(P) basis set which affords one set of polarization functions for non-hydrogen atoms.[6,7] For the Os atoms, a 60-electron scalar relativistic effective core potential was used.[8]Geometry optimizations for the carbene osmium complex **3** were performed for both the lowest-energy singlet and triplet electronic states. The results show a clear energetic preference of the singlet, by around 40 kcal/mol (BP/SV(P)). For comparison, geometry optimizations for the free carbene ligand in the singlet and triplet states was also carried out. Here, only the triplet was found to be stable. All attempts to obtain an optimized singlet geometry failed. Due to an isomerization process, the singlet optimizations led to a 2-vinyl-[6]helicene system.

Time-dependent DFT (TDDFT) optical rotation (OR) and circular dichroism (CD) calculations for **2** and **3** (singlet states) were performed with the BHLYP functional[9,10] and the SV(P) basis set. The optical rotation parameters were computed at the sodium *D*-line wavelength λ = 589.3 nm. The CD calculations reported here cover 120 and 60 lowest singlet and triplet excited states, respectively. Additional OR and CD calculations were performed with the NWChem package[11,12] at the LC-PBE0[13-15]/SV(P) level. The simulated spectra shown are the sums of Gaussian functions centered at the vertical singlet excitation energies and scaled using the calculated rotatory strengths as previously described in Reference 16. For the root mean square width, the parameter of σ = 0.2 eV was used in all cases. The BHLYP/SV(P)//BP/SV(P) data for the parent helicene ligand, labeled here as **1**, were taken from Reference 17.

As it was recently emphasized by Peach et al., TDDFT calculations, especially with functionals incorporating a large amount of exact exchange, may significantly underestimate triplet excitation energies due to an underlying triplet (near-)instability of the ground state.[18,19] The proposed approach[18,20] that is assumed to eliminate most of the problem and provide much improved triplet excitations is the use of the Tamm-Dancoff approximation (TDA).[21,22] Both full TDDFT and TDDFT/TDA triplet excitation computations were performed for the Os systems studied here. Test calculations employing TDA were also carried out for singlet excitations at the BHLYP/SV(P) level. The singlet ground-state of the osmium systems was indeed confirmed to have a triplet instability at the Hartree-Fock (HF) level. This may render TDDFT results obtained with functionals incorporating a large amount of exact exchange (both BHLYP and LC-PBE0) unreliable. As clearly visible in Figure S1 and Tables S2-S3, a comparison of the full TDDFT and TDDFT/TDA results shows the expected behavior, namely a pronounced blue-shift of the triplet excitations after applying TDA. Although successful performance of the TDA approach have been emphasized in recent benchmark studies,[18,19,23] we note in passing that in some cases – including ligand-field transitions in some metal complexes – the TDA method may also result in undesirable blue shifts of electronictransitions.[24-27]An un-wanted blue-shift can in fact also be observed when comparing BHLYP/SV(P) singlet results for TDDFT and TDDFT/TDA (Figure S1). Further in-depth studies are thus needed to assess the performance of the TDA approximation, in particular in conjunction with hybrid functionals, for metal complexes such as the systems studied here.

Additional calculated data

Table S1. Experimental and calculated molar rotations, $[\phi]_D$, (in degree cm^2/dmol) of enantiopure ethynyl-[6]helicene *P*-**1** and the corresponding vinyl- and carbene-osmium(II)-grafted helicene derivatives, *P*-**2**, and -**3**.

	1	**2**	**3**
BHLYP	17002	23915	17557
LC-PBE0 [a]	13800	17435	14173
Expt. (23°C)	11030	18000	9600

[a] Modified velocity gauge (MVG)[28] used in the calculations.

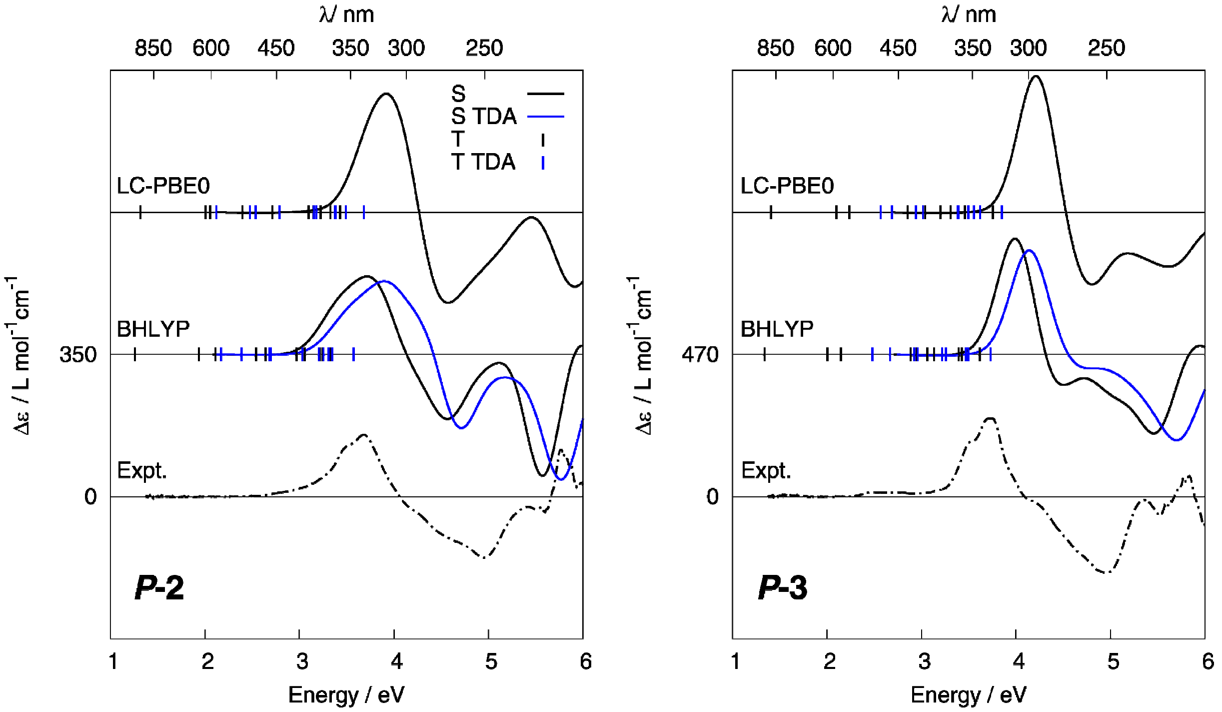

Figure S1. Comparison of the experimental (dashed lines) and TDDFT (solid lines) CD spectra of *P*-**2** and *P*-**3** with indication of the lowest ten triplet (T) excitations (TDDFT – black, TDDFT/TDA – blue). No spectral shift has been applied. SV(P) basis set used in the calculations.

Table S2. The BHLYP/SV(P) lowest ten triplet excitation energy values of *P*-**2** and -**3**.

Excitation	TDDFT		TDDFT/TDA	
	E / eV	*λ* / nm	*E* / eV	*λ* / nm
		2		
#1	1.26	982	2.17	571
#2	1.94	640	2.39	520
#3	2.11	587	2.69	462
#4	2.54	488	2.70	459
#5	2.64	469	3.03	409
#6	2.97	418	3.21	387
#7	3.06	406	3.26	381
#8	3.21	386	3.31	374

#9	3.25	382	3.34	371
#10	3.33	372	3.57	347
		3		
#1	1.34	927	2.48	500
#2	2.00	619	2.67	465
#3	2.15	578	2.92	424
#4	2.89	430	2.96	419
#5	2.95	421	3.22	385
#6	3.06	405	3.26	381
#7	3.13	396	3.47	358
#8	3.40	365	3.47	357
#9	3.43	362	3.50	355
#10	3.61	343	3.73	332

Table S3. The LC-PBE0/SV(P) lowest ten triplet excitation energy values of *P*-**2** and -**3**.

Excitation	TDDFT		TDDFT/TDA	
	E / eV	λ / nm	E / eV	λ / nm
		2		
#1	1.32	939	2.12	585
#2	2.00	619	2.48	500
#3	2.06	603	2.54	488
#4	2.40	517	2.79	445
#5	2.71	457	3.15	393
#6	3.10	400	3.18	390
#7	3.15	394	3.37	368
#8	3.23	384	3.38	366
#9	3.33	373	3.49	355
#10	3.43	362	3.68	337
		3		
#1	1.41	881	2.57	483

#2	2.10	590	2.69	461
#3	2.23	555	2.94	422
#4	2.85	435	3.02	411
#5	3.04	408	3.38	367
#6	3.20	387	3.39	366
#7	3.31	375	3.49	355
#8	3.46	359	3.56	349
#9	3.46	358	3.62	342
#10	3.75	330	3.85	322

Table S4. Selected dominant singlet excitations and occupied (occ) – unoccupied (unocc) molecular orbital (MO) pair contributions (greater than 10%) of *P*-**2** and -**3**. TDDFT BHLYP/SV(P) calculations.

Excitation	E / eV	λ / nm	R / 10^{-40} cgs	occ no.	unocc no.	%
			2			
#2	3.32	373	62.22	202	209	78.0
#3	3.38	367	141.87	206	207	65.1
				205	208	11.1
				204	207	10.3
#4	3.50	354	212.12	206	208	60.3
				205	207	15.7
#6	3.81	319	515.43	205	208	36.6
				205	207	35.7
			3			
#5	4.02	309	1236.94	215	218	49.6
				214	216	34.6

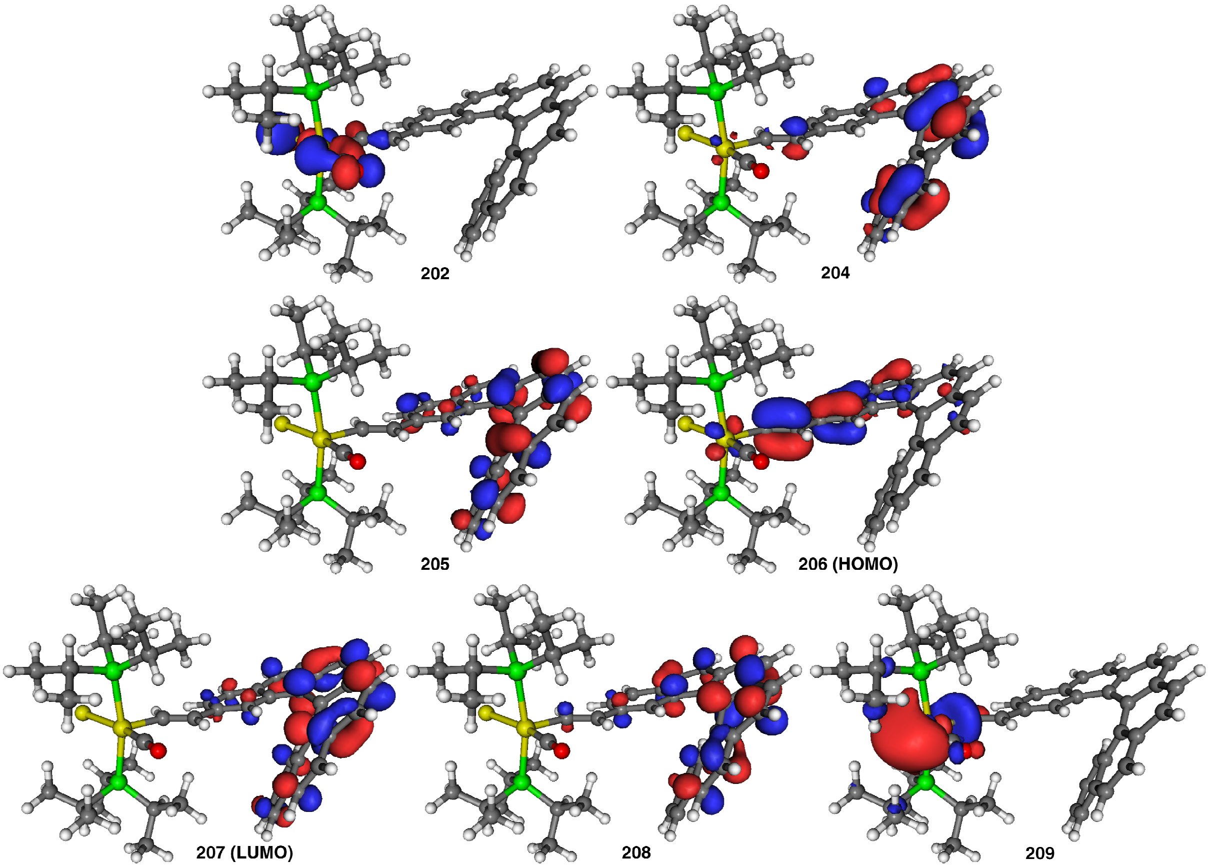

Figure S2. Isosurfaces (0.04 au) of MOs involved in selected transitions of *P*-**2**.

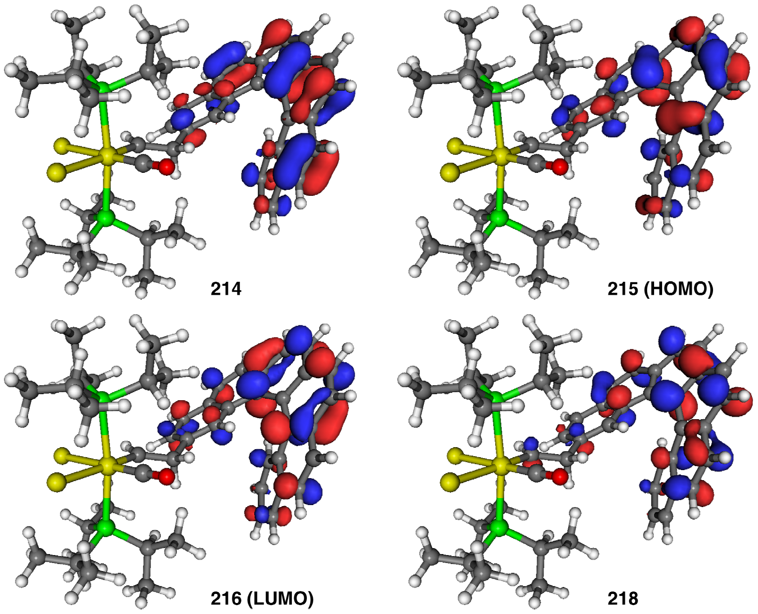

Figure S3. Isosurfaces (0.04 au) of MOs involved in selected transitions of *P*-**3**.

Optimized BP/SV(P) geometries of complexes 2 and 3

The atomic symbol followed by three Cartesian coordinates, in Å.

2

Os	-1.0894743	2.3568376	-0.3292936
Cl	-1.2074644	3.8446959	-2.2987874
P	0.8614986	3.6874491	0.3461107
P	-3.2945101	1.4640898	-1.0001629
O	-1.2633643	1.3103815	2.5049771
C	-0.0513923	0.7685032	-0.9904201
H	0.1214960	0.9294563	-2.0788828
C	0.4705382	-0.3624419	-0.4253996
H	0.3448518	-0.5280546	0.6609370
C	1.2579879	-1.3916979	-1.1171375
C	1.4577127	-1.3984210	-2.5356954
H	0.9500586	-0.6500962	-3.1651463
C	2.3068261	-2.3175389	-3.1266832
H	2.4859128	-2.2814480	-4.2152087
C	3.0015203	-3.2975323	-2.3579579
C	4.0006701	-4.1277751	-2.9578502
H	4.1656154	-4.0592276	-4.0465269
C	4.8048321	-4.9242404	-2.1736017
H	5.6457560	-5.4850274	-2.6150045
C	4.5826905	-5.0316794	-0.7592448
C	5.5399996	-5.7170343	0.0563874
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C	5.4199688	-5.7046346	1.4280853
H	6.2169448	-6.1152341	2.0706371
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C	3.1402036	-4.7284412	1.2348823
C	3.4412469	-4.4034266	-0.1546499
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C	1.8809290	-2.4107417	-0.3688351
H	1.7323714	-2.4103093	0.7210979
C	-1.1969324	1.6610088	1.3763498
C	0.2555640	5.2934671	1.1644530
H	1.1550466	5.7300503	1.6526982
C	-0.2956727	6.3309023	0.1701664
H	0.4886352	6.7235343	-0.5111804
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3

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H	-5.2992453	1.9377259	-4.1021873
H	-5.9531131	2.0248613	-0.3377852
H	-5.2519487	4.0346769	-1.6619907
H	-4.3450926	4.6656537	-0.2406566
H	-6.1421162	4.5022785	-0.1776187
H	-5.1875886	1.5971297	2.0051823
H	-6.0926037	3.1398376	1.8951458
H	-4.2935588	3.1689589	2.0061635
H	-1.2385191	-1.0466626	-0.8422189
H	-0.1397218	-0.7468481	0.5087367

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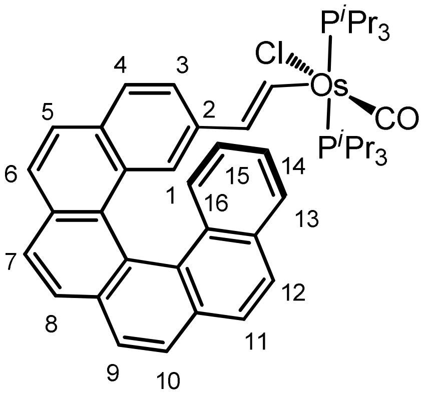
Synthesis

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran, diethyl ether) or from phosphorus pentoxide (pentane, dichloromethane). Preparative separations were performed by gravity column chromatography on basic alumina (Aldrich, Type 5016A, 150 mesh, 58 Å) or silica gel (Merck Geduran 60, 0.063-0.200 mm) in 3.5-20 cm columns. SEC separations were conducted on Bio-beads S-X beads from Bio-Rad. ^{1}H, ^{13} C, and ^{31} P NMR spectra were recorded on a Bruker AM300, AV400 or AV500. ^{1}H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 and were decoupled from the proton. Assignment of proton atoms is based on COSY experiment. Assignment of carbon atoms is based on HMBC, HMQC and DEPT-135 experiments. Elemental analyses were performed by the CRMPO, University of Rennes 1. Specific rotations (in deg cm^2 g^{-1}) were measured in a 1 dm thermostated quartz cell on a Perkin Elmer-341 polarimeter. Circular dichroism (in M^{-1} cm^{-1}) was measured on a Jasco J-815 Circular Dichroism Spectrometer (IFR140 facility - Université de Rennes 1). UV/vis/NIR spectroscopy was conducted on a Varian Cary 5000 spectrometer.

P-(+) and *M*-(-)-2-Ethynylcarbo[6]helicene **1**,[1] and $OsHClCO(P\textit{i}Pr_3)_2$[2] were prepared according to literature procedures.

Complex (±)-2.



To a solution of 2-ethynylcarbo[6]helicene (±)-**1** (20 mg, 0.05 mmol) in 2 mL of toluene under argon was added $OsHClCO(P^iPr_3)_2$[2] (33 mg, 0.05mmol) and the reaction mixture was stirred for 3 days at room temperature. (±)-**2** (37 mg, 70%) was obtained as a red solid after precipitation using cold pentane.

The same procedure was applied to enantioenriched *P*-(+) and *M*-(-)-1[1] to prepare *P*-(+) and *M*-(-)-**2a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-8.10 (m, 7H), 7.88-7.76 (m, 3H), 7.71-7.65 (m, 2H), 7.24-7.16 (m, 2H), 6.90 (s, 1H), 6.72 (ddd, 1H, J = 8.4, 6.9, 1.4 Hz, H^{15}), 4.80 (dt, 1H, $^3J_{H\text{-}H}$ = 13.4 Hz, $^3J_{P\text{-}H}$ = 1.8 Hz, OsCH=C*H*), 2.82 (m, 6H, PC*H*), 1.34-1.21 (m, 18H, C*H* ^{i}Pr), 1.20-1.07 (m, 18H, C*H*$_3$ ^{i}Pr).

^{31}P NMR (121 MHz, $CDCl_3$) δ 23.96 (s), 23.92 (s).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 182.2 (t, $^2J_{P\text{-}C}$ = 9.1 Hz, *C*O), 136.8 (t, $^4J_{P\text{-}C}$ = 1.6 Hz, *C*), 133.9 (t, $^3J_{P\text{-}C}$ = 3.8 Hz, OsCH=*C*H), 133.2 (*C*), 132.1 (*C*), 131.9 (*C*), 131.4 (*C*), 130.9 (*C*), 130.2 (*C*), 129.4 (*C*), 128.4 (*C*), 128.3

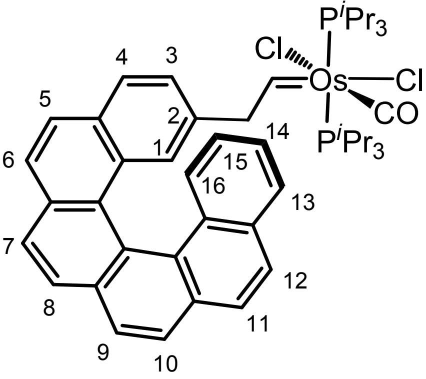
(*C*), 128.2 (*C*H), 128.0 (*C*H), 127.9 (*C*H), 127.6 (*C*H), 127.5 (*C*H), 127.4 (*C*H), 127.3 (*C*H), 126.9 (*C*H), 126.7 (*C*H), 126.5 (*C*H), 125.7 (*C*H), 124.7 (*C*H), 124.4 (*C*), 124.3 (*C*H), 123.0 (*C*H), 122.7 (*C*H), 121.1 (t, $^2J_{\text{P-C}}$ = 7.7 Hz, Os*C*H=CH), 24.9 (dt, *J* = 13.7, 10.4 Hz, *C*H ^{i}Pr x 6), 20.1 (*C*H$_3$ ^{i}Pr x 3), 20.0 (*C*H$_3$ ^{i}Pr x 3), 19.9(*C*H$_3$ ^{i}Pr x 3), 19.5(*C*H$_3$ ^{i}Pr x 3).

Elemental analysis, calcd. (%) for $C_{47}H_{59}ClOP_2Os$: C 60.86, H 6.41; found : C 59.91, H 6.55. Calculated for **2**.H_2O: C, 59.70; H, 6.50.

UV/Vis (2 10^{-5} M, CH_2Cl_2): 316 (46300), 341 (32000), 357 (22400), 396 (12800), 504 (1030).

IR (ν_{CO}) 1893 cm^{-1}.

Carbene-osmium complex (±)-3.



To a solution of complex (±)-**2** (20 mg, 0.022 mmol) in 2 mL of toluene under argon was added a toluene HCl solution (0.01M, 2.5 mL, 0.025mmol) and the reaction mixture was stirred for 10 minutes at room temperature. Complex (±)-**3** (18 mg, 86%) was obtained as a yellow solid after evaporation of the solvent and purification by size exclusion chromatography (toluene).

The same procedure was applied to enantioenriched *P*-(+)-**2** to prepare *P*-(+)-**3**.

^{31}P NMR (162 MHz, C*D*$_2$Cl$_2$) δ 11.13 (s).

^{1}H NMR (300 MHz, *C*D$_2$Cl$_2$) δ 18.07 (t, 1H, *J* = 6.6 Hz, C*H*=Os), 8.16-8.02 (m, 3H), 8.02-7.94 (m, 2H), 7.91 (d, 1H, *J* = 7.7 Hz), 7.86 (d, 1H, *J* = 8.2 Hz), 7.61 (d, 1H, *J* = 8.2 Hz), 7.54 (s, 1H), 7.33-7.12 (m, 5H), 6.71 (t, 1H, *J* = 7.2 Hz), 3.13 (dd, 1H, *J* = 18.4, 7.7 Hz), 2.85 (dd, 1H, *J* = 18.3, 5.4 Hz), 2.76-2.54 (m, 3H, C*H* ^{i}Pr), 2.51-2.27 (m, 3H, C*H* ^{i}Pr), 1.33-0.97 (m, 24H, C*H*$_3$ ^{i}Pr), 1.05 (dd, 6H, *J* = 13.7, 7 Hz, C*H*$_3$ ^{i}Pr), 0.88 (dd, 6H, *J* = 13.7, 7 Hz, C*H*$_3$ ^{i}Pr).

^{13}C NMR (75 MHz, C*D*$_2$Cl$_2$) δ 296.7 (dd, $^2J_{\text{P-C}}$ = 8, 5 Hz, Os=*C*H), 178.4 (t, $^2J_{\text{P-C}}$ = 9.2 Hz, *C*O), 137.2 (*C*), 133.9 (*C*), 132.4 (*C*), 131.1 (*C*), 130.8 (*C*), 130.7(*C*), 130.0 (*C*), 129.1 (*C*), 129.0 (*C*), 128.2 (*C*H), 127.4 (*C*H), 127.3 (*C*H), 126.9 (*C*H), 126.8 (CH), 126.7 (*C*H), 126.5 (*C*H), 126.3 (*C*H), 126.2 (C), 125.6 (*C*H), 125.4 (*C*H), 125.0 (*C*H), 124.9 (*C*H), 124.5 (*C*H), 123.8 (*C*H), 123.1 (*C*), 66.5 (*C*H$_2$), 24.5 (d, $^1J_{\text{P-C}}$ = 13.1 Hz, *C*H ^{i}Pr), 24.2 (d, $^1J_{\text{P-C}}$ = 13.1 Hz, *C*H ^{i}Pr), 20.4 (*C*H$_3$ ^{i}Pr), 18.7 (d, $^2J_{\text{P-C}}$= 12.4 Hz, *C*H$_3$ ^{i}Pr), 18.2 (d, $^2J_{\text{P-C}}$= 11 Hz, *C*H$_3$ ^{i}Pr), 15.5 (*C*H$_3$ ^{i}Pr).

UV/Vis (2 10^{-5} M, CH_2Cl_2): 315 (35500), 349 (21000), 385 (7000), 430 (6400), 497 (4950), 780 (3000).

IR (ν_{CO}) 1932 cm^{-1}.

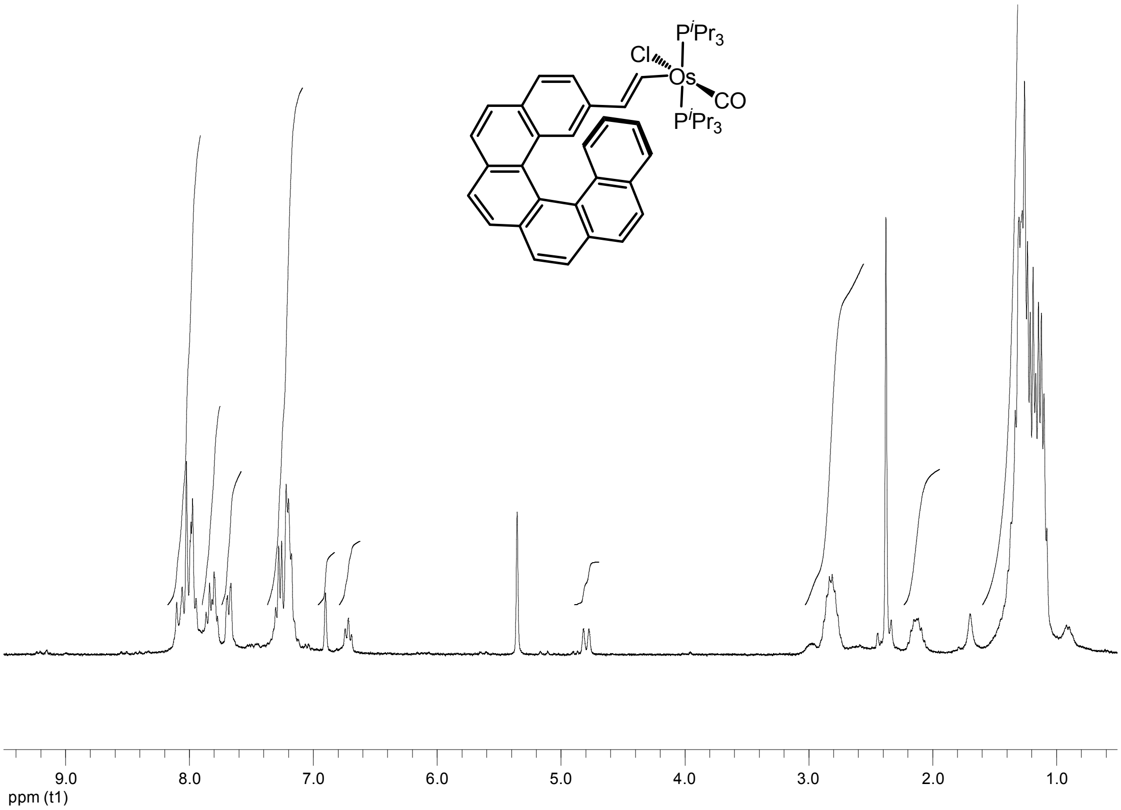


Figure S1. ^{1}H NMR spectrum in CD_2Cl_2 of vinyl-osmium helicene complex **2**

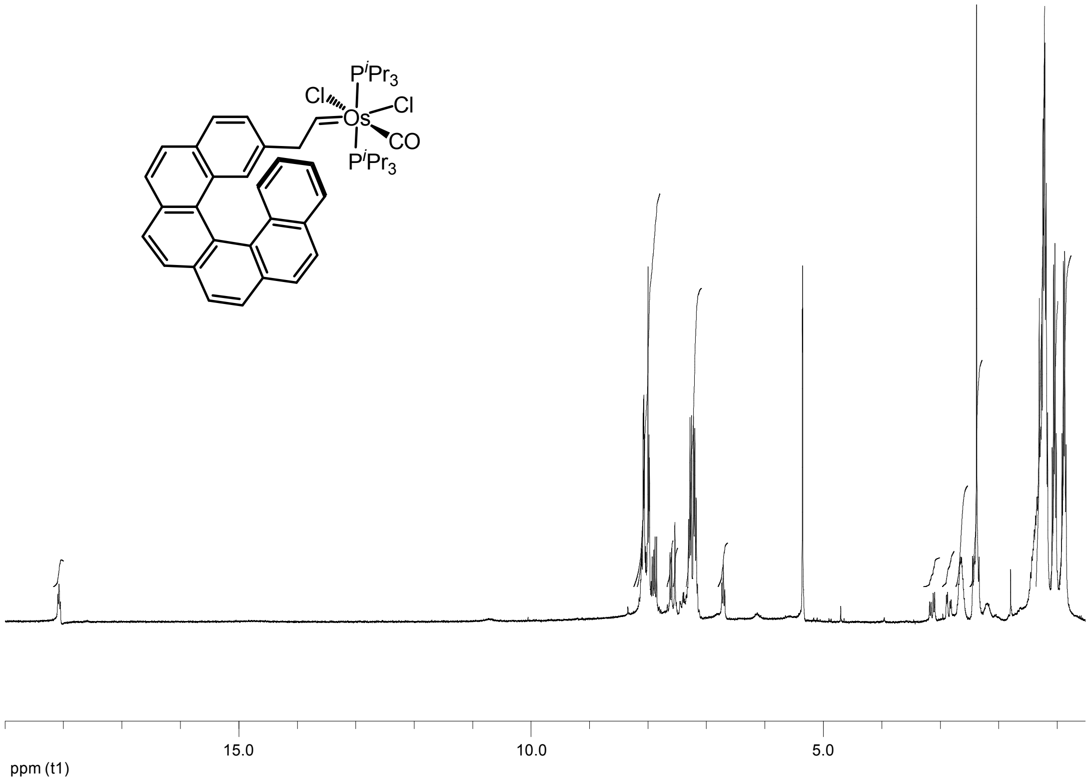


Figure S2. ^{1}H NMR spectrum in CD_2Cl_2 of carbene-osmium helicene complex **3**

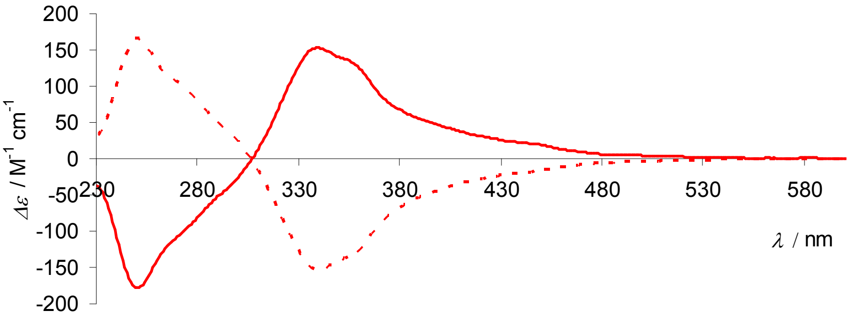


Figure S3. ECD spectra in CH_2Cl_2 (5 10^{-5} M) of vinyl-osmium helicene complexes *P*- and *M*-**2**

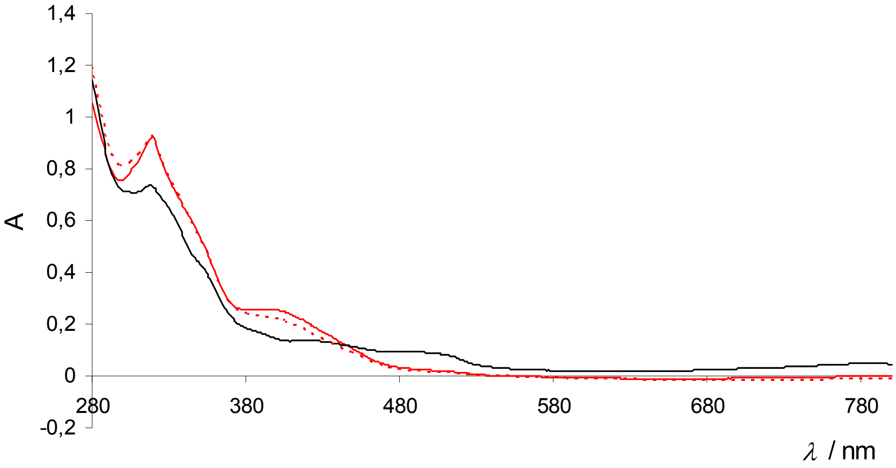


Figure S3. Reversibility test of the (carbene/vinyl)-osmium **2**↔ **3** transformation. UV-vis spectra of vinyl-Os-helicene **2** (plain red lines), carbene-Os-helicene **3,** and UV-vis spectrum obtained after **3**→**2** transformation in dashed red lines.

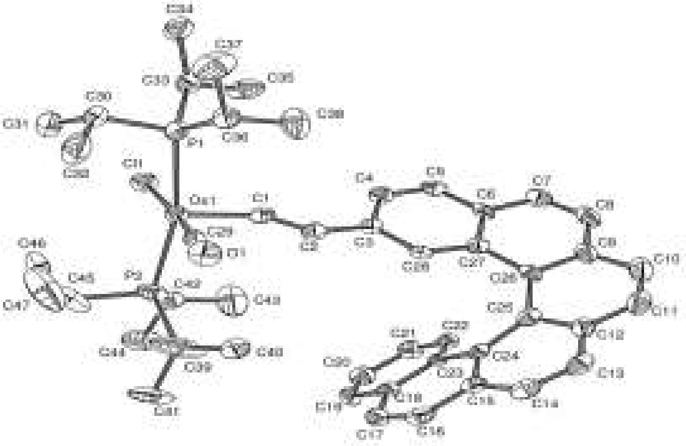


Figure S4. ORTEP diagram of Osmium (II) complex (±)-**2** with ellipsoids at 50% probability.

Table S5. Crystal data and structure refinement for (±)-**2**.

Identification code	**2**
CCDC	870662
Empirical formula	C47 H59 Cl O Os P2
Formula weight	927.53
Temperature	163(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.8261(3) A alpha = 83.893(2)deg. b = 13.8895(3) A beta = 78.095(2)deg. c = 14.4115(3) A gamma = 86.848(2)deg.
Volume	2107.18(9) A^3
Z, Calculated density	2, 1.462 Mg/m^3
Absorption coefficient	3.199 mm^-1
F(000)	944
Crystal size	0.288 x 0.176 x 0.147 mm
Theta range for data collection	2.63 to 27.00 deg.
Limiting indices	-12<=h<=13, -17<=k<=17, -18<=l<=18
Reflections collected / unique	21911 / 8436 [R(int) = 0.0603]
Completeness to theta = 27.00	91.7 %
Absorption correction	Analytical
Max. and min. transmission	0.71718 and 0.55591
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8436 / 0 / 469
Goodness-of-fit on F^2	0.923
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0693
R indices (all data)	R1 = 0.0596, wR2 = 0.0726
Largest diff. peak and hole	1.354 and -1.126 e.A^-3

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