## **Supporting Information for**

## **Multiple Aromatic C-H Bond Activations by a Dirhenium Carbonyl Complex** Richard D. Adams\*, Poonam Dhull and Jonathan 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. <sup>1</sup>H NMR and <sup>13</sup>C 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. Re<sub>2</sub>(CO)<sub>10</sub> and anthracene were obtained from STREM and Sigma Aldrich and used without further purification. Re<sub>2</sub>(CO)<sub>8</sub>( $\mu$ -C<sub>6</sub>H<sub>5</sub>)( $\mu$ -H), **1** was prepared according to previously reported procedure.<sup>1</sup> Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å *F*<sub>254</sub> glass plates.

#### Preparation of $\text{Re}_2(\text{CO})_8(\mu-\text{H})(\mu-\eta^2-1,2-\text{C}_{14}\text{H}_9)$ , 2.

30.0 mg (0.0445 mmol) 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 CH<sub>2</sub>Cl<sub>2</sub> and separated by TLC by using hexane solvent to yield a yellow band of Re<sub>2</sub>(CO)<sub>8</sub>( $\mu$ -H)( $\mu$ - $\eta$ <sup>2</sup>-1,2-C<sub>14</sub>H<sub>9</sub>), **2**, 25.0 mg (73% yield). Spectral data for **2**: IR  $v_{CO}$  (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 2111(m), 2083(s), 2016(vs), 1989(s), 1969(vs), 1954(sh). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz,  $\delta$  in ppm): 8.51 (s, 1H, H9), 8.31 (s, 1H, H10), 8.09-8.12 (d-d, 1H, H8, <sup>3</sup>J = 6.3 Hz, <sup>4</sup>J = 3.3 Hz), 8.04-8.07 (d-d, 1H, H5, <sup>3</sup>J =

6.3 Hz, <sup>4</sup>J =3.3 Hz), 8.02-8.05 (d, 1H, H4, <sup>3</sup>J = 8.7 Hz), 7.57-7.60 (d-d, 2H, H6, H7, <sup>3</sup>J = 6.6 Hz, <sup>4</sup>J =3.3 Hz), 7.43-7.46 (d, 1H, H3, <sup>3</sup>J = 8.7 Hz), -13.02 (s, 1H, H2, hydride). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 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. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, DEPT, 100.66 MHz,δ in ppm): 146.77, 128.18, 128.12, 127.94, 126.98, 126.61, 126.50, 126.16, and 113.02. Mass Spec. EI/MS *m/z*: 774, M<sup>+</sup>, 718, M<sup>+</sup>-2CO. Elemental analysis (mass %) Calculated for Re<sub>2</sub>O<sub>8</sub>C<sub>22</sub>H<sub>10</sub>: C, 34.11; H, 1.30. Found: C, 33.84; H, 1.29.

#### Preparation of Re<sub>2</sub>(CO)<sub>8</sub>(μ-H)(μ-η<sup>2</sup>-1,2-μ-η<sup>2</sup>-3,4-C<sub>14</sub>H<sub>8</sub>)Re<sub>2</sub>(CO)<sub>8</sub>(μ-H), 3.

20.0 mg (0.0258 mmol) of **1** and 16.0 mg (0.0237 mmol) of **2** were dissolved in 1.6 mL CD<sub>2</sub>Cl<sub>2</sub> in a 5 mm NMR tube. The NMR tube was evacuated and filled with N<sub>2</sub> gas. The NMR tube was then allowed to sit for 24 h at 40 °C. A <sup>1</sup>H NMR spectrum obtained after this period showed two new hydride resonances at  $\delta$  = -13.15 and -13.68. The contents were then transferred to a flask and solvent was removed in *vacuo*. The residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and separated by TLC by using hexane solvent to give a yellow band of Re<sub>2</sub>(CO)<sub>8</sub>(µ-H)(µ-η<sup>2</sup>-1,2-µ-η<sup>2</sup>-3,4-C<sub>14</sub>H<sub>8</sub>)Re<sub>2</sub>(CO)<sub>8</sub>(µ-H), **3**, 18.0 mg (56% yield). Spectral data for **3**: IR *v*<sub>CO</sub> (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 2108(m), 2083(s), 2023(vs), 1990(sh), 1976(s), 1958(sh). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$  in ppm) 8.67 (s, 1H, H9), 8.28 (s, 1H, H10), 8.06-8.09 (d-d, 2H, H5, H8, <sup>3</sup>J = 6.3 Hz, <sup>4</sup>J = 3.3 Hz), 7.60-7.63 (d-d, 1H, H6, H7, <sup>3</sup>J = 6.3 Hz, <sup>4</sup>J = 3.3 Hz), 7.43 (s, 1H, H3), 7.02 (s, 1H, H1), -13.15 (s, 1H, H2, hydride), -13.68 (s, 1H, H4, hydride). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100.66 MHz, $\delta$  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. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, DEPT, 100.66 MHz, $\delta$  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<sup>+</sup>, 1344, M<sup>+</sup>-CO. Elemental analysis (mass %) Calculated for  $\text{Re}_4\text{O}_{16}\text{C}_{30}\text{H}_{10}$ : C, 26.28; H, 0.74. Found: C, 27.22; H, 1.42. This double activated compound has some long term stability issues that appear to be affecting the elemental analyses and lead to values slightly outside the traditionally accepted ranges.

#### Preparation of Re<sub>2</sub>(CO)<sub>8</sub>(μ-H)(μ-1,μ-3-C<sub>6</sub>H<sub>4</sub>)Re<sub>2</sub>(CO)<sub>8</sub>(μ-H), 4.

25.0 mg (0.0371 mmol) of 1 was dissolved in 1.6 mL CD<sub>2</sub>Cl<sub>2</sub> in a 5 mm NMR tube. The NMR tube was evacuated and filled with N<sub>2</sub> gas. The NMR tube was then allowed to sit for 24 h at 40 °C. A <sup>1</sup> H NMR spectrum obtained after this period showed new hydride resonance at  $\delta$  = -12.27. The contents were then put into a flask and solvent was removed in *vacuo*. The residue was extracted in CH<sub>2</sub>Cl<sub>2</sub> and separated by TLC by using hexane to give a yellow band of Re<sub>2</sub>(CO)<sub>8</sub>(µ-H)(µ-1,µ-3-C<sub>6</sub>H<sub>4</sub>)Re<sub>2</sub>(CO)<sub>8</sub>(µ-H), **4**, 12.0 mg (51% yield). Spectral data for **4**: IR *v*<sub>CO</sub> (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 2107(w), 2085(m), 2020(vs), 1993(sh), 1969(sh), 1958(s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$  in ppm) 8.68 (s, 1H, H2, <sup>4</sup>J = 1.5 Hz), 8.06-8.09 (d-d, 2H, H4, H6, <sup>3</sup>J = 7.2 Hz, <sup>4</sup>J = 1.5 Hz), 7.05-7.10 (t, 1H, H5, <sup>3</sup>J = 7.2 Hz), -12.27 (s, 2H, H1, H3, hydride). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100.66 MHz, $\delta$  in ppm): 186.28, 184.47, 184.11, 180.94, 175.59, 147.18, 128.88, and 124.56. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, DEPT, 100.66 MHz, $\delta$  in ppm): 175.59, 147.18 and 128.88. Mass Spec. EI/MS *m/z*: 1272. Elemental analysis (mass %) Calculated for Re<sub>4</sub>O<sub>16</sub>C<sub>22</sub>H<sub>6</sub>: C, 20.79; H, 0.48. Found: C, 21.68; H, 0.47. This double activated compound has some long term stability issues that appear to be affecting the elemental analyses and lead to values slightly outside the traditionally accepted ranges.

**Crystallographic Analyses**: Yellow single crystals of **2** and **4** suitable for x-ray diffraction analyses were obtained by slow evaporation of solvent from a solution in pure hexane at 15 °C. Yellow single crystals of **3** suitable for x-ray diffraction analyses was obtained by slow evaporation of a hexane solvent mixture at 15 °C. Each data crystal was glued onto the end of a thin glass fiber.

X-ray intensity data for compounds 2 and 4 was measured by using a Bruker SMART APEX CCD-based diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073$ Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.<sup>2</sup> 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 least-squares on F2, using the SHELXTL software packages<sup>3</sup>. 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. X-ray intensity data from a yellow plate of **3** having approximate dimensions 0.03 x 0.10 x 0.14 mm<sup>3</sup> was collected at 302(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å).<sup>1</sup> The data collection strategy consisted of five 180°  $\omega$ -scans at different  $\varphi$  settings and two 360°  $\varphi$ -scans, with a scan width per image of 0.5° The crystal-to-detector distance was 5.0 cm and each image was measured for 15 s. The average reflection redundancy was 19.0. The raw area detector data frames were reduced, scaled and corrected for absorption effects using the SAINT<sup>4</sup> and SADABS<sup>5</sup> programs (Estimated minimum / maximum transmission = 0.3446 / 0.4599). Final unit cell parameters were determined by leastsquares refinement of 9645 reflections in the range  $5.306^{\circ} < 2\theta < 55.325^{\circ}$  taken from the data set.



**Figure S1**. An ORTEP diagram of the molecular structure of  $\text{Re}_2(\text{CO})_8(\mu-\text{H})(\mu-\eta^2-1,2-C_{14}\text{H}_9)$ , **2**, 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 S2.** An ORTEP diagram of the molecular structure of  $\text{Re}_2(\text{CO})_8(\mu-\text{H})(\mu-\mu-\eta^2-1,2-\mu-\eta^2-3,4-C_{14}\text{H}_8)\text{Re}_2(\text{CO})_8(\mu-\text{H})$ , **3**, showing 25% thermal ellipsoid probability. Selected interatomic bond distances(Å) are as follow: Re(1)-Re(2)=3.0566(4), 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 S3. An ORTEP diagram of the molecular structure of  $Re_2(CO)_8(\mu-H)(\mu-1,\mu-3 C_6H_4$ )Re<sub>2</sub>(CO)<sub>8</sub>(µ-H), 4, showing 30% 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 S4. The <sup>1</sup>H NMR spectra of compound **2**.



Figure S5. The <sup>13</sup>C NMR spectra of compound **2**.



Figure S6. The <sup>1</sup>H NMR spectra of compound **3**.



Figure S7. The <sup>13</sup>C NMR spectra of compound **3** 



Figure S8. The <sup>1</sup>H NMR spectrum of compound **4**.



Figure S9. The <sup>13</sup>C NMR spectra of compound **4**.

Compound	2	3	4
Empirical formula	Re <sub>2</sub> O <sub>8</sub> C <sub>22</sub> H <sub>10</sub>	Re <sub>4</sub> O <sub>16</sub> C <sub>30</sub> H <sub>10</sub>	Re <sub>4</sub> O <sub>16</sub> C <sub>22</sub> H <sub>6</sub>
Formula weight	774.70	1371.18	1271.07
Crystal system	Monoclinic	Monoclinic	Triclinic
Lattice parameters			
<i>a</i> (Å)	13.5703(6)	9.3222(4)	8.8829(3)
<i>b</i> (Å)	13.8800(6)	17.8131(8)	11.4074(4)
<i>c</i> (Å)	11.6405(5)	21.1743(9)	15.4729(5)
$\alpha$ (deg)	90.000	90.000	86.520(10)
$\beta$ (deg)	95.129(10)	101.801(10)	80.180(10)
γ (deg)	90.000	90.000	67.418(10)
V (Å <sup>3</sup> )	2183.78(16)	3441.8(3)	1426.44(8)
Space group	P2 <sub>1</sub> /c	$P2_1/n$	<i>P</i> -1
Z value	4	4	2
$\rho_{calc}$ (g/cm <sup>3</sup> )	2.356	2.646	2.959
μ (Mo Kα) (mm <sup>-1</sup> )	11.122	14.094	16.99
Temperature (K)	302(2)	294(2)	301(2)
$2\theta_{max}(^{\circ})$	55.34	56.52	56.62
No. Obs. (I>2σ(I))	5151	8551	7112
No. Parameters	293	459	387
Goodness of fit (GOF)	1.056	1.052	1.112
Max. shift/error on final	0.002	0.002	0.002
cycle			
Residuals*: R1; wR2	0.0233; 0.0385	0.0373; 0.0931	0.0211; 0.0422
Absorption Correction,	Multi-Scan	Multi-Scan	Multi-Scan
Max/min	0.7314/0.3050	1.000/0.572	0.4604/0.2545
Largest peak in Final	1.064	2.486	1.209
Diff. Map (e <sup>-/</sup> Å <sup>3</sup> )			

 Table S1. Crystal data, and results of the analyses for compounds 2 - 4.

<sup>a</sup> R1 =  $\Sigma_{hkl}(||F_{obs}| - |F_{calc}||)/\Sigma_{hkl}|F_{obs}|; wR2 = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF^2_{obs}]^{1/2};$  $w = 1/\sigma^2(F_{obs}); GOF = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}.$ 

Computational Analyses

All calculations were performed with ADF2014 program by using the PBEsol-D3 functional with ZORA scalar relativistic correction<sup>6</sup> and valence triple- $\zeta$  + 1 polarization, relativistically optimized (TZP) 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.<sup>7</sup> 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 systems <sup>8</sup> and for metal clusters.<sup>9</sup> This is also consistent with our own testing of various functionals for the structures and relative energetics in organometallic cluster complexes. The dispersion corrections by Grimme et al <sup>6h</sup> were included upon additional testing, once they became available in the current release of ADF.



Figure S10. Drawing of the geometry optimized structure of 3.

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

Re	4.14002756	-2.01067455	-0.08441739
Re	1.91749038	-2.73622949	-2.01018440
Re	-1.64887182	-4.18898858	0.76360341
Re	-1.17697926	-1.80154811	2.56655275
0	3.74289195	-4.64007337	1.57586021
0	4.90107604	-0.50300415	2.50943962
0	7.00863597	-3.10423306	-0.63698178

0	5.05250915	0.41350288	-1.85285369
0	1.95786708	-5.76588022	-1.17817517
Ο	-1.02732655	-2.79262302	-2.95941136
Ο	2.90436192	-3.65050456	-4.78714814
Ο	2.00433741	0.18719544	-3.14384778
Ο	0.69695416	-5.84218179	2.03268816
Ο	-1.19784830	-5.75885532	-1.86546137
0	-4.01910283	-2.69302682	-0.63873711
0	-3.66130070	-6.30022969	1.87045372
0	1.65243778	-2.83701455	3.44412996
0	-0.20151960	1.06635255	3.20880895
0	-2.06717490	-2.26660618	5.48267840
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
Η	1.48606581	-3.52142412	0.65063756
С	-0.38386164	-2.44875946	0.39479051
С	-0.87154513	-1.15018531	0.17858938
Η	-1.92590223	-0.99674368	-0.08278243
С	-0.00631075	-0.00577772	-0.02172503
С	-0.56034486	1.25188934	-0.20191576
Η	-1.65157899	1.35142085	-0.26324218
С	0.23495152	2.40994888	-0.25487908
С	-0.31199667	3.70557579	-0.42492319
Η	-1.39527383	3.81002962	-0.55006814
С	0.50424032	4.81186184	-0.42683435
Η	0.07314424	5.80931185	-0.55767497
С	1.90159355	4.67315987	-0.25801315
Η	2.53706266	5.56415847	-0.26291249
С	2.46293009	3.42945305	-0.08963792
Η	3.54512932	3.31598779	0.03649711
С	1.65147559	2.26852579	-0.08718333
С	2.19942093	0.97881970	0.04973384
Η	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
Η	3.76447586	-2.84024264	-1.69720140
Н	-1.94100609	-3.50366655	2.45872572

 Table S3. 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
Η	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
Η	3.33960020	-0.86004563	0.01464776
Н	-0.13231493	-3.42367903	-0.01864654
Н	2.34779648	-3.13062001	0.00003915

Figures S11 – S15 of Selected MO of Anthacene.

Figure S11. HOMO of Anthracene plus energy in eV, ISO value 0.05.



HOMO, -5.024 eV

Figure S12. HOMO-1 for Anthracene plus energy in eV, ISO value 0.05.



HOMO-1 -6.229 eV

Figure S13. HOMO-2 for Anthracene plus energy in eV, ISO value 0.05.



# HOMO-2 -6.531 eV

**Figure S14.** HOMO-3 for Anthracene plus energy in eV, ISO value 0.05.



HOMO-3 -7.546 eV

Figure S15. HOMO-4 for Anthracene plus energy in eV, ISO value 0.05.



HOMO-4 -7.672 eV



Figure S16. Drawing of the geometry optimized structure of 4.

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

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
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С	0.10411452	-2.42271297	-4.20533388
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С	-2.21969696	0.73600443	-2.00172033
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С	1.23367241	2.20115312	-3.27673556
Η	-0.60398226	0.36599755	3.55983687
Н	-0.36355127	-0.11781274	-3.65066174

### References

1. R. D. Adams, V. Rassolov and Y. O. Wong, Angew. Chem. Int. Ed., 2014, 53, 11006 - 11009.

2. SAINT+, version 6.2a, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2001.

3. G. M. Sheldrick, SHELXTL, version 6.1, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.

4. APEX3 Version 2016.5-0 and SAINT Version 8.37A. Bruker AXS, Inc. Madison, WI, USA.

5. SADABS Version 2016/2. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, J. *Appl. Cryst.*, 2015, **48**, 3-10.

6. (a) G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E.J. Baerends, J.G. Snijders and T. Ziegler, *J. Comp. Chem.*, 2001, 22, 931-967; (b) C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends Theoret, *Chem. Accts.*, 1998, 99, 391-403; (c) J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke *Phys. Rev. Lett.*, 2008, 100, 136406; (d) J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke *Phys. Rev. Lett.*, 2008, 100, 136406; (d) J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.*, 2009, 102, 039902; (e) E. van Lenthe, E. J. Baerends, J. G. Snijders, *J. Chem. Phys.*, 1993, 99, 4597; (f) E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1994, 101, 9783; (g) E. van Lenthe, A. E. Ehlers and E. J. Baerends, *J. Chem. Phys.*, 1999, 110, 8943; (h) S. Grimme, J. Anthony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, 132, 154104.

7. (a) R. D. Adams, Y. Kan, V. Rassolov and Q. Zhang, *Organometallics*, 2013, **730**, 20 – 31; (b) R. D. Adams, V. Rassolov and Y. O. Wong, *Angew.Chem. Int. Ed.*, 2016, **55**, 1324 - 1327.

8. G. I. Csonca, A. Ruzisinsky, J. P. Perdew and S. Grimme, *J. Chem. Theor. Comp.*, 2008, 4, 888-891.

9. (a) R. Koitz, T. M. Soini, A. Genest, S. B. Trickey and N. Rosch, *J. Chem. Phys.*, 2008, **137**, 034102; (b) M. P. Johansson, A. Lechtken, D. Schooss, M. M. Kappes and F. Furche, *Phys. Rev.*, 2008, **77**, 035202.