SUPPORTING INFORMATION

Photophysics of Tungsten Benzylidyne complexes derived form *s*-indacene: Synthesis, Characterization and DFT Studies

Cesar A. Morales-Verdejo,*[a] Ximena Zarate,[b] Eduardo Schott,[a] Sebastián Correa,[a] Iván Martinez-Díaz,[a]

a).- Universidad Bernardo O Higgins, Departamento de Ciencias Químicas y Biológicas, Laboratorio de Bionanotecnología, General Gana 1780, Santiago, Chile .
b).- Dirección de Postgrado e Investigación, Universidad Autónoma de Chile, Av. Pedro de Valdivia 641, Santiago, Chile.

Contents

Table S6. Cartesian Coordinates (Å) of DFT Optimized Geometry of **1***
Table S7. Cartesian Coordinates (Å) of DFT Optimized Geometry of **2***

D. References

A. Syntheses, Spectra, and Reactions

General Procedures. All manipulations were carried out under pure dinitrogen atmosphere using a Vacuum Atmospheres drybox equipped with a Model HE 493 Dri-Train purifier or a vacuum line using standard Schlenk-tube techniques. Reagent grade solvents were distilled under dinitrogen from sodium/benzophenone (tetrahydrofuran, toluene, petroleum ether) or from P_2O_5 (dichloromethane). The starting compounds [W≡CPh$(CO)_2(py)_2$Br], [1] and 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (Ic'H_2) [2] were prepared according to published methods. Elemental analyses (C and H) were made with a Fissions EA 1108 microanalyzer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-400, Bruker AC-200P and Bruker AC 80 Spectrometers. Chemical shifts were reported in ppm relative to residual solvents and were assigned using 2D NMR tools. All peaks reported were singlets, unless otherwise specified. Mass spectra (EI, 70 eV) were recorded on HP-5889A spectrometer. IR spectra on a Perkin-Elmer 1600 FT-IR spectrometer or Bruker Vector 22.

Synthesis of [$(CO)_2$PhC≡W(Ic'H)] (1). A *n*-Butyllithium solution (1.6 M in hexanes, 0.52 ml, 0.80 mmol) was slowly added to a solution of 2,6.diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (0.20 g, 0.80 mmol) in THF (30ml) at -80°C. The mixture was stirred for 2 h at room temperature to yield the monolithiated ligand. The solution was cooled to -80°C, and a solution of [W≡CPh$(CO)_2(py)_2$Br] (0.50 g, 0.90 mmol) in THF (30ml) was added via syringe. The mixture was allowed to reach room temperature and was then refluxed for 12 h. Then, the solvent was removed and the product was dissolved with diethyl ether, filtered to remove the insoluble LiBr, and washed three times. After removal of the solvent via vacuum, orange crystals were obtained. Yield: 90% (0.45 g).

Anal.Calc. for $C_{27}H_{26}O_2W$ (566.14 g·mol^{-1}): C: 57.26; H: 4.63. Found: C: 57.20; H: 4.61 %.

IR: (C≡O), 1978(s), 1887(s) cm^{-1}

^{1}H NMR (400 MHz, ppm in CD_2Cl_2): δ 0.80 (t, 6H, C*H*$_3$–CH$_2$–C$_{(2,6)}$); 2.34 (s, 6H, C*H*$_3$–C$_{(4,8)}$); 2.56 (q, 4H, CH$_3$–C*H*$_2$–C$_{(2,6)}$); 3.23 (s, 2H, C$_{(5)}$*H*); 4.67 (s, 2H, C$_{(1,3)}$*H*); 6.63 (s, 1H, C$_{(7)}$*H*); 7.37 (t, 2H, H$_m$-C_6H_5); 7.84 (t, 1H, H$_p$-C_6H_5); 9.14 (d, 2H, H$_o$-C_6H_5)

^{13}C NMR (100 MHz, ppm in CD_2Cl_2): δ 14.1 (*C*H$_3$-C$_{(4,8)}$); 14.7(C$_{(2)}$CH$_2$*C*H$_3$); 15.5(C$_{(6)}$CH$_2$*C*H$_3$); 25.3 (C$_{(6)}$*C*H$_2$CH$_3$); 30,5 (C$_{(2)}$*C*H$_2$CH$_3$); 40.2 (C$_{(1,3,5,7)}$); 122.5 (C$_{(7)}$); 124.4 (C$_{(2)}$); 125.9 (C$_{(6)}$); 128.6(C-

C_6H_5); 129.9(C_m-C_6H_5); 129.6(C_p-C_6H_5); 138.9,141.2, 151.0, 154.3 ($C_{(3a,4,4a,7a,8,8a)ar\text{-}indacene}$); 154.4 ($C_o$-$C_6H_5$); 221.4 (CO); 259.9 (W≡C).

Synthesis of [{$(CO)_2PhC{\equiv}W\}_2$(Ic')] (2). To a solution of 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (0.20 g, 0.80 mmol) in THF (30 ml) at -80°C, was added dropwisely a *n*-Butyllithium solution (1.6 M in hexanes, 1.06 ml, 1.7 mmol) with constant stirring. The mixture was stirred for 2 h at room temperature, producing the consequent lithiated salt of *s*-indacene ligand. Then the mixture was once again cooled at -80°C, and a solution of [W≡CPh$(CO)_2(py)_2$Br] (0.96 g, 1.70 mmol) in THF (30 ml) was added via syringe. The solution was allowed to warm to room temperature and was then refluxed for 12 h. Then, the solvent was removed and the product was extracted with hexanes filtering out the LiBr precipitate and washed five times with hexanes. After removal of the solvent via vacuum, red powder were obtained. Yield: 56 % (0.32 g).

Anal.Calc. for $C_{30}H_{30}O_4W_2$ (709.06 g·mol^{-1}): C: 48.35; H: 3.38. Found: C: 48.23; H: 3.19 %.

IR: (C≡O), 1979(s), 1890(s) cm^{-1}.

^{1}H NMR (400 MHz, ppm in CD_2Cl_2): δ 0.87 (t, 6H, CH_3–CH_2–$C_{(2,6)}$); 2.34 (s, 6H, CH_3–$C_{(4,8)}$); 2.53 (q, 4H, CH_3–CH_2–$C_{(2,6)}$); 4.38 (s, 2H, $C_{(1,3,5,7)}H$); 7.19 (t, 2H, H_m-C_6H_5); 7.84 (t, 1H, H_p-C_6H_5); 9.14 (d, 2H, H_o-C_6H_5)

^{13}C NMR (100 MHz, ppm in CD_2Cl_2): δ 13.2 (CH_3-$C_{(4,8)}$); 14.1($C_{(6)}CH_2CH_3$); 14.9($C_{(2)}CH_2CH_3$); 24.7 ($C_{(2,6)}CH_2CH_3$); 29.7 ($C_{(7,5)}$); 39.9 ($C_{(1,3)}$); 123.6 ($C_{(2,6)}$); 125.4(C-C_6H_5); 128.1(C_m-C_6H_5); 129.2 (Cp-C_6H_5); 138.1,140.3, 150.7 ($C_{(3a,4,4a,7a,8,8a)ar\text{-}indacene}$); 153.5 ($C_o$-$C_6H_5$); 220.6 (CO); 263.2 (W≡C).

Mass spectroscopy results: MS (EI, m /z, 6 %): [M]•+ 893; [M•+- ($(CO)_2PhC{\equiv}W$))]•+ 569.

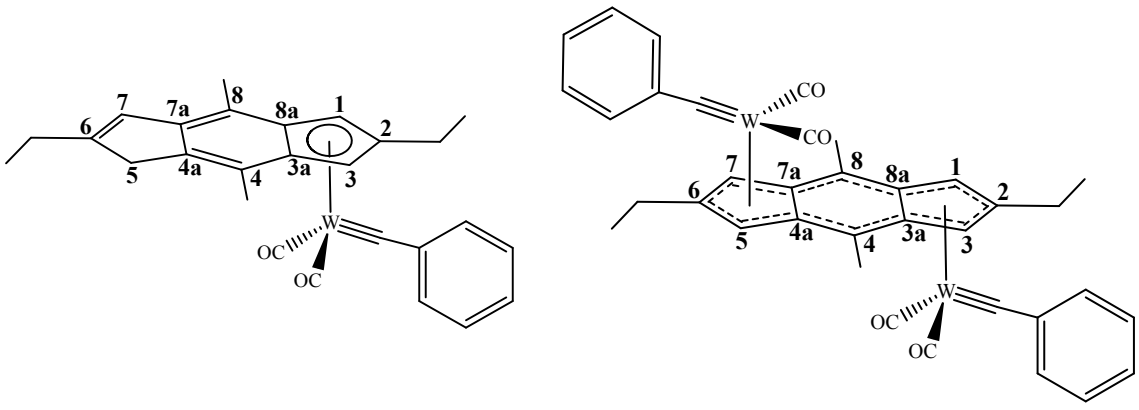

Chart S1. NMR assignment of the tetraalkylated *s*-indacene ligand for the here reported complexes.

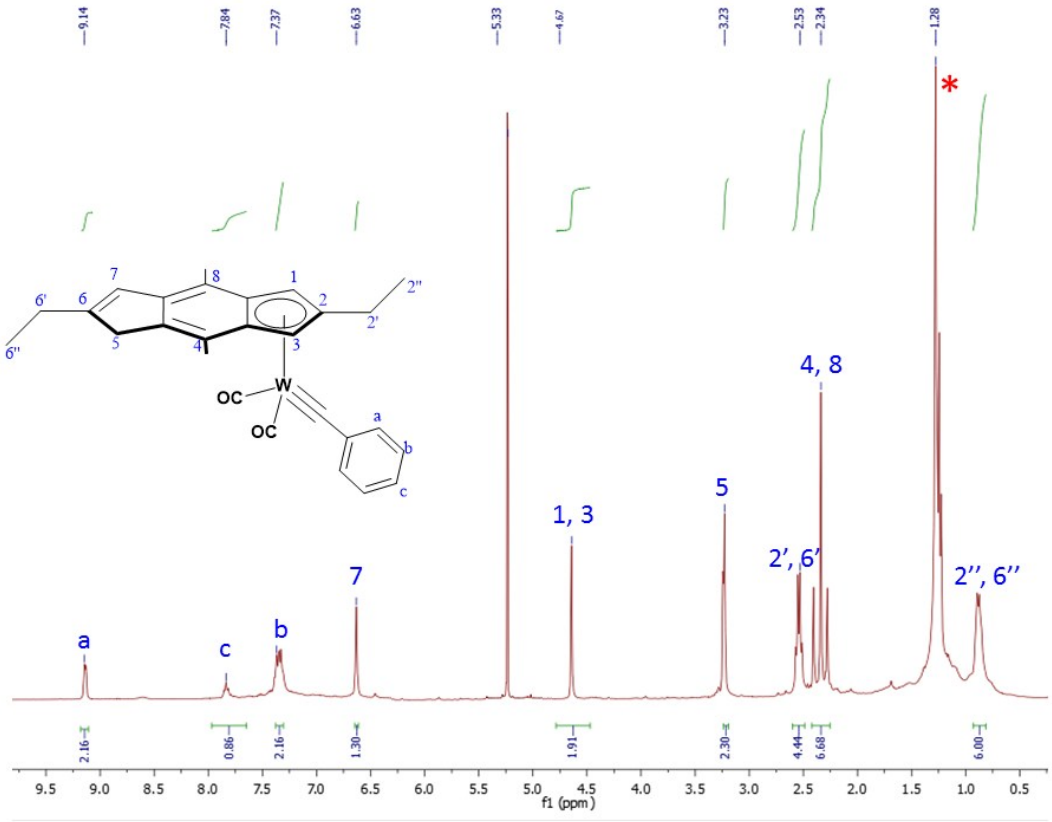

Figure S1. ^{1}H NMR spectrum of **1** in CD_2Cl_2 at 295 K. (* grease)

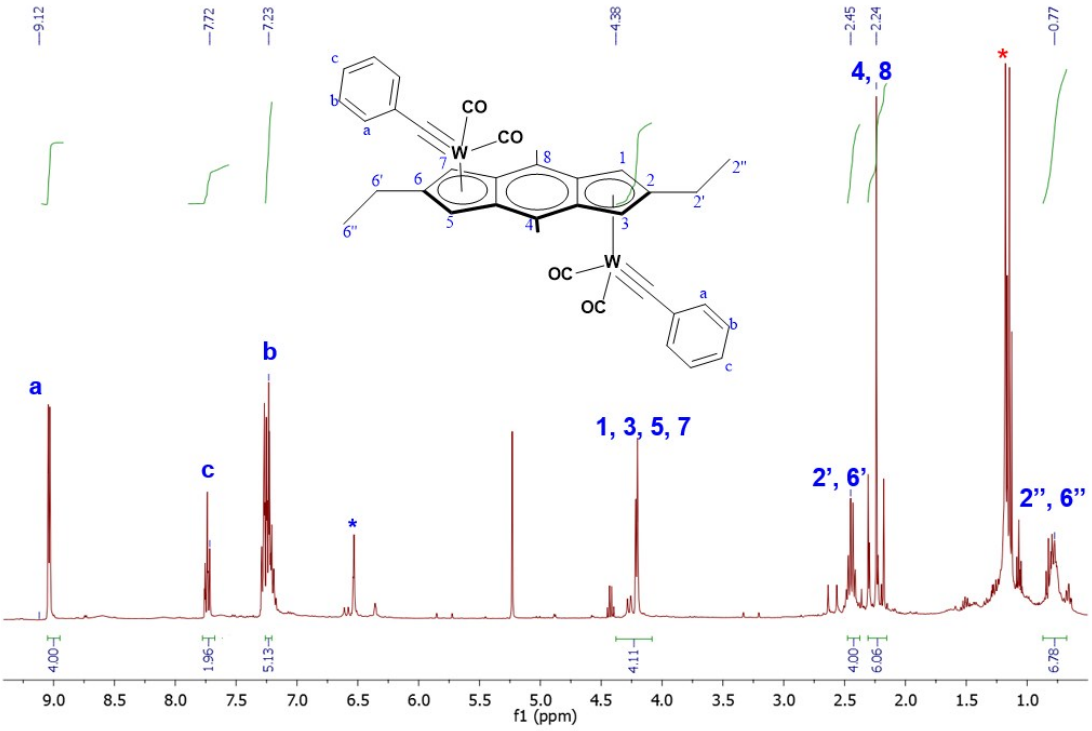

Figure S2. ^{1}H NMR spectrum of **2** in CD_2Cl_2 at 295 K. (* grease and free ligand)

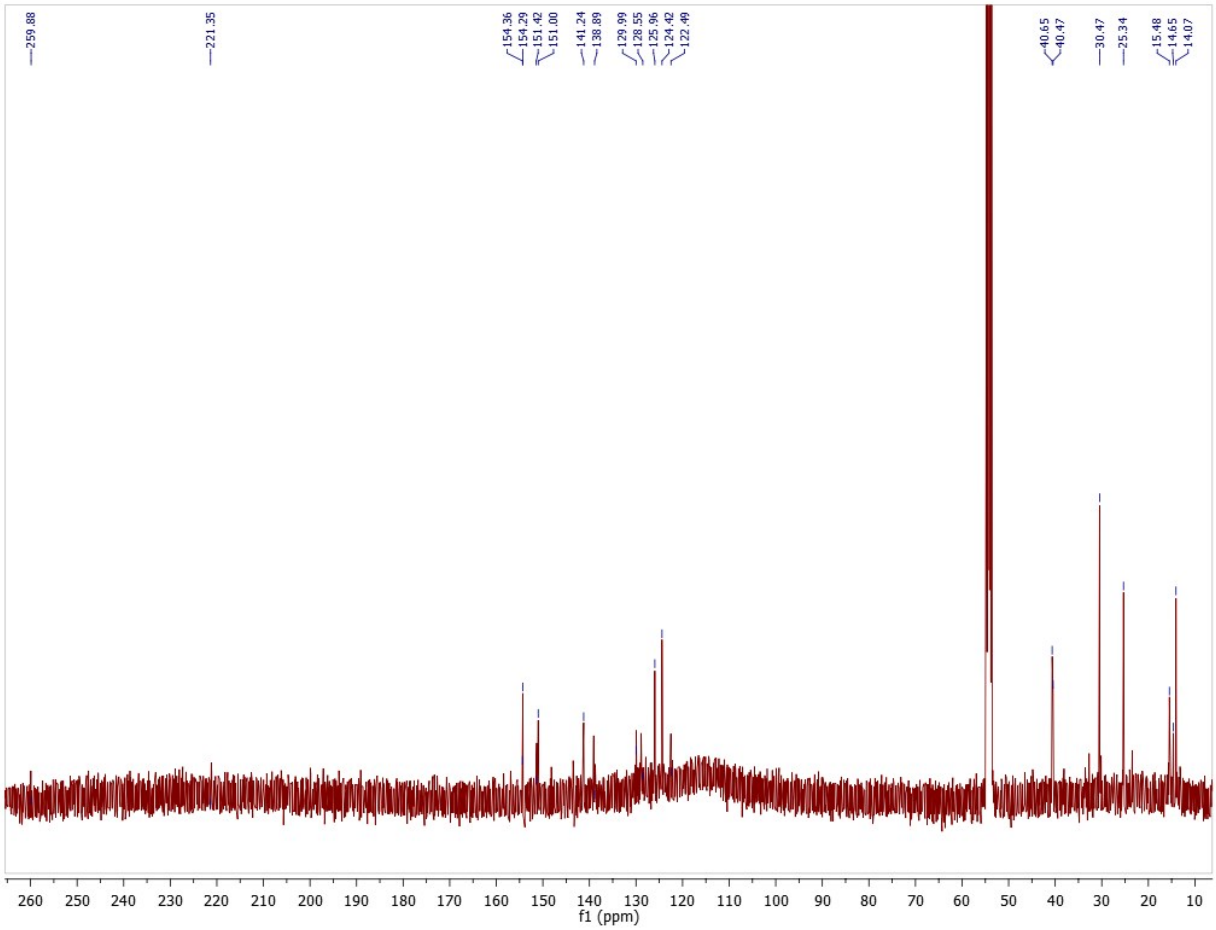

Figure S3. ^{13}C NMR spectrum of **1** in CD_2Cl_2 at 295 K

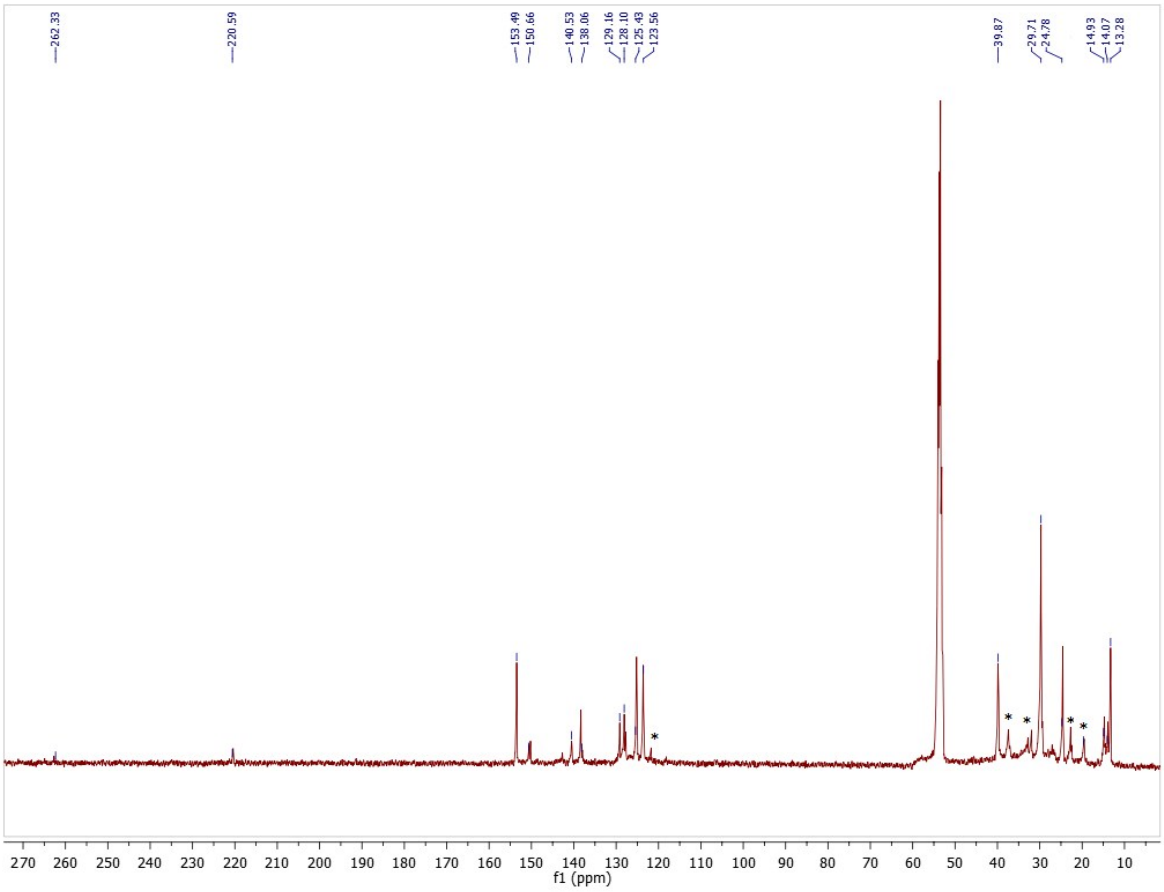

Figure S4. ^{13}C NMR spectrum of **2** in CD_2Cl_2 at 295 K (* free ligand)

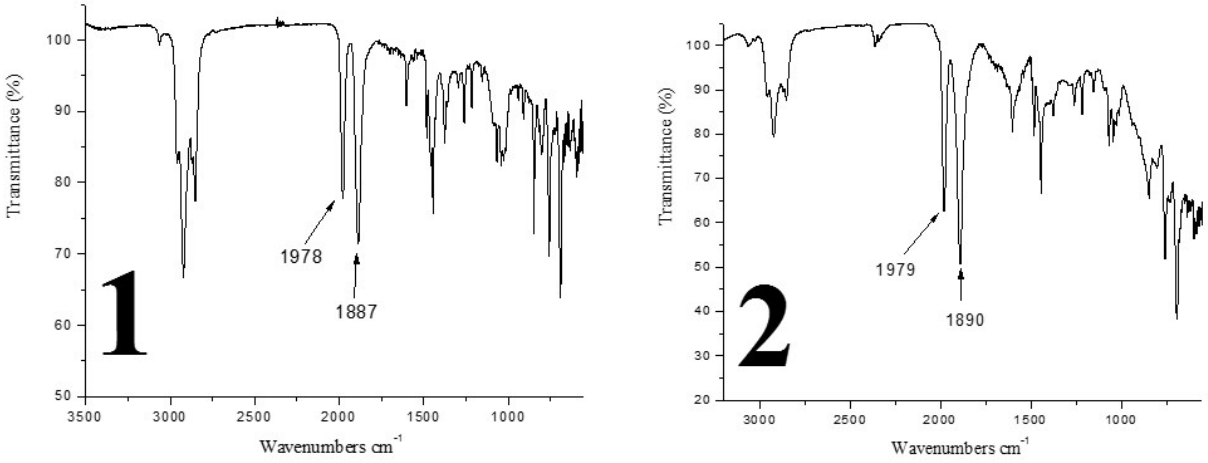

Figure S5. FT-IR spectra of compounds **1** and **2**.

```
Print of window 80: Apex Mass Spectrum of Peak 0.202 of CESAR_WW004.D
Data File  : D:\DATA\HOPKINS\HUNTER\CESAR_WW004.D
Sample Name : Cesar_WW
======================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : E449 Agilent 6130 LCMS          Location : FIA
Injection Date  : 7/23/2014 1:40:43 PM
                                                  Inj Volume : 5.000 µl
Method          : C:\CHEM32\1\METHODS\DEFAULT METHODS\FIA-P-SINGLE.M
Last changed    : 7/23/2014 1:40:06 PM by SYSTEM
                  (modified after loading)
Flow Injections :
          Inj. InjTime   Location   FIA Sample Name    Fragmentor
               [min]                                    [V]
          ----|-------|-----------|------------------|----------|
             1   0.000   Vial 1                              40
```

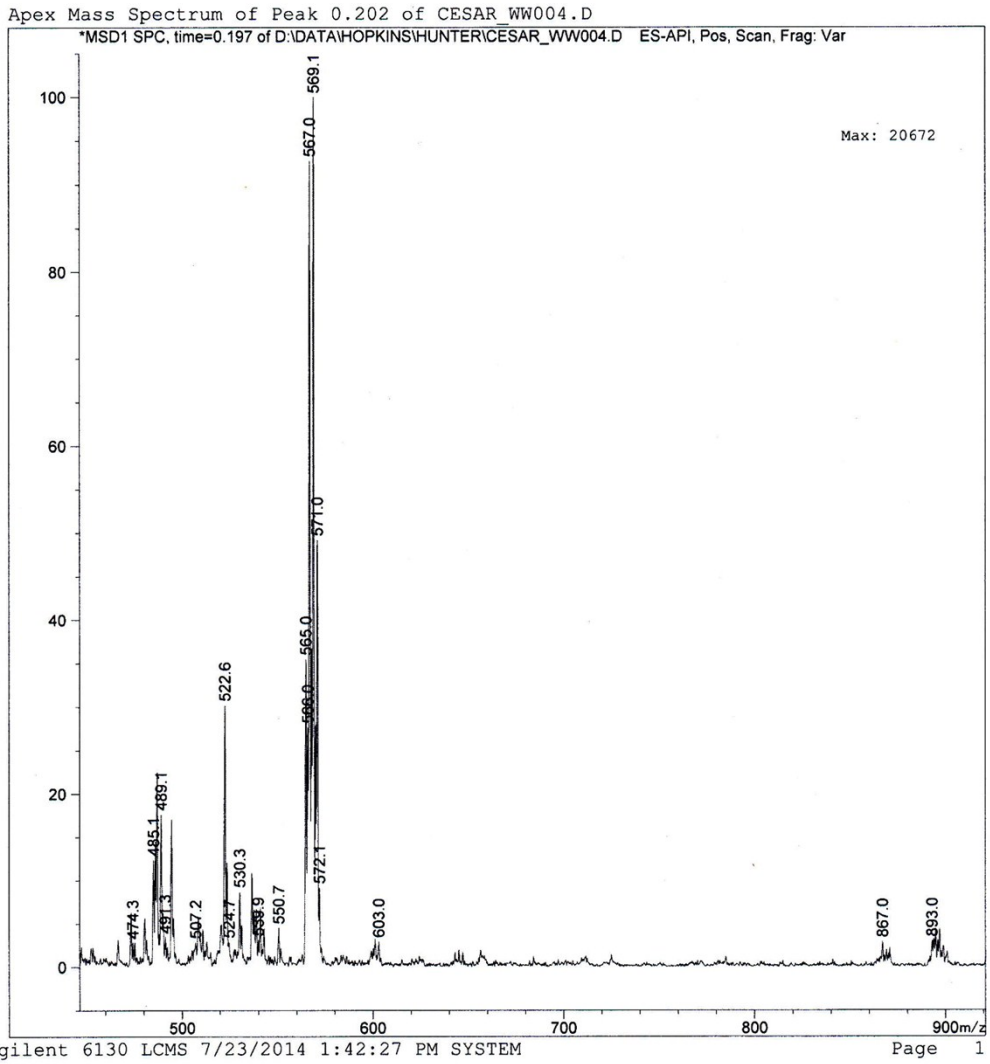

Figure S6. Mass Spectrum of compound **2.**

B. Physical Characterization Methods

General Procedures. Electronic-absorption spectra were recorded using an Agilent Technologies 8453 UV-visible spectrophotometer of samples sealed in quartz cuvettes. Emission spectra were recorded on a PTI Quantmaster fluorimeter equipped with Peltier-cooled photomultiplier tube (R928) and InGaAs array detectors; emission intensities were corrected for instrument sensitivity.[3] Samples for emission measurements were prepared on vacuum line, degassed with multiple freeze/pump/thaw cycles, and sealed under purified nitrogen. Emission quantum yields were determined relative to $[Ru(bpy)_3]Cl_2$ in N_2-saturated H_2O (ϕ_{em}= 0.063),[4] using absorbance-matched reference and analyte samples; a correction for the refractive index of the solvent was applied.[5]

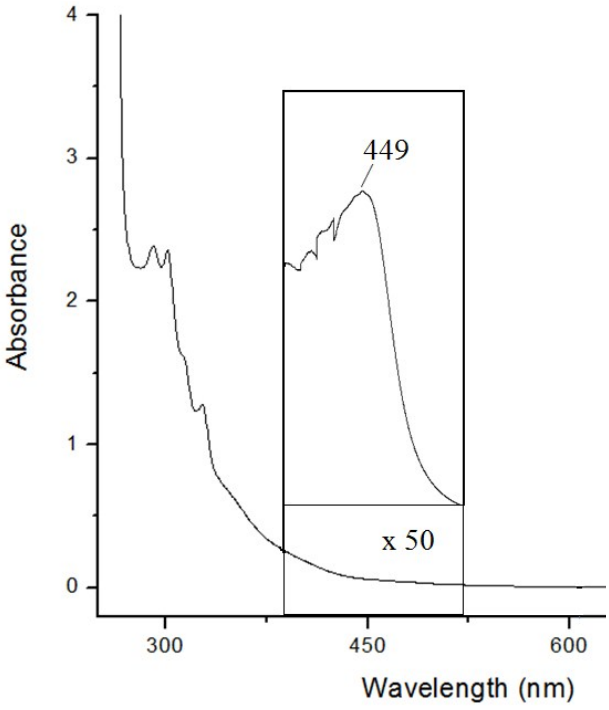

Figure S7. UV-vis spectrum of **1** in toluene at 295 K

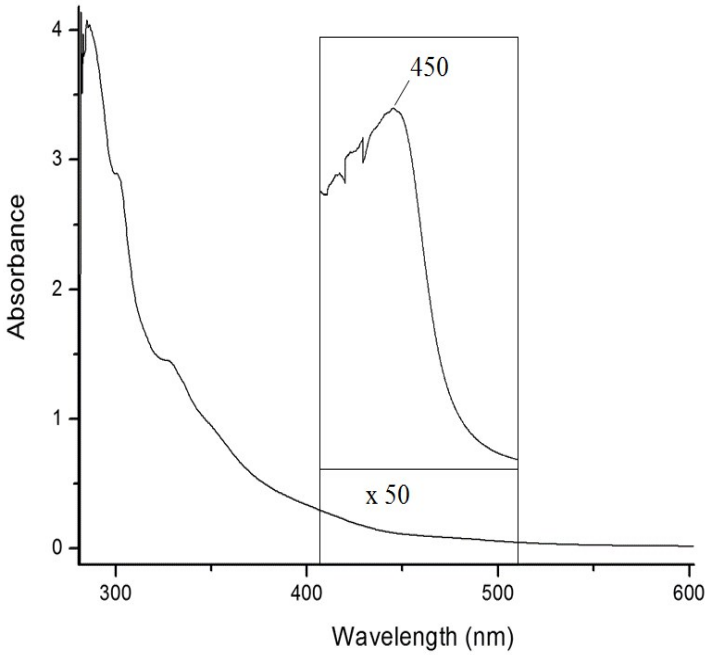

Figure S8. UV-vis spectrum of **2** in toluene at 295 K

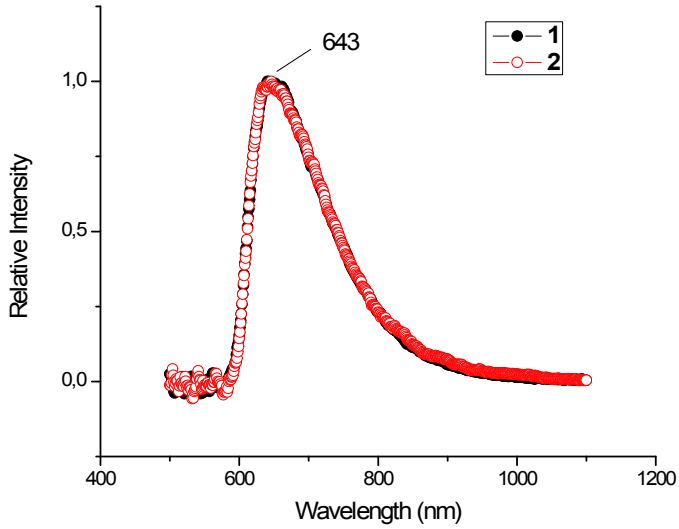

Figure S9. Emission spectra of **1** and **2** in toluene at 295 K

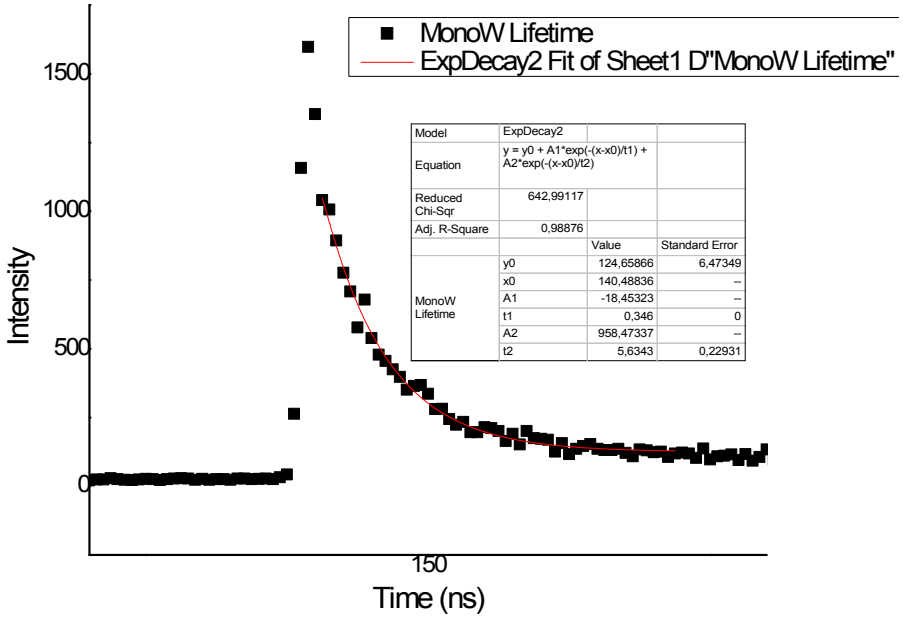

Figure S10. Lifetime Exponential Decay of **1**

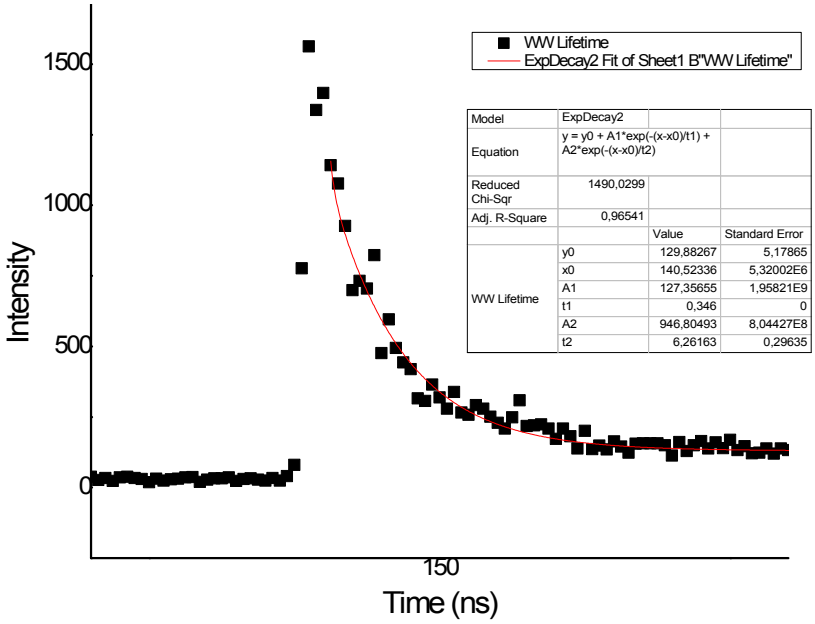

Figure S11. Lifetime Exponential Decay of **2**

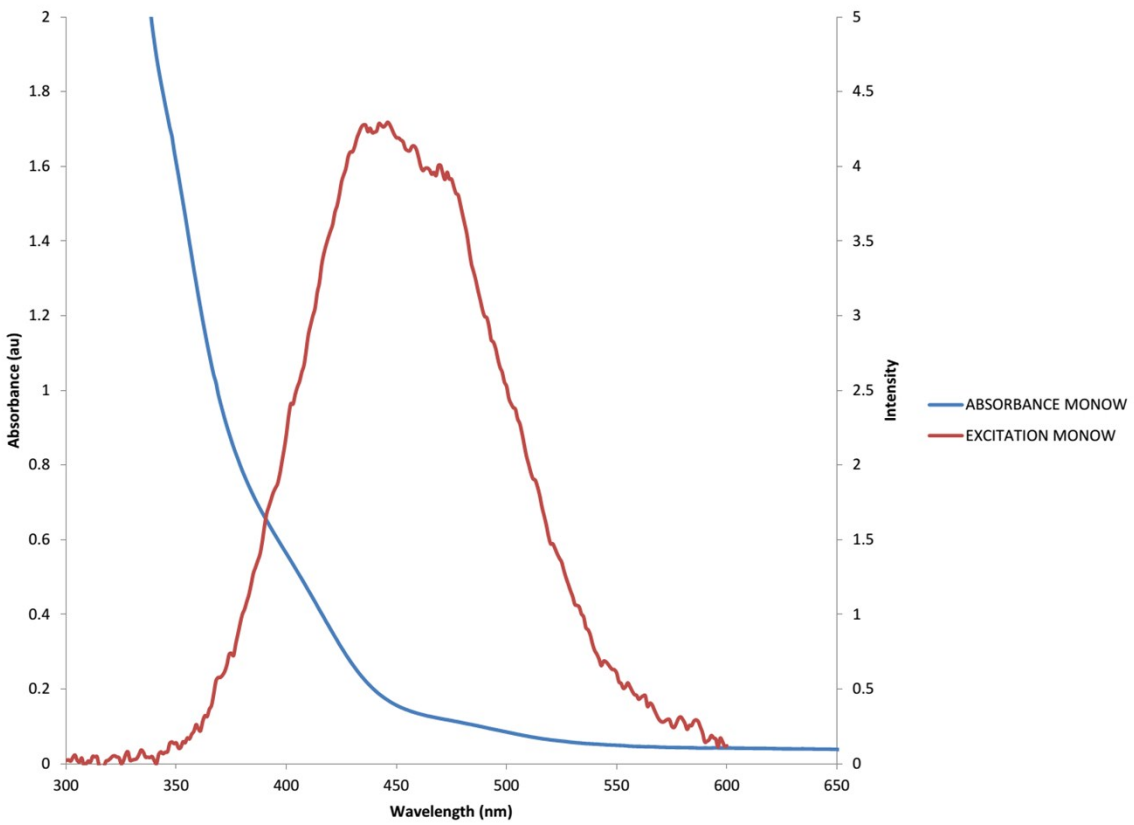

Figure S12. Emission Excitation Spectrum **1**

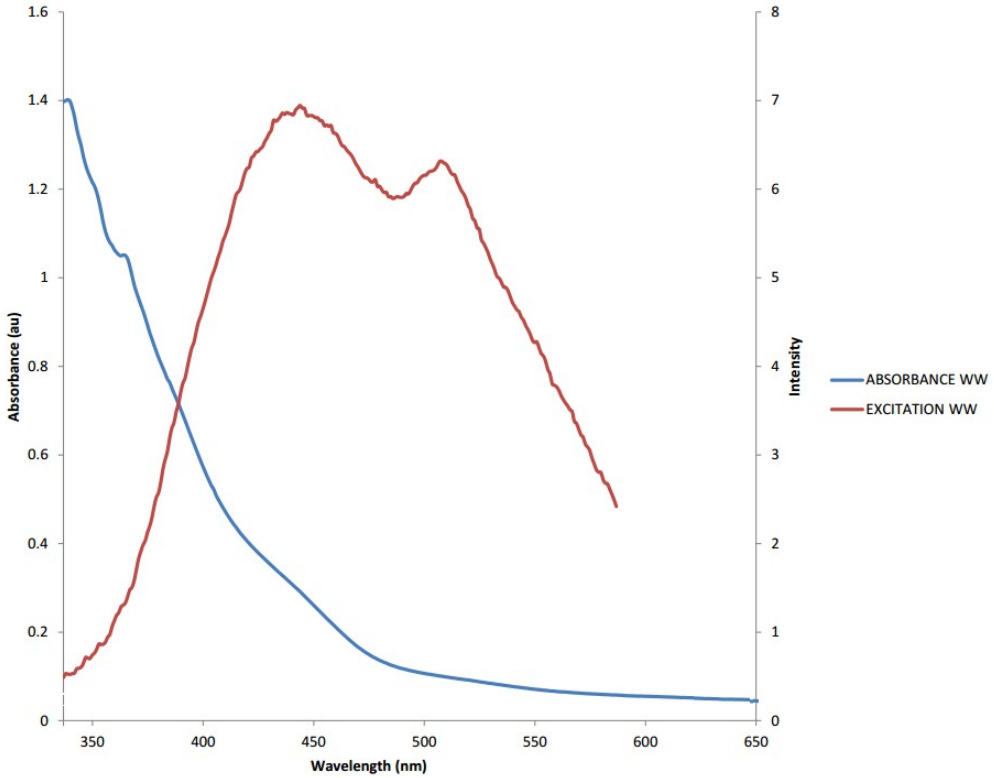

Figure S13. Emission Excitation Spectrum **2**

Table S1. Emission data.

Complex	λ (nm)	τ (ns)	Φ
$[(CO)_2PhC{\equiv}W\text{-}(Ic`H)]$ (**1**)	643	5.6	2.28×10^{-3}
$[\{(CO)_2PhC{\equiv}W\}_2(Ic`)]$ (**2**)	643	6.3	2.90×10^{-3}

C. Density Functional Theory Calculation

Methodology. All calculations were performed at density functional theory (DFT) level, as implemented in the Amsterdam density functional package (ADF2010).[6] The relativistic scalar effects were incorporated via the Zeroth order regular approximation (ZORA) Hamiltonian.[7,8] Uncontracted type IV basis set were employed, using triple-f accuracy sets of Slater type orbitals (STO) with two polarization functions (TZ2P).[9,10] The ground and excited states were fully optimized via generalized-gradient approximation (GGA) employing the BP86 functional.[11,12] The excitation energies were estimated by Time Dependent Density Functional Theory (TDDFT).[13,14] This methodology is based on the linear response formalism within the iterative Davison procedure implemented in the ADF2009 code. The calculations performed by first-principles method let to obtain accurate excitation energies.

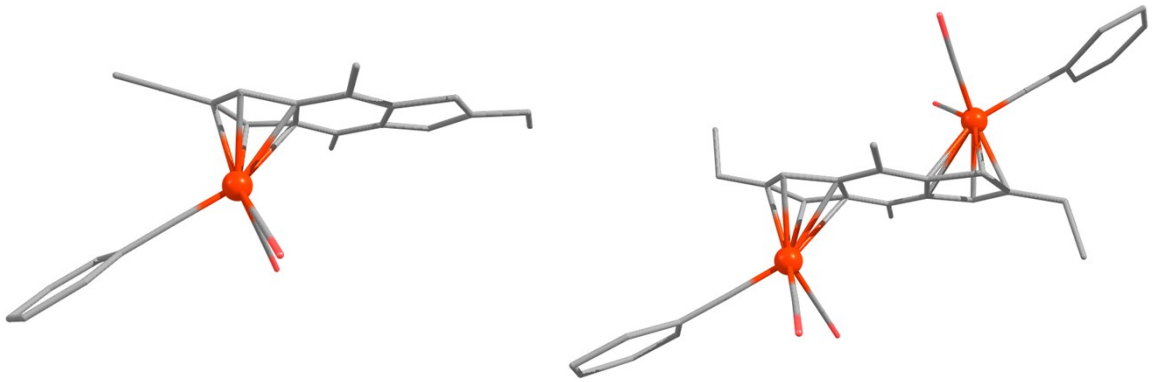

Figure S14. Calculated (DFT) structure of **1** and **2.**

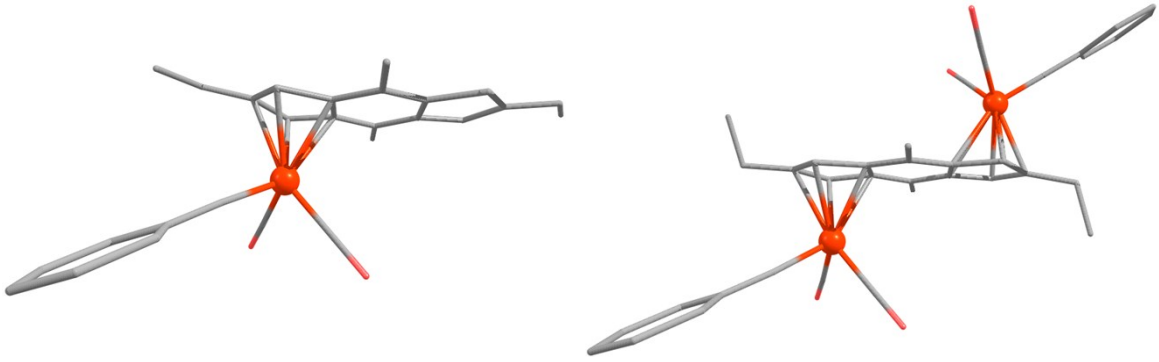

Figure S15. Calculated (DFT) structure of **1*** and **2***

Table S2. TDDFT data of calculated transitions.

Compound	λ(nm) exp	E(eV)	λ(nm) calc.	*f*	% Orbital Contribution			
$[(CO)_2PhC{\equiv}W\text{-}(Ic`H)]$ (**1**)	330	3.782	328	9.49E-003	8γ1/2	→	15γ1/2	60
	449	2.917	425	1.82E-002	5γ1/2	→	10γ1/2	61
$[\{(CO)_2PhC{\equiv}W\}_2(Ic`)]$ (**2**)	330	3.564	348	6.74E-003	1γ1/2	→	9γ1/2	66
	450	3.076	403	2.65E-002	4γ1/2	→	10γ1/2	68

Table S3. Selected bond distances (Å), angles and the calculated δ of the compounds **1** and **2**

Parameter	Complex 1	Complex 1*S	Complex 2	Complex 2*S
d W1-C_2	2,351	2,454	2,335	2,433
d W1-$C_{1,3}$ [c]	2,368	2,387	2,361	2,374
d W1-$C_{3a,8a}$ [c]	2,549	2,441	2,589	2,427
d W2-C_6	-	-	2,336	2,333
d W2-$C_{5,7}$ [c]	-	-	2,362	2,388
d W2-$C_{4a,7a}$ [c]	-	-	2,583	2,606
dihedral W1-C	-3,0	-38,9	0,0	-30,6
dihedral W2-CBz	-	-	0,0	2,6
d W1-CO Average	1,981	1,975	1,987	1,989
d W2-CO Average	-	-	1,987	1,986
d W1-C	1,831	1,883	1,825	1,877
d W2-C	-	-	1,825	1,825
δW1	8	-1	11	0
δW2	-	-	11	12

$\delta = [(W\text{-}C_{3a,8a})\text{-}(W\text{-}C_2)]/W\text{-}C_2$ [15]

Table S4. Cartesian Coordinates (Å) of DFT Optimized Geometry of **1**

C	2.236874000	-0.359800000	0.940993000	H	6.218679000	-1.526006000	1.287436000
C	3.457728000	-0.896925000	1.653306000	H	5.402684000	-3.035774000	1.606570000
C	4.226745000	-1.607575000	0.559610000	C	6.224740000	-2.892276000	-0.394751000
C	0.227176000	0.828394000	0.497208000	H	5.599640000	-3.675333000	-0.845075000
C	3.547428000	-1.520444000	-0.611866000	H	6.426259000	-2.137551000	-1.167441000
C	2.310541000	-0.759918000	-0.440428000	H	7.182161000	-3.347584000	-0.111405000
C	0.291994000	0.421805000	-0.885784000	C	-3.328853000	3.549665000	0.104325000
C	-0.901535000	1.725888000	0.640624000	H	-4.020231000	4.315359000	-0.269874000
C	-0.815137000	1.056134000	-1.575564000	H	-3.920729000	2.756727000	0.581483000
C	-1.478291000	1.937335000	-0.655684000	H	-2.701590000	4.018431000	0.874570000
C	1.340801000	-0.410964000	-1.373191000	W	-2.011722000	-0.262323000	-0.020652000
C	1.209338000	0.406013000	1.446712000	C	-3.842753000	-0.281431000	-0.036017000
H	3.196580000	-1.585849000	2.473184000	C	-5.270605000	-0.311094000	-0.025571000
H	3.877550000	-1.942980000	-1.558022000	C	-6.002976000	-0.246901000	-1.235587000
H	-1.163898000	2.263491000	1.544903000	C	-5.980388000	-0.404748000	1.196135000
H	-0.997424000	1.021136000	-2.644109000	C	-7.395733000	-0.275036000	-1.218110000
C	1.123286000	0.846982000	2.881958000	C	-7.372651000	-0.439234000	1.201402000
H	1.940866000	0.435469000	3.482538000	C	-8.084496000	-0.373099000	-0.002856000
H	1.161224000	1.943423000	2.962857000	H	-5.462658000	-0.177535000	-2.178404000
H	0.173897000	0.529562000	3.337243000	H	-5.423048000	-0.452128000	2.130352000
C	1.387019000	-0.802117000	-2.824833000	H	-7.948106000	-0.224591000	-2.155380000
H	2.244808000	-1.443034000	-3.050039000	H	-7.906440000	-0.516814000	2.147538000
H	0.475566000	-1.343249000	-3.118745000	C	-2.027379000	-1.969240000	-1.024838000
H	1.448916000	0.084779000	-3.473156000	O	-2.037923000	-2.951147000	-1.660195000
C	-2.484238000	2.992628000	-1.043285000	C	-2.088316000	-1.220933000	1.712216000
H	-1.916655000	3.818637000	-1.503971000	O	-2.145574000	-1.751921000	2.752590000
H	-3.132675000	2.599015000	-1.837923000	H	-9.173224000	-0.399152000	0.005892000
C	5.544616000	-2.268333000	0.825878000	H	4.060289000	-0.098251000	2.115240000

Table S5. Cartesian Coordinates (Å) of DFT Optimized Geometry of **2**

C	2.266132000	-0.107260000	0.689346000	H	0.159076000	-0.583308000	-3.383791000
C	3.508350000	-0.643073000	1.227719000	H	1.461037000	0.585136000	-3.625364000
C	4.185112000	-1.356050000	0.184536000	C	-2.970372000	2.835402000	-0.614218000
C	0.137235000	0.953579000	0.487952000	H	-3.596523000	2.461206000	-1.435324000
C	3.492252000	-1.104175000	-1.044709000	H	-3.585944000	2.809387000	0.294976000
C	2.256277000	-0.396892000	-0.740818000	C	5.378075000	-2.259608000	0.359490000
C	0.128175000	0.666052000	-0.939523000	H	5.991510000	-2.230581000	-0.551139000
C	-1.092946000	1.668597000	0.792178000	H	6.003606000	-1.879709000	1.178478000
C	-1.106988000	1.210922000	-1.482101000	C	4.978124000	-3.715580000	0.657831000
C	-1.784362000	1.923142000	-0.437959000	H	4.392250000	-3.785188000	1.584683000
C	1.184500000	-0.018936000	-1.571834000	H	4.379601000	-4.139439000	-0.160272000
C	1.203726000	0.565331000	1.322678000	H	5.876909000	-4.335389000	0.777290000
H	3.779224000	-0.672462000	2.277327000	C	-2.560220000	4.289231000	-0.909263000
H	3.748734000	-1.541700000	-2.003226000	H	-3.454755000	4.914978000	-1.029834000
H	-1.344899000	2.109808000	1.750239000	H	-1.961017000	4.707994000	-0.089024000
H	-1.371164000	1.248154000	-2.533201000	H	-1.971408000	4.356713000	-1.834452000
C	1.204707000	0.874107000	2.792181000	W	-2.041837000	-0.352808000	0.020824000
H	1.888970000	0.220709000	3.344071000	C	-3.862859000	-0.473832000	0.055419000
H	1.516890000	1.913364000	2.979332000	C	-5.289438000	-0.528336000	0.076725000
H	0.201544000	0.760296000	3.223003000	C	-6.020297000	-0.739151000	-1.117920000
C	1.165375000	-0.303373000	-3.046048000	C	-6.000042000	-0.357207000	1.289736000
H	1.852369000	-1.113687000	-3.312312000	C	-7.412496000	-0.775033000	-1.094413000

C	-7.392331000	-0.396366000	1.301462000	C	8.403839000	0.886285000	-1.529677000
C	-8.102246000	-0.603859000	0.112286000	C	8.403489000	1.426339000	0.847406000
H	-5.479228000	-0.871467000	-2.053536000	C	9.795580000	0.943997000	-1.536485000
H	-5.443603000	-0.193858000	2.211326000	C	9.795172000	1.482112000	0.828601000
H	-7.963812000	-0.936843000	-2.019655000	C	10.495040000	1.240903000	-0.360171000
H	-7.927938000	-0.263730000	2.240451000	H	7.855547000	0.655104000	-2.441577000
C	-1.997964000	-1.985246000	-1.110643000	H	7.855080000	1.611524000	1.769665000
O	-1.990324000	-2.919323000	-1.812715000	H	10.338839000	0.756678000	-2.461651000
C	-1.982143000	-1.421965000	1.694564000	H	10.338251000	1.713681000	1.743813000
O	-1.966740000	-2.013606000	2.702050000	C	4.365848000	1.978646000	-1.958477000
H	-9.190893000	-0.632087000	0.125866000	O	4.340913000	2.561266000	-2.971044000
W	4.437271000	0.918726000	-0.279231000	C	4.385985000	2.551623000	0.851889000
C	6.257021000	1.053695000	-0.318280000	O	4.373284000	3.484444000	1.555434000
C	7.683083000	1.126770000	-0.334502000	H	11.583241000	1.284691000	-0.369913000

Table S6. Cartesian Coordinates (Å) of DFT Optimized Geometry of **1***

C	1.900331000	-0.470492000	0.955000000	H	5.768137000	-1.532332000	2.024957000
C	2.971111000	-1.048520000	1.847332000	H	5.010748000	-3.102638000	1.965866000
C	3.990231000	-1.596373000	0.876303000	C	6.228309000	-2.653963000	0.226036000
C	-0.036176000	0.698314000	0.210292000	H	5.769873000	-3.392950000	-0.444875000
C	3.560266000	-1.396199000	-0.401651000	H	6.537660000	-1.792081000	-0.381367000
C	2.282970000	-0.706992000	-0.405714000	H	7.132081000	-3.104646000	0.655076000
C	0.356141000	0.468229000	-1.169476000	C	-3.466831000	3.437301000	-0.607998000
C	-1.190434000	1.565188000	0.186297000	H	-4.146258000	4.173633000	-1.055240000
C	-0.628003000	1.131892000	-2.002327000	H	-4.070084000	2.622883000	-0.184932000
C	-1.498272000	1.894363000	-1.167712000	H	-2.933936000	3.933726000	0.214564000
C	1.509098000	-0.282084000	-1.499323000	W	-1.872829000	-0.505344000	-0.816196000
C	0.745511000	0.200424000	1.305042000	C	-3.614884000	-0.315951000	-0.126501000
H	2.583867000	-1.838997000	2.510851000	C	-4.893967000	-0.256667000	0.413633000
H	4.099893000	-1.690046000	-1.298598000	C	-6.049014000	0.048072000	-0.386602000
H	-1.698954000	1.959277000	1.058663000	C	-5.113225000	-0.493328000	1.816659000
H	-0.601976000	1.190700000	-3.084944000	C	-7.313212000	0.102543000	0.181729000
C	0.340385000	0.474894000	2.724328000	C	-6.388667000	-0.433312000	2.358309000
H	0.979474000	-0.054037000	3.438005000	C	-7.506050000	-0.136270000	1.555815000
H	0.401208000	1.550941000	2.945517000	H	-5.915439000	0.236690000	-1.451188000
H	-0.700042000	0.171889000	2.904266000	H	-4.257203000	-0.727345000	2.447969000
C	1.921720000	-0.506083000	-2.925806000	H	-8.169623000	0.332950000	-0.452185000
H	2.540912000	-1.402982000	-3.031728000	H	-6.522442000	-0.624021000	3.423864000
H	1.051115000	-0.609697000	-3.583817000	C	-2.652428000	-1.241856000	-2.466885000
H	2.510475000	0.347027000	-3.297880000	O	-3.107898000	-1.642632000	-3.470633000
C	-2.495208000	2.907976000	-1.663356000	C	-1.607605000	-2.377392000	-0.224964000
H	-1.915328000	3.748322000	-2.079729000	O	-1.453130000	-3.489918000	0.126591000
H	-3.048064000	2.484981000	-2.513319000	H	-8.503089000	-0.092077000	1.991118000
C	5.263476000	-2.231645000	1.336149000	H	3.417434000	-0.293761000	2.514720000

Table S7. Cartesian Coordinates (Å) of DFT Optimized Geometry of **2***

C	2.429146	-0.259617	0.216970	C	0.141191	0.645437	-1.129964
C	3.695327	-0.856874	0.584192	C	-0.808123	1.684000	0.735537
C	4.239817	-1.541115	-0.543556	C	-1.105406	1.255356	-1.521760
C	0.336534	0.917487	0.283317	C	-1.645722	1.964145	-0.395436
C	3.387533	-1.277346	-1.654400	C	1.103081	-0.057902	-1.902688
C	2.215748	-0.556278	-1.197947	C	1.497983	0.501753	0.971683

H	4.137760	-0.850392	1.574022
H	3.535325	-1.678040	-2.651174
H	-0.924749	2.122666	1.720374
H	-1.497894	1.297999	-2.532044
C	1.704237	0.810496	2.423602
H	2.755117	0.710228	2.715867
H	1.381913	1.832388	2.661964
H	1.114125	0.127204	3.055244
C	0.875486	-0.322425	-3.360677
H	1.775388	-0.701574	-3.854918
H	0.075132	-1.067367	-3.497052
H	0.560684	0.590049	-3.884183
C	-2.802669	2.929164	-0.428987
H	-3.553386	2.570429	-1.146083
H	-3.293318	2.939053	0.553714
C	5.485888	-2.379332	-0.556283
H	5.896029	-2.391537	-1.575680
H	6.244074	-1.903636	0.081320
C	5.244230	-3.823787	-0.081907
H	4.865444	-3.845458	0.948856
H	4.513195	-4.338093	-0.720577
H	6.182860	-4.393368	-0.109686
C	-2.371755	4.357914	-0.805838
H	-3.243692	5.025972	-0.817697
H	-1.644433	4.758794	-0.086899
H	-1.909363	4.384664	-1.801906
W	-1.959871	-0.295388	0.095242
C	-3.775034	-0.355711	0.269864
C	-5.193154	-0.407763	0.411218
C	-6.015081	-0.784739	-0.678237
C	-5.811056	-0.069288	1.639284
C	-7.399165	-0.818779	-0.539611
C	-7.196233	-0.105366	1.766227
C	-7.995493	-0.478408	0.679794
H	-5.544883	-1.051286	-1.623658
H	-5.183397	0.215603	2.482441
H	-8.019166	-1.113933	-1.385650
H	-7.658055	0.156059	2.717877
C	-2.020502	-2.007523	-0.914292
O	-2.065857	-2.987019	-1.544524
C	-1.790291	-1.288847	1.803480
O	-1.691295	-1.823262	2.835145
H	-9.079591	-0.505858	0.783739
W	4.198921	0.849897	-0.993670
C	5.924113	1.105398	-0.299373
C	7.210377	1.202448	0.228105
C	8.349409	0.724389	-0.498625
C	7.444629	1.781744	1.517394
C	9.622681	0.815656	0.041233
C	8.728305	1.862066	2.034678
C	9.830389	1.379926	1.310334
H	8.197486	0.290870	-1.485987
H	6.595484	2.163167	2.082915
H	10.472387	0.445357	-0.532785
H	8.879805	2.308994	3.017477
C	4.920636	1.179408	-2.806728
O	5.370903	1.323729	-3.873065
C	3.818575	2.809879	-0.878933
O	3.589142	3.950069	-0.819719

D. References

(1) McDermott, G.A.; Dorries, A.M.; Mayr, A. *Organometallics* **1987**, *6*, 925.

(2) Dahrouch, M.R.; Jara, P.; Mendez, L.; Portilla, Y.; Abril, D.; Alfonso, G.; Chávez, I.; Manriquez, J.M.; Riviere-Baudet, M.; Riviere, P.; Castel, A.; Rouzaud, J.; Gornitzka, H.; *Organometallics*, **2001**, *20*, 5591.

(3) Parker, C.A.; Rees, W.T. *Analyst* **1960**, *85*, 587.

(4) Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishic, S.; Tobita, S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9850.

(5) Caspar, J.V.; Meyer, T.J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.

(6) Amsterdam Density Functional (ADF) Code, Release 2010, Vrije Universiteit, Amsterdam, The Netherlands.

(7) van Lenthe, E.; Baerends, E.J.; Snijders, J.G. *J. Chem. Phys.* **1994**, *101*, 9783.

(8) Velde, G.T.; Bickelhaupt, F.M.; van Gisberger, S.; Fonseca-Guerra, C.; Baerends, E.J.; Snijders, J.G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

(9) Snijder, J.G.; Baerends, E.J.; Vernooijs, P. *At. Data Nucl. Data Tables* **1982**, *26*, 483.

(10) Vernooijs, P.; Snijders, J.G.; Baerends, E.J. Slater Type Basis Functions for the Whole Periodic System, Internal Report, Free University of Amsterdam, The Netherlands, **1981**.

(11) Becke, A.D. *Phys. Rev. A* **1988**, *38*, 3098.

(12) Perdew, J.P. *Phys. Rev. B* **1986**, *33*, 8822.

(13) Runge, E.; Gross, E.K.U. *Phys. Rev. Lett.* **1984**, *52*, 997.

(14) Wang, F.; Ziegler, T.; van Lenthe, E.; van Gisbergen, S.; Baerends, E.J. *J. Chem. Phys.* **2005**, *122*, 204103.

(15) S. Bendjaballah, S. Kahlal, K. Costuas, E. Bévillon, J.Y. Saillard, *Chem. Eur. J.* **2006**, *12*, 2048