Supporting Information for

Multiple Aromatic C-H Bond Activations by a Dirhenium Carbonyl Complex Richard D. Adams*, Poonam Dhull, Mark D. Smith and Jonathan D. Tedder

Experimental Details

General Data. All reactions were performed under a nitrogen atmosphere by using the standard Schlenk glassware techniques. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet IS10 Midinfrared FT-IR spectrophotometer. ¹H NMR and ¹³C NMR were recorded on a on Bruker Advance III-HD spectrometer operating at 300 and 400MHz respectively. Mass spectrometric (MS) measurements performed by a direct-exposure probe by using electron impact ionization (EI) were made on a VG 70S instrument. Re₂(CO)₁₀ and anthracene were obtained from STREM and Sigma Aldrich and used without further purification. Re₂(CO)₈(μ -C₆H₅)(μ -H), **1** was prepared according to previously reported procedure.¹ Re₂(CO)₈(μ -H)(μ - η ²-1,2-C₁₀H₇), **2**, was synthesized as previously reported.² Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å *F*₂₅₄ glass plates.

Preparation of [Re₂(CO)₈(µ-H)](µ-1,µ-3-C₆H₄)[Re₂(CO)₈(µ-H)], 3.³

25.0 mg (0.0371 mmol) of **1** was dissolved in 1.6 mL CD₂Cl₂ in a 5 mm NMR tube. The NMR sample was evacuated and filled with N₂ gas. The NMR sample was then heated to 40 °C for 24 h. A ¹H NMR spectrum obtained after this period showed new hydride resonance at δ = -12.27. The contents of the tube were then put into a flask and the solvent was removed in *vacuo*. The residue was extracted in CH₂Cl₂ and then separated by TLC by using hexane to give a yellow band of 12.0 mg of [Re₂(CO)₈(µ-H)](µ-1,µ-3-C₆H₄)[Re₂(CO)₈(µ-H)], **3**, 51% yield. Spectral data for **3**: IR *v*_{CO} (cm⁻¹ in CH₂Cl₂): 2107(w), 2085(m), 2020(vs), 1993(sh), 1969(sh), 1958(s). ¹H NMR

 $(CD_2Cl_2, \delta \text{ in ppm}) 8.68 \text{ (s, br, 1H)}, 8.08 \text{ (dd, 2H, }^3J = 7.2 \text{ Hz}, {}^4J = 1.5 \text{ Hz}), 7.08 \text{ (t, 1H, H5, }^3J = 7.2 \text{ Hz}), -12.27 \text{ (s, 2H, hydride)}. {}^{13}C \text{ NMR} (CD_2Cl_2, 100.66 \text{ MHz}, \delta \text{ in ppm}): 186.28, 184.47, 184.11, 180.94, 175.59, 147.18, 128.88, and 124.56. {}^{13}C \text{ NMR} (CD_2Cl_2, DEPT, 100.66 \text{ MHz}, \delta \text{ in ppm}): 175.59, 147.18 \text{ and } 128.88. \text{ Mass Spec. EI/MS } m/z: 1272. \text{ Elemental analysis: Calculated for Re}_{4O_{16}C_{22}H_6}: C, 20.79\%; H, 0.48\%. \text{ Found: C, 21.68\%; H, 0.47\%}.$

Reaction of 1 with naphthalene.

A 50.0 mg (0.074 mmol) amount of 1 and 3.0 mg (0.0234 mmol) of naphthalene, $C_{10}H_8$, were dissolved in 1.6 mL CD₂Cl₂ in a 5 mm NMR tube. The NMR sample was evacuated and filled with nitrogen. The sample was then heated to 40 °C for 24 h. A ¹H NMR spectrum obtained after this period showed new hydride resonances. The contents were then put into a flask and solvent was removed in *vacuo*. The residue was extracted in CH₂Cl₂ and separated by TLC by using hexane to give a yellow band of 20.0 mg of $[Re_2(CO)_8(\mu-H)](\mu-\eta^2-1,2-\mu-\eta^2-3,4-C_{10}H_6)[Re_2(CO)_8(\mu-H)]$, 4, 41% yield as major product and yellow band of 5.0 mg of $[\text{Re}_2(\text{CO})_8(\mu-\text{H})](\mu-\eta^2-1,2-\mu-\eta^2-5,6-1)$ $C_{10}H_6$ [Re₂(CO)₈(μ -H)], 5, 10% yield along with 3.0 mg of compound 3, 6% yield and 7.0 mg of known compound Re₂(CO)₈(μ -H)(μ - η^2 -1,2-C₁₀H₇), **2**, 13% yield. Spectral data for **4**: IR v_{CO} (cm⁻ ¹ in CH₂Cl₂): 2108(m), 2084(s), 2023(vs), 1991(sh), 1976(s), 1959(sh). ¹H NMR (CD₂Cl₂, δ in ppm) 8.19-8.22 (m, 1H), 7.81-7.84 (m, 1H), 7.62-7.65 (m, 2H), 7.52 (d, 1H, ⁴J=1.5Hs), 6.90 (s,br, 1H), -13.10 (s, 1H, hydride) and -13.63 (s, 1H, hydride). Mass Spec. EI/MS m/z: 1322, M⁺, 1238, M⁺-3CO. Spectral data for 5: IR v_{CO} (cm⁻¹ in CH₂Cl₂): 2110(m), 2084(s), 2023(vs), 1991(sh), 1969(s), 1961(sh). ¹H NMR (CD₂Cl₂, δ in ppm) 8.35 (d, 2H, ³J = 7.2 Hz), 7.57 (d, 2H, ³J = 7.2 Hz), 7.21 (s, 2H), -12.66 (s, 2H, hydride).

Preparation of 4 and 5 from the reaction of 1 with 2.

30.0 mg (0.0445 mmol) of **1** and 20.0 mg (0.0276 mmol) of **2** were dissolved in 1.6 mL CD₂Cl₂ in a 5 mm NMR tube. The NMR sample was evacuated and filled with nitrogen. The NMR sample was then heated to 40 °C for 24 h. A ¹H NMR spectrum obtained after this period showed the hydride resonances of **4** and **5**. The contents were then put into a flask and solvent was removed in *vacuo*. The residue was then redissolved in CH₂Cl₂ and separated by TLC by using hexane solvent to give in order of elution, a yellow band of **4**, 17.0 mg, 47% yield and a yellow band of **5**, 3.0 mg, 8% yield.

Reaction of 1 with anthracene in 1 / 2 ratio.

A 30.0 mg (0.0445 mmol) amount of **1** and 14.0 mg (0.078 mmol) of anthracene, $C_{14}H_{10}$, were dissolved in 15 mL of methylene chloride. The solution was then heated to reflux for 15 h. The solution was then cooled, and the solvent was removed in *vacuo*. The residue was redissolved in CH₂Cl₂ and separated by TLC by using hexane solvent to yield a yellow band of Re₂(CO)₈(μ -H)(μ - η^2 -1,2-C₁₄H₉), **6**, 25.0 mg (73% yield). Spectral data for **6**: IR v_{CO} (cm⁻¹ in CH₂Cl₂): 2111(m), 2083(s), 2016(vs), 1989(s), 1969(vs), 1954(sh). ¹H NMR (CD₂Cl₂, 300 MHz, δ in ppm): 8.51 (s, 1H), 8.31 (s, 1H), 8.09-8.12 (dd, 1H, ³J = 6.3 Hz, ⁴J =3.3 Hz), 8.02-8.05 (m, 2H,), 7.57-7.60 (dd, 2H, H6, H7, ³J = 6.6 Hz, ⁴J =3.3 Hz), 7.43-7.46 (d, 1H, ³J = 8.7 Hz), 7.31 s, 1H), -13.02 (s, 1H, H2, hydride). ¹³C NMR (CD₂Cl₂, 100.66 MHz, δ in ppm): 186.05, 185.02, 183.66, 181.52, 146.77, 135.13, 132.72, 132.49, 130.56, 129.85, 128.18, 128.12, 127.94, 126.98, 126.61, 126.50, 126.16, and 113.02. Mass Spec. El/MS *m/z*: 774, M⁺, 718, M⁺-2CO.

Reaction of 1 with anthracene in a 3/1 ratio.

62.4 mg (0.0927 mmol) of **1** and 6.0 mg (0.033 mmol) of anthracene were dissolved in 1.6 mL CD_2Cl_2 in a 5 mm NMR tube. The NMR sample was evacuated and filled with nitrogen gas. The

NMR sample was then heated to 40 °C for 24 h. A ¹H NMR spectrum obtained after this period showed three new hydride resonances at $\delta = -13.15$, -13.68 and -12.94 in addition to the one of **6**. The contents were then transferred to a flask and solvent was removed in *vacuo*. The residue was then dissolved in CH₂Cl₂ and separated by TLC by using hexane solvent to give in order of elution: a yellow band of 15.0 mg of $[\text{Re}_2(\text{CO})_8(\mu-\text{H})](\mu-\eta^2-1,2-\mu-\eta^2-3,4-\text{C}_{14}\text{H}_8)[\text{Re}_2(\text{CO})_8(\mu-\text{H})], 7, 24\%$ yield and a yellow band of 30.0 mg of $[Re_2(CO)_8(\mu-H)](\mu-\eta^2-1,2-\mu-\eta^2-5,6-C_{14}H_8)[Re_2(D-\eta^2-1,2-\mu-\eta^2-2,2-\mu-$ H)], 8, 47% yield along with 5.0 mg of 6, 7% yield and 10.0 mg of compound 3, 17% yield. Spectral data for 7: IR v_{CO} (cm⁻¹ in CH₂Cl₂): 2108(m), 2083(s), 2023(vs), 1990(sh), 1976(s), 1958(sh). ¹H NMR (CD₂Cl₂, δ in ppm) 8.67 (s, 1H), 8.28 (s, 1H), 8.26 (s, 1H), 8.08 (dd, 2H, ³J = 6.3 Hz, ${}^{4}J$ =3.3 Hz), 7.62 (d-d, 2H, ${}^{3}J$ = 6.3 Hz, ${}^{4}J$ =3.3 Hz), 7.43 (s, 1H), 7.02 (s, 1H), -13.15 (s, 1H, H2, hydride), -13.68 (s, 1H, H4, hydride). ¹³C NMR (CD₂Cl₂, 100.66 MHz,δ in ppm): 149.12, 141.49, 139.04, 135.87, 135.84, 133.36, 132.47, 128.54, 127.77, 127.49, 127.20, 126.85, 125.72 and 105.69. ¹³C NMR (CD₂Cl₂, DEPT, 100.66 MHz, δ in ppm): 135.87, 128.54, 127.77, 127.49, 127.20, 126.85, 125.72 and 105.69. Mass Spec. EI/MS m/z: 1372, M⁺, 1344, M⁺-CO. Elemental analysis (mass %) Calculated for Re₄O₁₆C₃₀H₁₀: C, 26.28; H, 0.74. Found: C, 27.22; H, 1.42. Spectral data for 8: IR v_{CO} (cm⁻¹ in CH₂Cl₂): 2110(m), 2084(s), 2019(vs), 1990(sh), 1970(s), 1958(sh). ¹H NMR (CD₂Cl₂, δ in ppm) 8.40 (s, 2H), 8.17 (d, 2H, ³J = 8.7 Hz), 7.54(d, 2H, ³J = 8.7 Hz), 7.54(d, 2H, ³J = 8.7 Hz) Hz), 7.33 (s, 2H), -12.95 (s, 2H, hydride). Elemental analysis (mass %) Calculated for Re₄O₁₆C₃₀H₁₀: C, 26.28; H, 0.74. Found: C, 26.00; H, 0.80.

Preparation of 7 and 8 from 6.

25.0 mg (0.0371 mmol) of **1** and 20.0 mg (0.0276 mmol) of **6** were dissolved in 1.6 mL CD_2Cl_2 in a 5 mm NMR tube. The NMR sample was evacuated and filled with nitrogen. The NMR sample was then heated to 40 °C for 24 h. A ¹H NMR spectrum obtained after this period showed new hydride resonances. The contents were then put into a flask and solvent was removed in *vacuo*. The residue was extracted in CH_2Cl_2 and separated by TLC by using hexane to give a yellow band of 10.0 mg of **7**, 28% yield and 15.0 mg of **8**, 43% yield. The yield of **7** is higher (56%) if the ratio of **1/6** is 1/1.

Preparation of [Re₂(CO)₈(µ-H)]₄(µ-η²-1,2-µ-η²-3,4-µ-η²-5,6-µ-η²-7,8-C₁₄H₆), 9

60.0 mg (0.089 mmol) of **1** and 3.2 mg (0.0178 mmol) of anthracene were dissolved in 1.6 mL CD₂Cl₂ in a 5 mm NMR tube. The NMR sample was evacuated and filled with nitrogen. The NMR sample was then heated to 40 °C for 24 h. The contents were then transferred to a flask and solvent was removed in *vacuo*. The residue was redissolved in CH₂Cl₂ and separated by TLC by using hexane solvent to give a yellow band of 3.0 mg of $[\text{Re}_2(\text{CO})_8(\mu-\text{H})]_4(\mu-\eta^2-1,2-\mu-\eta^2-3,4-\mu-\eta^2-5,6-\mu-\eta^2-7,8-C_{14}H_6)$, **9**, 5% yield along with 12.0 mg of complex **3**, 22% yield, 15.0 mg of complex **7**, 24% yield and 20.0 mg of complex **8**, 33% yield. Spectral data for **9**: IR *v*_{CO} (cm⁻¹ in CH₂Cl₂): 2110(m), 2084(s), 2020(vs), 1990(sh), 1971(s), 1958(sh). ¹H NMR (CD₂Cl₂, δ in ppm) 8.59 (s, 2H), 7.44 (s, 2H), 6.77 (s, 2H,), -13.04 (s, 2H, H2, H6, hydride), -13.64 (s, 2H, H4, H8, hydride). **Thermolysis of 7 at 40 °C.**

20.0 mg (0.0146 mmol) of 7 was dissolved in 1.6 mL CD_2Cl_2 in a 5 mm NMR tube. The NMR sample was evacuated and filled with nitrogen. The NMR sample was then heated to 40 °C for 40 h. ¹H NMR spectrum taken after 17 h showed hydride resonances for **6**, **8** and anthracene, after 40 h. An ¹H NMR spectrum showed that the solution contained a mixture of **6**, **7**, **8** and anthracene. A TLC workup provided the following amounts of the products: 4.5 mg anthracene, 2.0 mg of compound **6**, 0.5 mg of **7**, 0.5 mg of **8** and 3.0 mg of Re₂(CO)₁₀.



Figure S1. An ORTEP diagram of the molecular structure of $\text{Re}_2(\text{CO})_8(\mu-\text{H})(\mu-1,\mu-3-C_6\text{H}_4)\text{Re}_2(\text{CO})_8(\mu-\text{H})$, **3**, showing 15% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follow: Re(1)-Re(2)=3.0046(2), Re(3)-Re(4)=3.0240(2), Re(1)-H(1)=1.85(5), Re(2)-H(1)=1.89(5), Re(3)-H(3)=1.92(5), Re(4)-H(3)=1.72(5), Re(1)-C(1)=2.224(4), Re(2)-C(1)=2.417(4), Re(3)-C(3)=2.424(4), Re(4)-C(3)=2.224(4), C(1)-C(2)=1.410(5), C(2)-C(3)=1.421(5), C(1)-C(6)=1.431(5), C(3)-C(4)=1.413(5), C(4)-C(5)=1.393(6), C(5)-C(6)=1.367(6).



Figure S2. An ORTEP diagram of the molecular structure of $\text{Re}_2(\text{CO})_8(\mu-\text{H})(\mu-\eta^2-1,2-\mu-\eta^2-3,6-C_{10}\text{H}_6)\text{Re}_2(\text{CO})_8(\mu-\text{H})$, **4**, showing 50% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follow: Re(1)-Re(2)=3.0433(2), Re(3)-Re(4)=3.0792(2), Re(1)-H(2)=1.88(4), Re(2)-H(2)=1.92(4), Re(3)-H(4)=1.78(4), Re(4)-H(4)=1.88(4), Re(1)-C(1)=2.526(3), Re(1)-C(2)=2.474(3), Re(2)-C(2)=2.201(3), Re(3)-C(3)=2.482(3), Re(3)-C(4)=2.489(3), Re(4)-C(4)=2.219(3), C(1)-C(2)=1.398(5), C(2)-C(3)=1.476(5), C(3)-C(4)=1.411(5).



Figure S3. An ORTEP diagram of the molecular structure of $\text{Re}_2(\text{CO})_8(\mu-\text{H})(\mu-\eta^2-1,2-\mu-\eta^2-5,6-C_{10}\text{H}_6)\text{Re}_2(\text{CO})_8(\mu-\text{H})$, **5**, showing 50% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follow: Re(1)-Re(2)=3.0431(2), Re(1)-H(2)=1.93(4), Re(2)-H(2)=1.87(4), Re(1)-C(1)=2.578(3), Re(1)-C(2)=2.448(3), Re(2)-C(2)=2.201(3), C(1)-C(2)=1.406(5), C(2)-C(3)=1.450(5), C(3)-C(4)=1.363(5).



Figure S4. An ORTEP diagram of the molecular structure of $\text{Re}_2(\text{CO})_8(\mu-\text{H})(\mu-\eta^2-1,2-C_{14}H_9)$, **6**, showing 25% thermal ellipsoid probability. Selected interatomic bond distances(Å) are as follow: Re(1)-Re(2)=3.0450(3), Re(1)-H(2)=1.84(5), Re(2)-H(2)=1.76(5), Re(1)-C(2)=2.431(4), Re(1)-C(1)=2.571(3), Re(2)-C(2)=2.205(4), C(1)-C(2)=1.389(5), C(1)-C(11)=1.446(5), C(2)-C(3)=1.472(5), C(3)-C(4)=1.337(5), C(4)-C(12)=1.429(5), C(11)-C(12)=1.423(5).



Figure S5. An ORTEP diagram of the molecular structure of $\text{Re}_2(\text{CO})_8(\mu-\text{H})(\mu-\eta^2-1,2-\mu-\eta^2-3,4-C_{14}\text{H}_8)\text{Re}_2(\text{CO})_8(\mu-\text{H})$, **7**, showing 25% thermal ellipsoid probability. Selected interatomic bond distances(Å) are as follow: Re(1)-Re(2)=3.0566(4), Re(1)-H(2)=1.92(7), Re(2)-H(2)=1.65(8), Re(3)-H(4)=1.81(6), Re(4)-H(4)=1.80(6), Re(1)-C(1)=2.500(6), Re(1)-C(2)=2.463(6), Re(2)-C(2)=2.202(6), Re(3)-Re(4)=3.0484(3), Re(3)-C(3)=2.519(6), Re(3)-C(4)=2.462(6), Re(4)-C(4)=2.217(5), C(1)-C(2)=1.383(9), C(1)-C(11)=1.459(8), C(2)-C(3)=1.474(8), C(3)-C(4)=1.403(8), C(4)-C(12)=1.470(8), C(11)-C(12)=1.428(8).



Figure S6. An ORTEP diagram of the molecular structure of $\text{Re}_2(\text{CO})_8(\mu-\text{H})(\mu-\eta^2-1,2-\mu-\eta^2-5,6-C_{14}\text{H}_8)\text{Re}_2(\text{CO})_8(\mu-\text{H})$, **8**, showing 50% thermal ellipsoid probability. Selected interatomic bond distances(Å) are as follow: Re(1)-Re(2)=3.0543(18), Re(1)-H(2)=1.88(6), Re(2)-H(2)=1.85(6), Re(1)-C(2)=2.456(3), Re(1)-C(1)=2.520(3), Re(2)-C(2)=2.186(3), C(1)-C(2)=1.404(4), C(2)-C(3)=1.460(4), C(3)-C(4)=1.358(4).



Figure S7. An ORTEP diagram of the molecular structure of $[\text{Re}_2(\text{CO})_8(\mu-\text{H})]_4(\mu-\eta^2-1,2-\mu-\eta^2-3,4-\mu-\eta^2-5,6-\mu-\eta^2-7,8-C_{14}H_6)$, **9** showing 30% thermal ellipsoid probability. Re(1)-Re(2)=3.0393(4), Re(1)-H(2)=1.80(2), Re(2)-H(2)=1.80(2), Re(3)-H(4)=1.78(4), Re(4)-H(4)=1.88(4), Re(1)-C(1)=2.520(7), Re(1)-C(2)=2.429(6), Re(2)-C(2)=2.202(6), Re(3)-Re(4)=3.0221(4), Re(3)-C(3)=2.543(7), Re(3)-C(4)=2.438(7), Re(4)-C(4)=2.216(7), C(1)-C(2)=1.388(9), C(1)-C(11)=1.445(9), C(2)-C(3)=1.472(10), C(3)-C(4)=1.417(9), C(4)-C(12)=1.479(9), C(11)-C(12)=1.424(9).



Figure S8. The ¹H NMR spectrum of compound **3** in CD_2Cl_2 solvent.



Figure S9. The ¹³C NMR spectra of compound **3** in CD_2Cl_2 solvent.



Figure S10. The ¹H NMR spectrum of compound 4 in CD₂Cl₂ solvent.



Figure S11. The ¹H NMR spectrum of compound 5 in CD_2Cl_2 solvent.



Figure S12. The ¹H NMR spectrum of compound **7** in CD_2Cl_2 solvent.



FigureS13. The ¹³C NMR spectra of compound **7** in CD_2Cl_2 solvent.



Figure S14. The ¹H NMR spectra of compound 8 in CD₂Cl₂ solvent.



Figure S15. The ¹H NMR spectra of compound 9 in CD₂Cl₂ solvent.

Crystallographic Analyses: Yellow single crystals of **3**, **4**, **5** and **6** suitable for x-ray diffraction analyses were obtained by slow evaporation of solvent from a solution in pure hexane at 20 °C. Yellow single crystals of compounds **7**, **8** and **9** suitable for x-ray diffraction analyses were obtained by slow evaporation of a hexane and methylene chloride solvent mixture at 20 °C. Each

data crystal was glued onto the end of a thin glass fiber. X-ray intensity data for compounds were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo K α radiation (λ = 0.71073Å). The raw data frames were integrated with the SAINT+ program by using a narrowframe integration algorithm.⁴ Correction for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections were applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix leastsquares on F2, using the SHELXTL software packages.⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Xray intensity data from a pale yellow needle of 9 approximate dimensions 0.02 x 0.03 x 0.28 mm³ were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K_{α} radiation, 1 = 0.71073 Å).⁶ The data collection consisted of diffraction images from six 180° ω -scans at different φ settings and two 360° ϕ -scans at different ω settings, with an individual image angular width of 0.5°. The crystal-to-detector distance was 5.0 cm and each image were measured for 20 s. The average reflection redundancy was 15.7. The raw area detector data frames were reduced, scaled and corrected for absorption effects using the SAINT⁶ and SADABS⁷ programs (Estimated minimum / maximum transmission =0.0411 / 0.0989). Final unit cell parameters were determined by leastsquares refinement of 9045 reflections in the range $4.937^{\circ} \le 2\theta \le 60.038^{\circ}$ taken from the data set. Compound 9 cocrystallized with one equivalent of disordered CH₂Cl₂ in the crystal lattice. Crystallographic data including CCDC deposit numbers and a summary of the results of the refinements are presented in Table S1.

Compound	3	4	5
CCDC Deposit No.	1581217	1877208	1877209
Empirical formula	Re ₄ O ₁₆ C ₂₂ H ₆	Re ₄ O ₁₆ C ₂₆ H ₈	Re ₄ O ₁₆ C ₂₆ H ₈
Formula weight	1271.07	1321.12	1239.07
Crystal system	Triclinic	Triclinic	Monoclinic
Lattice parameters			
<i>a</i> (Å)	8.8829(3)	8.4047(3)	14.6327(5)
<i>b</i> (Å)	11.4074(4)	11.5141(5)	8.9569(3)
<i>c</i> (Å)	15.4729(5)	16.8411(7)	24.1799(18)
α (deg)	86.520(1)	109.760(2)	90
β (deg)	80.180(1)	92.532(2)	106.430(1)
γ (deg)	67.418(1)	102.400(2)	90
V (Å ³)	1426.44(8)	1485.87(10)	3039.70(18)
Space group	<i>P</i> -1	<i>P</i> -1	C2/c
Z value	2	2	4
ρ_{calc} (g/cm ³)	2.959	2.953	2.887
μ (Mo Kα) (mm ⁻¹)	16.99	16.317	15.952
Temperature (K)	301(2)	100(2)	100(2)
$2\theta_{max}(^{\circ})$	56.62	60.18	60.20
No. Obs. (I>2 σ (I))	7112	7390	3987
No. Parameters	387	424	212
Goodness of fit (GOF)	1.112	1.041	1.212
Max. shift/error on final cycle	0.002	0.002	0.001
Residuals*: R1; wR2 (I> $2\sigma(I)$)	0.0211; 0.0422	0.0226; 0.0329	0.0205; 0.0390
Absorption Corr., Max/min	Multi-Scan 0.4604/0.2545	Multi-Scan 0.2980/0.1727	Multi-Scan 0.1716/0.0872
Largest peak in Final Diff. (e ^{-/} Å ³)	1.209	0.956	0.774

Table S1. Crystal data, and results of the analyses for compounds 3, 4 and 5.^a

^aR1 = $\Sigma_{hkl}(||F_{obs}| - |F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; wR2 = $[\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF_{obs}]^{1/2}$; w = $1/\sigma^2(F_{obs})$; GOF = $[\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

Compound	6	7	8	9
CCDC Deposit No.	1581215	1581216	1877210	1877211
Empirical formula	Re2O8C22H10	Re ₄ O ₁₆ C ₃₀ H ₁₀	Re ₄ O ₁₆ C ₃₀ H ₁₀	Re ₈ O ₃₂ Cl ₂ C ₄₇ H ₁₀
Formula weight	774.70	1371.18	1371.18	2647.05
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Lattice parameters				
<i>a</i> (Å)	13.5703(6)	9.3222(4)	8.6699(3)	17.3695(7)
<i>b</i> (Å)	13.8800(6)	17.8131(8)	8.7057(3)	9.2110(4)
<i>c</i> (Å)	11.6405(5)	21.1743(9)	12.5081(5)	19.6782(8)
α (deg)	90.000	90.000	75.118(1)	90
β (deg)	95.129(1)	101.801(1)	78.274(1)	109.393(2)
γ (deg)	90.000	90.000	64.698(1)	90
V (Å ³)	2183.78(16)	3441.8(3)	820.15(5)	2969.7(2)
Space group	P2 ₁ /c	P2 ₁ /n	<i>P</i> -1	<i>P2/n</i>
Z value	4	4	1	2
ρ_{calc} (g/cm ³)	2.356	2.646	2.776	2.960
μ (Mo Kα) (mm ⁻¹)	11.122	14.094	14.786	16.415
Temperature (K)	302(2)	100(2)	100(2)	100(2)
2 _{θmax} (°)	55.34	56.52	65.30	60.04
No. Obs. (I>2σ(I))	5151	8551	5374	6835
No. Parameters	293	459	231	413
Goodness of fit (GOF)	1.056	1.052	1.070	1.089
Max. shift/error on	0.002	0.002	0.002	0.003
final cycle	0.0222:	0.0272.	0.0216:	0.0267:0.0716
$(I \ge 2\sigma(I))$	0.0235,	0.0373,	0.0210,	0.0307, 0.0710
Absorption Corr	Multi-Scan	Multi-Scan	Multi-Scan	Multi-Scan
Max/min	0.7314/0.3050	1.000/0.572	0.1595/0.0317	0.0989/0.0411
Largest peak in Final Diff. (e ⁻ /Å ³)	1.064	2.486	2.578	3.976

 Table S1 cont. Crystal data, and results of the analyses for compounds 6 - 9.

Computational Analyses

All calculations were performed with ADF2014 program by using the PBEsol-D3 functional with ZORA scalar relativistic correction⁸ and valence triple- ζ + 2 polarization, relativistically optimized (TZ2P) Slater-type basis set, with small frozen cores. All computations are done in gas phase. This choice of computational model is based on prior testing of various functionals and basis sets.⁹ The PBEsol functional, which was originally developed primarily for solids, was shown to be superior to other functionals in the PBE family in the structural parameters of large organic systems¹⁰ and for metal clusters.¹¹ This is also consistent with our own testing of various functionals for the structures and relative energetics in organometallic cluster complexes.⁹ The dispersion corrections by Grimme et al.^{8h} were included upon additional testing, once they became available in the current release of ADF. The coordinates for the initiation of the geometry-optimization refinements were obtained from the crystal structure analyses.



Figure S16. Drawing of the geometry optimized structure of **3**, Re = orange, gray = C and red = O.

Table S2. Cartesian Coordinates for the DFT Geometry Optimized structure of **3**.

Re	-0.54627261	-1.39730031	2.97151612
Re	0.20838193	1.43454716	2.24477105
Re	0.72078572	-1.34389785	-2.74253033
Re	-0.47598173	1.43118416	-2.64307309
0	2.03792921	-1.92005924	4.66689335
0	-2.18740646	-1.93408408	5.57140369

0	-0.45057532	-4.34652552	2.04169095
0	-3.28969231	-1.09472545	1.48280824
0	3.04127429	1.04500616	3.53379055
0	-0.24759517	3.54671365	4.43582501
0	1.57535634	3.47330265	0.36059600
0	-2.65885981	2.19985488	1.21659378
0	-1.65217101	-2.57622294	-1.09866462
0	2.52073608	-3.62555090	-1.67608374
0	-0.27841239	-3.06449566	-5.08995930
0	3.02884373	-0.39879007	-4.64941644
0	-3.26116256	0.37747037	-1.65471068
0	-1.09022727	4.05962757	-1.12853398
0	-1.85640802	2.41084041	-5.26265305
0	2.21452871	2.69702221	-3.63315683
С	0.60464639	-0.69715173	1.24687056
С	-0.02245157	-0.05180583	0.15381925
Н	-1.11751034	-0.04151953	0.13411969
С	0.63274030	0.38839881	-1.06835806
С	2.02299306	0.12141756	-1.10765353
Н	2.64979736	0.61142894	-1.86042288
С	2.69475241	-0.55597575	-0.04620138
Н	3.76972989	-0.74630594	-0.13464351
С	2.02239100	-0.93330142	1.08006587
Н	2.57400850	-1.42937321	1.88595150
С	1.10478008	-1.69455319	4.02316896
С	-1.57922871	-1.74878451	4.60332297
С	-0.49980692	-3.24785948	2.40971827
С	-2.26339526	-1.17553758	2.00683324
С	2.00312960	1.13157768	3.04307173
С	-0.06976409	2.75714590	3.60750913
С	1.03639628	2.72018066	1.05534599
С	-1.61181860	1.87652186	1.57035892
С	-0.78794447	-2.07776354	-1.67379516
С	1.84403637	-2.77414365	-2.07212898
С	0.10411452	-2.42271297	-4.20533388
С	2.18733920	-0.70649525	-3.92538061
С	-2.21969696	0.73600443	-2.00172033
С	-0.83803910	3.07993928	-1.69681503
С	-1.36089161	2.06478183	-4.27507848
С	1.23367241	2.20115312	-3.27673556
Н	-0.60398226	0.36599755	3.55983687
Н	-0.36355127	-0.11781274	-3.65066174



Figure S17. HOMO and HOMO-1 of 3 plus energy in eV, isovalue 0.05.



HOMO-14 -8.450 eV

Figure S18. HOMO-14 of 3 plus energy in eV, isovalue 0.05.



HOMO-21 -10.40 eV

Figure S19. HOMO-21 of 3 plus energy in eV, isovalue 0.05.



HOMO-22 -10.48 eV

Figure S20. HOMO-22 of 3 plus energy in eV, isovalue 0.05.



Figure S21. Drawing of the geometry-optimized structure of naphthalene.

Table S3. Cartesian Coordinates for the DFT Geometry Optimized structure of naphthalene.

С	5.03363823	4.83590937	1.97562902
Н	5.33944485	4.16176470	2.78031173
С	4.01727833	4.47427465	1.12351642
Н	3.50712760	3.51313836	1.24312915
С	3.60575525	5.33543526	0.07940413
С	2.56145054	4.99505232	-0.81207022
Н	2.05747300	4.03139103	-0.68679340
С	2.18684246	5.85304073	-1.81873629
Н	1.37986367	5.57587575	-2.50247098
С	2.83936177	7.09409099	-1.97562902
Н	2.53355515	7.76823566	-2.78031173
С	3.85572167	7.45572571	-1.12351642
Н	4.36587240	8.41686200	-1.24312915
С	4.26724475	6.59456510	-0.07940413
С	5.31154946	6.93494804	0.81207022
Н	5.81552700	7.89860933	0.68679340
С	5.68615754	6.07695963	1.81873629
Н	6.49313633	6.35412461	2.50247098



LUMO+2 -0.55 eV Figure S22. LUMO+2 of Naphthalene plus energy in eV, isovalue 0.05.



LUMO+1 -1.36 eV

Figure S23. LUMO+1 of Naphthalene plus energy in eV, isovalue 0.05.



LUMO -2.12 eV

Figure S24. LUMO of Naphthalene plus energy in eV, isovalue 0.05.



HOMO -5.55 eV

Figure S25. HOMO of Naphthalene plus energy in eV, isovalue 0.05.



HOMO-1 -6.29 eV

Figure S26. HOMO-1 of Naphthalene plus energy in eV, isovalue 0.05.



HOMO-2 -7.24 eV Figure S27. HOMO-2 of Naphthalene plus energy in eV, isovalue 0.05



HOMO-3 -7.91 eV

Figure S28. HOMO-3 of Naphthalene plus energy in eV, isovalue 0.05.



HOMO-4 -8.11 eV

Figure S29. HOMO-4 of Naphthalene plus energy in eV, isovalue 0.05.



HOMO-5 -8.25 eV

Figure S30. HOMO-5 of Naphthalene plus energy in eV, isovalue 0.05.



Figure S31. Drawing of the geometry-optimized structure of **4**, Re = orange, gray = C and red = O and white = H.

Table S4. Cartesian Coordinates for the DFT Geometry Optimized structure of 4

Re	1.81829036	0.35717279	5.66723260
Re	1.62764522	-0.13069358	2.68486099
Re	1.26384919	4.54273772	1.96886669
Re	3.39327161	5.76140417	3.73911299
0	4.55976132	1.85175152	5.42099954
0	1.33908387	1.91876095	8.28803032
0	3.35876315	-1.83935716	7.16908900
0	-0.78272241	-1.29930025	6.22959741
0	4.63916860	0.56175423	2.17083136
0	1.03362401	0.76865790	-0.20934070
0	2.21497131	-3.05114674	1.78870516
0	-1.40141440	-0.85845653	2.97711848
0	-1.04361405	2.58937854	1.34488622
0	0.60957602	6.21248658	-0.53044176
0	3.32483695	2.99928420	0.17653082
0	-0.89417434	6.26910454	3.43994476
0	4.66758511	5.82974861	6.55203108
0	5.31775697	7.88021050	2.52289325
0	5.55756425	3.69554124	2.82275206
0	1.61907079	8.25563771	4.39452089
С	0.17352873	1.92893221	4.64413404
Н	-0.68668542	1.25051319	4.62141349

С	1.25326458	1.72929180	3.76971016
С	2.10855098	2.91001322	3.59031958
Н	3.06164482	2.71007131	3.09266892
С	1.97453612	4.15669666	4.24660415
С	0.75841013	5.31725915	6.12153633
Н	1.50440853	6.11311880	6.09237534
С	-0.29415842	5.39928673	7.01675441
Н	-0.37563346	6.26536896	7.67842714
С	-1.25006674	4.38154304	7.07253113
Н	-2.09353738	4.45448398	7.76374280
С	-1.10310364	3.26711568	6.26806888
Н	-1.81796004	2.43971820	6.33089418
С	-0.02030196	3.15533024	5.38332861
С	0.90489648	4.22568252	5.25335682
С	3.54336713	1.31894153	5.46169026
С	1.52173263	1.34377201	7.30459019
С	2.77877257	-1.01227278	6.61050138
С	0.15449829	-0.68220745	5.98452846
С	3.53252315	0.32894006	2.38662730
С	1.24131131	0.43977393	0.88078989
С	2.00423361	-1.95833223	2.09585613
С	-0.28341076	-0.59275203	2.89852066
С	-0.16367736	3.30254203	1.56953841
С	0.84991393	5.58611332	0.40874388
С	2.58013947	3.54630506	0.85686271
С	-0.07833563	5.63078682	2.94567993
С	4.20476621	5.81056060	5.49224692
С	4.60130269	7.10221347	2.98734781
С	4.72392649	4.41253429	3.16603264
С	2.21594804	7.29215989	4.18479750
Н	2.18136977	-0.86069083	4.29241622
Н	2.62268844	5.83568586	2.05873707



LUMO -3.57 eV Figure S32. LUMO of 4 plus energy in eV, isovalue 0.05.



HOMO -6.34 eV

Figure S33. HOMO of **4** plus energy in eV, isovalue 0.05.



HOMO-1 -6.39 eV

Figure S34. HOMO-1 of **4** plus energy in eV, isovalue 0.05.



HOMO-2 -6.54 eV

Figure S35. HOMO-2 of **4** plus energy in eV, isovalue 0.05.



HOMO-9 -7.25 eV

Figure S36. HOMO-9 of **4** plus energy in eV, isovalue 0.05.



HOMO-13 -7.86 eV

Figure S37. HOMO-13 of 4 plus energy in eV, isovalue 0.05.



Figure S38. Drawing of the geometry optimized structure of **5**, Re = orange, gray = C and red = O.

Table S5. Cartesian Coordinates for the DFT Geometry Optimized structure of **5**.

Re	0.65907896	0.90981953	3.58320745
Re	-0.50602382	3.64051371	3.03389303
0	-2.15267113	-0.28167970	4.28581031
0	1.54655696	-1.91350531	2.70280913
0	1.39395902	0.33785819	6.50702895
0	3.61082166	1.91562387	3.27969669
0	-3.30925247	2.96355621	4.25338007
0	-1.92454851	5.46446747	0.98565827
0	-0.22485512	5.84769831	5.21043408
0	2.22799565	4.60165684	1.85521751
С	0.63507613	1.39934300	1.07488316
Н	1.55329419	1.99706527	1.08395075
С	-0.52608576	1.88855558	1.72308755
С	-1.74539636	1.19092429	1.38392947
Н	-2.67920273	1.51329608	1.85447703
С	-1.78906311	0.16211723	0.48451811
Н	-2.74621539	-0.31233198	0.24097692
С	0.61380184	0.30965780	0.14984165
С	-1.14778110	0.18682177	3.98801969
С	1.21212223	-0.85953064	3.03538278
С	1.11692254	0.54937768	5.40550068

С	2.51449795	1.57834211	3.35092150
С	-2.27204749	3.17579077	3.79974174
С	-1.38817090	4.79550737	1.76062758
С	-0.34123313	5.03791177	4.39527465
С	1.23399512	4.21529715	2.29235894
Н	0.26436470	2.57874584	4.34588905
С	-0.63507613	-1.39934300	-1.07488316
Н	-1.55329419	-1.99706527	-1.08395075
С	0.52608576	-1.88855558	-1.72308755
С	1.74539636	-1.19092429	-1.38392947
Н	2.67920273	-1.51329608	-1.85447703
С	1.78906311	-0.16211723	-0.48451811
Н	2.74621539	0.31233198	-0.24097692
С	-0.61380184	-0.30965780	-0.14984165
Re	-0.65907896	-0.90981953	-3.58320745
Re	0.50602382	-3.64051371	-3.03389303
0	2.15267113	0.28167970	-4.28581031
0	-1.54655696	1.91350531	-2.70280913
0	-1.39395902	-0.33785819	-6.50702895
0	-3.61082166	-1.91562387	-3.27969669
0	3.30925247	-2.96355621	-4.25338007
0	1.92454851	-5.46446747	-0.98565827
0	0.22485512	-5.84769831	-5.21043408
0	-2.22799565	-4.60165684	-1.85521751
С	1.14778110	-0.18682177	-3.98801969
С	-1.21212223	0.85953064	-3.03538278
С	-1.11692254	-0.54937768	-5.40550068
С	-2.51449795	-1.57834211	-3.35092150
С	2.27204749	-3.17579077	-3.79974174
С	1.38817090	-4.79550737	-1.76062758
С	0.34123313	-5.03791177	-4.39527465
С	-1.23399512	-4.21529715	-2.29235894
Н	-0.26436470	-2.57874584	-4.34588905



LUMO+1 -3.47 eV Figure S39. LUMO+1 of 5 plus energy in eV, isovalue 0.05.



Figure S40. LUMO of 5 plus energy in eV, isovalue 0.05.



HOMO -6.32 eV

Figure S41. HOMO of **5** plus energy in eV, isovalue 0.05.



HOMO-10 -7.57 eV

Figure S42. HOMO-10 of 5 plus energy in eV, isovalue 0.05.



HOMO-13 -7.92 eV

Figure S43. HOMO-13 of 5 plus energy in eV, isovalue 0.05.



HOMO-15 -8.43 eV

Figure S44. HOMO-15 of 5 plus energy in eV, isovalue 0.05.



HOMO-20 -9.68 eV

Figure S45. HOMO-20 of 5 plus energy in eV, isovalue 0.05.

Table S6. Cartesian Coordinates for the DFT Geometry Optimized Structure of Anthracene.

С	-0.56723759	4.83769265	0.00562455
С	-1.11782538	3.58274202	-0.00246691
С	-0.29303150	2.42276268	-0.00041980
С	-0.82589623	1.13050573	-0.00850830
С	1.14001490	2.59213049	0.01037720
С	1.67136129	3.91260077	0.01854835
С	0.84312489	5.00442941	0.01625080
Н	-1.21396089	5.72106700	0.00393269
Н	-2.20576462	3.45049262	-0.01067592
Н	-1.91545287	1.00182125	-0.01671705
Н	2.76021715	4.03740859	0.02673925
Н	1.26615052	6.01412602	0.02261838
С	-0.00617931	-0.00168350	-0.00640536
С	1.95973181	1.45994126	0.01248014
С	1.42686708	0.16768431	0.00439164
С	-0.53752570	-1.32215378	-0.01457651
Н	3.04928846	1.58862573	0.02068889

С	2.25166096	-0.99229503	0.00643875
С	0.29071069	-2.41398242	-0.01227896
Н	-1.62638156	-1.44696160	-0.02276741
С	1.70107317	-2.24724566	-0.00165271
Н	3.33960020	-0.86004563	0.01464776
Н	-0.13231493	-3.42367903	-0.01864654
Н	2.34779648	-3.13062001	0.00003915



HOMO, -5.024 eV

Figure S46. HOMO of Anthracene plus energy in eV, isovalue 0.05.



HOMO-1 -6.229 eV Figure S47. HOMO-1 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-2 -6.531 eV

Figure S48. HOMO-2 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-3 -7.546 eV Figure S49. HOMO-3 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-4 -7.672 eV

Figure S50. HOMO-4 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-5 -7.87 eV

Figure S51. HOMO-5 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-6 -8.106 eV

Figure S52. HOMO-6 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-7 -8.08 eV

Figure S53. HOMO-7 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-8 -9.107 eV

Figure S54. HOMO-8 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-9 -9.10 eV

Figure S55. HOMO-9 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-10 -9.10 eV

Figure S56. HOMO-10 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-11 -9.964 eV

Figure S57. HOMO-11 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-12 -10.055 eV

Figure S58. HOMO-12 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-13 -10.062 eV

Figure S59. HOMO-13 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-14 -10.349 eV

Figure S60. HOMO-14 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-15 -10.33

Figure S61. HOMO-15 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-16 -11.03 eV

Figure S62. HOMO-16 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-17 -11.03 eV

Figure S63. HOMO-17 for Anthracene plus energy in eV, isovalue 0.05.



HOMO-18 -11.382 eV

Figure S64. HOMO-18 for Anthracene plus energy in eV, isovalue 0.05.



Figure S65. Drawing of the geometry optimized structure of **7**, Re = orange, gray = C and red = O.

Table S7. Cartesian	Coordinates for th	e DFT Geometry C	Optimized structure of 7.

4.14002756	-2.01067455	-0.08441739
1.91749038	-2.73622949	-2.01018440
-1.64887182	-4.18898858	0.76360341
-1.17697926	-1.80154811	2.56655275
3.74289195	-4.64007337	1.57586021
4.90107604	-0.50300415	2.50943962
7.00863597	-3.10423306	-0.63698178
5.05250915	0.41350288	-1.85285369
1.95786708	-5.76588022	-1.17817517
-1.02732655	-2.79262302	-2.95941136
2.90436192	-3.65050456	-4.78714814
2.00433741	0.18719544	-3.14384778
0.69695416	-5.84218179	2.03268816
-1.19784830	-5.75885532	-1.86546137
-4.01910283	-2.69302682	-0.63873711
-3.66130070	-6.30022969	1.87045372
1.65243778	-2.83701455	3.44412996
-0.20151960	1.06635255	3.20880895
-2.06717490	-2.26660618	5.48267840
	4.14002756 1.91749038 -1.64887182 -1.17697926 3.74289195 4.90107604 7.00863597 5.05250915 1.95786708 -1.02732655 2.90436192 2.00433741 0.69695416 -1.19784830 -4.01910283 -3.66130070 1.65243778 -0.20151960 -2.06717490	4.14002756-2.010674551.91749038-2.73622949-1.64887182-4.18898858-1.17697926-1.801548113.74289195-4.640073374.90107604-0.503004157.00863597-3.104233065.052509150.413502881.95786708-5.76588022-1.02732655-2.792623022.90436192-3.650504562.004337410.187195440.69695416-5.84218179-1.19784830-5.75885532-4.01910283-2.69302682-3.66130070-6.300229691.65243778-2.83701455-0.201519601.06635255-2.06717490-2.26660618

0	-4.05460928	-0.67842222	2.00607270
С	3.83493850	-3.66598463	0.96173126
С	4.63121494	-1.07982695	1.53972486
С	5.94938503	-2.68398585	-0.42872832
С	4.64965717	-0.44813039	-1.19543912
С	1.93054960	-4.64977763	-1.45762384
С	0.07029304	-2.79540652	-2.59074672
С	2.53327717	-3.30164809	-3.74782483
С	1.98031606	-0.86635216	-2.68097688
С	2.00528721	-1.52019273	0.07701221
С	1.08204172	-2.57318650	0.28143267
Н	1.48606581	-3.52142412	0.65063756
С	-0.38386164	-2.44875946	0.39479051
С	-0.87154513	-1.15018531	0.17858938
Н	-1.92590223	-0.99674368	-0.08278243
С	-0.00631075	-0.00577772	-0.02172503
С	-0.56034486	1.25188934	-0.20191576
Н	-1.65157899	1.35142085	-0.26324218
С	0.23495152	2.40994888	-0.25487908
С	-0.31199667	3.70557579	-0.42492319
Н	-1.39527383	3.81002962	-0.55006814
С	0.50424032	4.81186184	-0.42683435
Н	0.07314424	5.80931185	-0.55767497
С	1.90159355	4.67315987	-0.25801315
Н	2.53706266	5.56415847	-0.26291249
С	2.46293009	3.42945305	-0.08963792
Н	3.54512932	3.31598779	0.03649711
С	1.65147559	2.26852579	-0.08718333
С	2.19942093	0.97881970	0.04973384
Н	3.28197149	0.88739745	0.17154647
С	1.42177305	-0.16705459	0.03593476
С	-0.14917866	-5.20498753	1.57254271
С	-1.37146787	-5.15719357	-0.88798605
С	-3.14652129	-3.22438596	-0.09909637
С	-2.90169303	-5.53752899	1.44349021
С	0.61923132	-2.48317127	3.07827499
С	-0.55807912	-0.00755376	2.96783642
С	-1.73116681	-2.08756699	4.38940805
С	-2.99857747	-1.10682567	2.17695231
н	3.76447586	-2.84024264	-1.69720140
Н	-1.94100609	-3.50366655	2.45872572



LUMO -3.582 eV

Figure S66. LUMO for 7 plus energy in eV, isovalue 0.05.





Figure S68. Drawing of the geometry optimized structure of **8**, Re = orange, gray = C and red = O.

Table S8. Cartesian Coordinates for the DFT Geometry Optimized structure of 8.

Re	8.33369940	3.00646476	2.06049042
Re	8.22898340	5.90705675	2.90220661
0	11.22453364	3.31144858	0.89073144
0	8.92600479	0.01718359	2.55374420
0	7.45153541	2.46566548	-0.83238099
0	5.34648513	2.49966948	2.85967612
0	10.77589672	6.72378148	1.27414319
0	6.59745844	7.88904058	1.14054901
0	9.00847187	8.01675538	5.01810212
0	5.62177269	5.36157603	4.54292076
С	8.58156562	3.21429717	4.55959801
Н	7.51073726	3.31391488	4.76753774
С	9.26170399	4.25834117	3.89509532
С	10.71166011	4.20233168	3.99533182
Н	11.29468482	4.98490229	3.50077465
С	11.37294346	3.24099904	4.69526534
Н	12.46587989	3.26720216	4.76249937
С	10.67939311	2.18105907	5.35071506
С	9.25212749	2.17125846	5.29128203
С	8.54298512	1.17391247	5.95583295
Н	7.44796174	1.16717545	5.90918524

С	10.17972399	3.23614471	1.36143298
С	8.71227319	1.13628349	2.36442113
С	7.78449347	2.66610960	0.25545003
С	6.44499237	2.71799485	2.60175418
С	9.85039715	6.38821832	1.87218085
С	7.21195420	7.16836103	1.80220813
С	8.70470355	7.23483472	4.22260921
С	6.58391827	5.52969655	3.93086643
Н	7.80259265	4.73193292	1.53143940
С	11.30027630	-0.86269923	7.45957776
Н	12.37110467	-0.96231694	7.25163803
С	10.62013793	-1.90674323	8.12408045
С	9.17018182	-1.85073374	8.02384394
Н	8.58715711	-2.63330435	8.51840112
С	8.50889846	-0.88940110	7.32391043
Н	7.41596204	-0.91560422	7.25667639
С	9.20244882	0.17053887	6.66846071
С	10.62971444	0.18033948	6.72789373
С	11.33885680	1.17768547	6.06334282
Н	12.43388018	1.18442249	6.10999052
Re	11.54814253	-0.65486682	9.95868535
Re	11.65285852	-3.55545881	9.11696915
0	8.65730828	-0.95985064	11.12844433
0	10.95583714	2.33441435	9.46543157
0	12.43030652	-0.11406754	12.85155675
0	14.53535680	-0.14807154	9.15949965
0	9.10594521	-4.37218354	10.74503258
0	13.28438348	-5.53744264	10.87862676
0	10.87337006	-5.66515744	7.00107364
0	14.26006923	-3.00997809	7.47625501
С	9.70211794	-0.88454677	10.65774279
С	11.16956873	1.21531445	9.65475463
С	12.09734846	-0.31451166	11.76372574
С	13.43684956	-0.36639691	9.41742158
С	10.03144478	-4.03662038	10.14699491
С	12.66988773	-4.81676309	10.21696764
С	11.17713838	-4.88323678	7.79656655
С	13.29792366	-3.17809860	8.08830934
Н	12.07924928	-2.38033498	10.48773637



LUMO -3.63 eV Figure S69. LUMO for 8 plus energy in eV, isovalue 0.05.



HOMO -6.08 eV

Figure S70. HOMO for **8** plus energy in eV, isovalue 0.05.



HOMO-1 -6.30 eV

Figure S71. HOMO-1 for **8** plus energy in eV, isovalue 0.05.



HOMO-3 -6.62 eV

Figure S72. HOMO-3 for 8 plus energy in eV, isovalue 0.05.



HOMO-14 -7.93 eV

Figure S73. HOMO-14 for 8 plus energy in eV, isovalue 0.05



Figure S74. Drawing of the geometry optimized structure of **9**, Re = orange, gray = C and red = O.

Table S9. Cartesian Coordinates for the DFT Geometry Optimized structure of 9.

Re	7.81558300	4.59127979	5.47908827
Re	5.97911589	2.68526129	6.95447491
Re	9.65407274	0.00261114	8.19532242
Re	11.75577157	1.93863052	9.18422277
0	9.37627799	5.47334277	8.04818903
0	10.22700993	5.42448957	3.74143918
0	6.70806996	7.45822316	5.36149310
0	6.27655797	4.03317389	2.80450988
0	6.59741617	3.92346330	9.76457544
0	5.32436002	0.02357874	8.37729889
0	3.04382417	3.68741546	7.20314695
0	5.26060747	1.27417741	4.25470991
0	7.47623186	-0.96507453	6.23183122
0	7.62662901	0.73145799	10.47673577
0	9.79682612	-2.78941336	9.48173473
0	11.75046875	-1.07119452	6.13437012
0	13.35685469	4.51006659	8.58427221
0	14.10367361	0.22412653	8.02588428
0	13.13384276	1.41413073	11.92267026
0	9.70049496	3.59681345	10.86622179
С	8.60717846	2.27592066	5.18713002
Н	7.94894339	2.00372966	4.35384665
С	8.09005325	2.40660189	6.48640576
С	9.09526478	2.30219313	7.55624898
Н	8.75349168	2.64412887	8.53763092
С	10.48656553	2.10369510	7.39446978
С	12.30729324	2.12995475	5.67092074
Н	13.04678720	2.18159155	6.47404140
С	10.02550820	2.15565411	4.92681424
С	10.95598325	2.10911951	6.00205851
С	8.79511550	5.10773599	7.12745542
С	9.34605099	5.11122145	4.41707834
С	7.12439841	6.38300788	5.40108602
С	6.82926294	4.20013819	3.79628504
С	6.39647918	3.47633744	8.72277101
С	5.57598207	1.01230946	7.83066381
С	4.12812232	3.29807984	7.13512700
С	5.53441352	1.82088635	5.23006611
С	8.27349060	-0.59070165	6.97756419
С	8.35845224	0.49454203	9.62552705
С	9.74487809	-1.74512551	8.99432545
С	10.99142061	-0.63453964	6.87654641

С	12.75286678	3.55478334	8.83117382
С	13.20696491	0.85211528	8.38805016
С	12.63838579	1.60935712	10.89833488
С	10.41789643	2.98337496	10.20712481
Н	6.15896015	4.41525490	6.32833068
Н	10.91576932	0.32920014	9.54624979
С	14.18003880	2.27592083	4.09373119
Н	14.83827387	2.00372968	4.92701450
С	14.69716400	2.40660232	2.79445547
С	13.69195247	2.30219375	1.72461223
Н	14.03372556	2.64412969	0.74323036
С	12.30065173	2.10369566	1.88639139
С	10.47992402	2.12995493	3.60994044
Н	9.74043006	2.18159187	2.80681979
С	12.76170906	2.15565419	4.35404695
С	11.83123401	2.10911978	3.27880266
Re	14.97163420	4.59128003	3.80177339
Re	16.80810136	2.68526187	2.32638638
Re	13.13314457	0.00261188	1.08553835
Re	11.03144569	1.93863140	0.09663837
0	13.41093919	5.47334348	1.23267281
0	12.56020725	5.42448942	5.53942264
0	16.07914717	7.45822341	3.91936912
0	16.51065924	4.03317365	6.47635167
0	16.18980105	3.92346441	-0.48371391
0	17.46285729	0.02357961	0.90356188
0	19.74339305	3.68741615	2.07771453
0	17.52660981	1.27417747	5.02615110
0	15.31098547	-0.96507413	3.04902935
0	15.16058828	0.73145922	-1.19587487
0	12.99039125	-2.78941238	-0.20087451
0	11.03674858	-1.07119423	3.14649043
0	9.43036251	4.51006731	0.69658943
0	8.68354369	0.22412713	1.25497653
0	9.65337452	1.41413212	-2.64180922
0	13.08672227	3.59681470	-1.58536032
С	13.99210169	5.10773654	2.15340634
С	13.44116620	5.11122145	4.86378343
С	15.66281875	6.38300813	3.87977599
С	15.95795428	4.20013813	5.48457655
С	16.39073805	3.47633835	0.55809043
С	17.21123521	1.01231022	1.45019715
С	18.65909491	3.29808049	2.14573441
С	17.25280375	1.82088660	4.05079501

С	14.51372673	-0.59070112	2.30329646
С	14.42876506	0.49454307	-0.34466619
С	13.04233926	-1.74512461	0.28653497
С	11.79579671	-0.63453920	2.40431423
С	10.03435045	3.55478412	0.44968764
С	9.58025238	0.85211597	0.89281077
С	10.14883148	1.60935832	-1.61747380
С	12.36932081	2.98337607	-0.92626346
Н	16.62825705	4.41525535	2.95253095
Н	11.87144798	0.32920111	-0.26538896



LUMO -3.93 eV Figure S75. LUMO for 9 plus energy in eV, isovalue 0.05.



HOMO -6.40 eV

Figure S76. HOMO for 9 plus energy in eV, isovalue 0.05.



HOMO-1 -6.49 eV

Figure S77. HOMO-1 for **9** plus energy in eV, isovalue 0.05.



HOMO-11 -6.95 eV

Figure S78. HOMO-11 for 9 plus energy in eV, isovalue 0.05.

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