

SUPPLEMENTARY INFORMATION

Organometallic Chemistry of New Carbon Material IV. Structure and Dynamic Behavior of Group 6 metal Tricarbonyl Complexes of Graphene and Perforated Graphene: A DFT Study

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Table S1. Selected bond lengths (Å) and angles (°) for the optimized structure of coronene **I**, comparison with previous DFT, X ray and electron diffraction data.

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Table S3. Calculated and experimental chemical shifts ¹H and ¹³C (ppm) for **I**, **II**, **Ia,b-M** and **IIa,b-M** (M=Cr,Mo). Atoms numbering as in Fig.3. Data for W were not calculated.

Table S4. Symmetrical (*A*) and unsymmetrical (*E*) ν_{CO} vibrational frequencies (in cm⁻¹) complexes **Ia,b-M** **IIa,b-M**. Vibrational frequencies of (η^6 -naphthalene)M(CO)₃ **V** (M=Cr, Mo, W) are presented for comparison.

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Table S6. Selected computed data for the optimized structures of **Ia,b-M**. Relative energies in kcal/mol, bond lengths in Å.

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S11. Experimental for related complexes and calculated IR ν_{CO} values for metal tricarbonyl complexes of graphene (cm⁻¹). Table S12. Computed bond lengths (Å) in model graphene **III**.

Table S1. Selected bond lengths (Å) and angles (°) for the optimized structure of coronene **I**, comparison with previous DFT, X ray and electron diffraction data.

Bond lengths	PBE/L2	X ray	Δ	B3LYP/6-31G	Δ (DFT)	Electron diffraction
C1-C4	1.423	1.405	0.018	1.426	-0.003	1.444
C1-C2	1.425	1.413	0.012	1.424	0.001	1.381
C2-C3	1.426	1.412	0.014	1.423	0.003	1.438
C4-C5	1.375	1.360	0.015	1.375	0.000	1.362
C-H	1.092	0.983	0.109	1.093	-0.001	1.090
C4-C1-C2	118.76	118.74	0.02	118.77	-0.01	
C1-C2-C3	120.00	118.84	1.16	120.00	0.00	
C5-C4-C1	121.26	122.02	-0.76	121.22	0.040	

Δ : Difference between X ray and our DFT results, J. M. Robertson and J. G. White, *J. Chem. Soc. (Resumed)*, 1945, 607.

Δ (DFT): Difference between our DFT results and DFT from the literature (G.R. Jenness and K.D. Jordan, *J. Phys. Chem. C*, 2009, **113**, 10242).

Table S2. Selected bond lengths (Å) and angles (°) for the optimized structure of kekulene **II** and comparison with X ray and previous DFT calculations.

Bond lengths	PBE/L2	X ray	Δ	B3LYP/6-31G	Δ (DFT)
C1-C2	1.439	1.445	-0.006	1.441	-0.002
C1-C6	1.366	1.350	0.016	1.362	0.004
C3-C4	1.457	1.456	0.001	1.460	-0.003
C4-C5	1.395	1.394	0.001	1.394	0.001
C-H _{in}	1.085	-	-	-	-
C-H _{out}	1.093	-	-	-	-
C6-C1-C2	121.8	122.0	-0.2	-	-
C2-C3-C4	119.9	119.9	0.0	-	-
C4-C5-C7	123.5	123.7	-0.2	-	-
C5-C7-C8	118.4	118.3	0.1	-	-

Δ : Difference between X ray and our DFT results (H. A. Staab, F. Diederich, C. Krieger and D. Schweitzer, *Chem. Ber.*, 1983, **116**, 3504).

Δ (DFT): Difference between our DFT and DFT from the literature (H. Jiao, P.V.R. Schleyer, *Angew. Chem. Int. Ed. in English*, 1996, **35**, 2383).

Table S3. Calculated and experimental chemical shifts ^1H and ^{13}C (ppm) for **I**, **II**, **Ia,b-M** and **IIa,b-M** (M=Cr,Mo). Atoms numbering as in Fig.3. Data for W were not calculated.

Atom	Ligand (exp.)		Cr		Mo			
	I ^a	II ^b	I	II	I	II		
a	C1	128.8	135.2	95.1	111.2	96.6	113.6	
	C2	128.8	138.4	95.2	110.5	96.8	114.7	
	C3	132.2	133.0	109.1	95.1	112.2	95.6	
	C4	135.9	138.4	106.0	107.8	109.2	110.7	
	C5	135.9	135.2	106.0	108.3	109.1	109.6	
	C6	-	119.7	-	81.8	-	84.6	
	C _{CO}	-	-	219.4; 227.7	228.2/ 228.5/229.4	220.3; 226.8	230.4/230.7	
	C _{npoc}	-	10.48	131.6-137.5	8.87	130.1-136.3	10.1/10.7/10.9	
	H _{coord(I)/} H _{inner(II)}	-	8.67; 9.05	6.41	6.68/7.64/ 8.04	6.54	6.76/7.44/ 7.89/8.1-8.7	
	H _{other(I)/} H _{outer(II)}	9.32	135.2	8.50-8.86	111.2	8.31-8.67	113.6	
b	C1	135.9	134.26	103.5	95.7	107.6	96.2	
	C2	135.9	134.26	95.7	95.5	100.8	96.2	
	C3	132.2	138.4	142.8	113.4	138.8	116.5	
	C4	128.8	135.2	131.8	110.3	131.5	113.3	
	C5	128.8	135.2	134.5	135.6	134.3	113.3	
	C6	-	138.4	-	110.4	-	116.5	
	C _{CO}	-	-	225.5	223.4/ 227.6	228.1	224.1/228.7	
	H(I)/ H _{inner(II)}	9.32	10.48	9.96; 9.77	10.83	9.30; 9.49	10.3/10.7/10.8	
	H _{outer(II)}		8.67; 9.05		6.64/ 6.65		6.5/8.1-8.7	
	a	Atom	Ligand (exp.)		Cr		Mo	
I ^a			II ^b	I	II	I	II	
C1		128.8	135.2	95.1	111.2	96.6	113.6	
C2		128.8	138.4	95.2	110.5	96.8	114.7	
C3		132.2	133.0	109.1	95.1	112.2	95.6	
C4		135.9	138.4	106.0	107.8	109.2	110.7	
C5		135.9	135.2	106.0	108.3	109.1	109.6	
C6		-	119.7	-	81.8	-	84.6	
C _{CO}		-	-	219.4; 227.7	228.2/ 228.5/229.4	220.3; 226.8	230.4/230.7	
C _{npoc}		-	10.48	131.6-137.5	8.87	130.1-136.3	10.1/10.7/10.9	
H _{coord(I)/} H _{inner(II)}		-	8.67; 9.05	6.41	6.68/7.64/ 8.04	6.54	6.76/7.44/ 7.89/8.1-8.7	
H _{other(I)/} H _{outer(II)}		9.32	135.2	8.50-8.86	111.2	8.31-8.67	113.6	
b		C1	135.9	134.26	103.5	95.7	107.6	96.2
		C2	135.9	134.26	95.7	95.5	100.8	96.2
		C3	132.2	138.4	142.8	113.4	138.8	116.5
		C4	128.8	135.2	131.8	110.3	131.5	113.3
		C5	128.8	135.2	134.5	135.6	134.3	113.3
		C6	-	138.4	-	110.4	-	116.5
		C _{CO}	-	-	225.5	223.4/ 227.6	228.1	224.1/228.7
		H(I)/ H _{inner(II)}	9.32	10.48	9.96; 9.77	10.83	9.30; 9.49	10.3/10.7/10.8
H _{outer(II)}		8.67; 9.05		6.64/ 6.65		6.5/8.1-8.7		

a) J. M. Robertson and J. G. White, *J. Chem. Soc. (Resumed)*, 1945, 607. b) H. A. Staab, F. Diederich, C. Krieger and D. Schweitzer, *Chem. Ber.*, 1983, **116**, 3504.

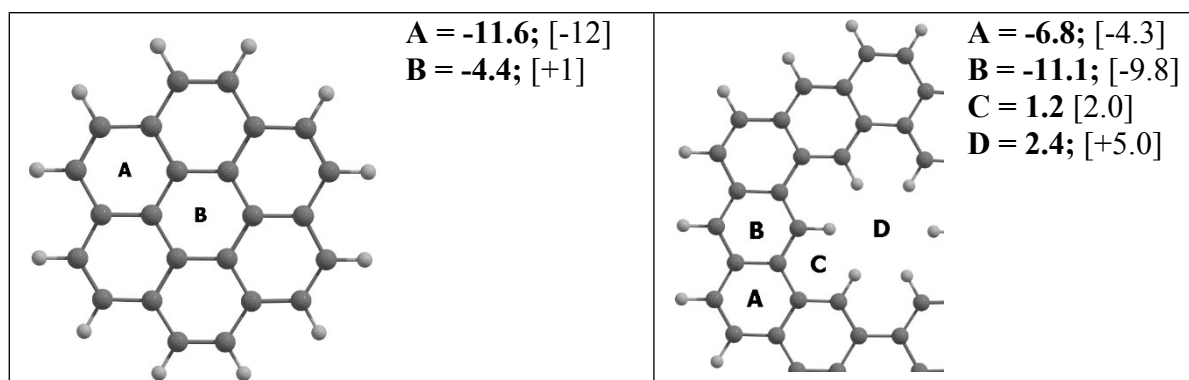
Table S4. Symmetrical (*A*) and unsymmetrical (*E*) ν_{CO} vibrational frequencies (in cm^{-1}) complexes **Ia,b-M** **IIa,b-M**. Vibrational frequencies of (η^6 -naphthalene) $\text{M}(\text{CO})_3$ **V** ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$) are presented for comparison.

PBE/L2	Ia-M	Ib-M	IIa-M	IIb-M	V Experiment*	V BLYP/JMW**
M=Cr $\nu_{\text{CO}}, \text{sm}^{-1}$	<i>E</i> : 1922.98	1915.93	1930.37	1919.61	1893 ^a	1917.6
	<i>E</i> : 1931.55	1916.34	1936.16	1934.49	1908	1928.3
	<i>A</i> : 1977.10	1969.46	1978.37	1978.07	1971	1978.2
M=Mo $\nu_{\text{CO}}, \text{sm}^{-1}$	<i>E</i> : 1912.74	1906.30	1919.46	1910.37	1859 ^b	-
	<i>E</i> : 1925.27	1906.32	1926.99	1925.79	1883	-
	<i>A</i> : 1975.23	1966.35	1974.12	1974.88	1960	-
M=W $\nu_{\text{CO}}, \text{sm}^{-1}$	<i>E</i> : 1916.02	1910.20	1922.40	1912.80	1854 ^b	-
	<i>E</i> : 1925.68	1910.32	1929.83	1924.65	1879	-
	<i>A</i> : 1974.91	1966.76	1976.42	1973.07	1956	-

* a) Yu.F. Oprunenko, N.G. Akhmedov, D.N. Laikov, S.G. Malyugina, V.I. Mstislavsky, V.A. Roznyatovsky and N.A. Ustynyuk, *J. Organomet. Chem.*, 1999, **583**, 136. b) data for **V** (Mo, W) were taken from Oprunenko, *Doctor of Science (Habilitation) Thesis*, Department of Chemistry, M.V. Lomonosov Moscow State University, 1999, Moscow

** B.V. Lokshin, N.E. Borisova, B.M. Senyavin and M.D. Reshetova, *Russ. Chem. Bull.*, 2002, **51**, 1656.

Table S5. NICS (1) data calculated for **I** and **II**. In brackets: NICS (0) extracted from literature



a) H. Jiao, P.V.R. Schleyer, *Angew. Chem. Int. Ed.in English*, 1996, **35**, 2383. b) F. De Proft and P. Geerlings, *Chem. Rev.*, 2001, **101**, 1451. c) J. M. Martin, *Chem. Phys. Lett.*, 1996, **262**, 97.

Table S6. Selected computed data for the optimized structures of **Ia,b-M**. Relative energies in kcal/mol, bond lengths in Å.

	Ia-M			Ib-M		
	Cr	Mo	W	Cr	Mo	W
ΔE	0.0	0.0	0.0	12.0	11.0	12.5
ΔG	0.0	0.0	0.0	12.7	10.1	12.4
M-ligand	1.768	1.909	1.880	1.811	2,025	1.991
C1-C2	1.403	1.403	1.408	1.436	1,438	1.440
C2-C3	1.436	1.441	1.443	1.438	1,435	1.439
C3-C4	1.434	1.435	1.437	1.416	1.417	1.416
C4-C5	1.443	1.447	1.449	1.383	1.380	1.381

Table S7. Selected computed data for the optimized structures **IIa,b-M**. Relative energies in kcal/mol; bond lengths in Å, for all **IIa-M** $\Delta G=0$ kcal/mol; for **IIb-M** $\Delta G=1.6$ kcal/mol (Mo) $\Delta G=3.1$ kcal/mol (W).

Parameter	IIa-M			IIb-M		
	Cr	Mo	W	Cr	Mo	W
ΔG	0.0	0.0	0.0	5.9	1.6	3.1
M-C1	2.313	2.478	2.438	2.206	2.356	2.337
M-C2	2.304	2.468	2.421	2.206	2.356	2.337
M-C3	2.202	2.362	2.372	2.342	2.501	2.477
M-C4	2.255	2.401	2.406	2.366	2.535	2.498
A	$\sim 6^\circ$	$\sim 6^\circ$	$\sim 8^\circ$	$\sim 1^\circ$	$\sim 2^\circ$	$\sim 2^\circ$
C1-C2	1.432	1.433	1.440	1.402	1.402	1.408
C2-C3	1.437	1.440	1.436	1.443	1.448	1.449
C3-C4	1.423	1.424	1.433	1.442	1.443	1.445
C4-C5	1.445	1.450	1.444	1.466	1.470	1.471

A: deviation of coordinated ring plane with respect to the uncoordinated part of the ligand ($^\circ$)

Table S8. Selected bond lengths in **TS(Ia-b)**, **IM(Ia-b)**, **TS' (Ia-b)** for Mo and W complexes, Å.

	Mo	W
TS	a=2.404 b=2.941 c=2.745 d=2.694	a=2.334 b=2.894 c=2.687 d=2.606
IM	a=2.373 b=2.735 c=2.842 d=2.736	a=2.298 b=2.679 c=2.761 d=2.677
TS'	a=2.381 b=2.719 c=2.885 d=2.718	a=2.316 b=2.640 c=2.848 d=2.640

Table S9. Selected bond lengths in **TS(Ia-a)** for Cr, Mo, W complexes, Å.

	Cr	Mo	W
a	2.155	2.335	2.273
b	2.495	2.647	2.605
c	2.495	2.647	2.605
d	2.640	2.837	2.722

Table S10. Selected bond lengths in **TS(IIa-b)** for Cr, Mo, W complexes, Å.

	Cr	Mo	W
a	2.159	2.353	2.301
b	2.296	2.445	2.356
c	2.485	2.677	2.612
d	2.745	2.962	2.930

Table. S11. Experimental (related complexes) and calculated IR ν_{CO} values for **IIIa** and **IIIe** complexes (cm^{-1}).

	Cr		Mo		W	
	DFT	Experiment*	DFT	Experiment**	DFT	Experiment**
IIIa	E:1948,91; 1948.93 A: 1988.50	E:1893; 1908 A:1971	E:1938,02; 1938.17 A: 1984.62	E:1859; 1883 A:1960	E:1943.63; 1943.65 A: 1987.43	E:1856; 1879 A:1956
IIIe	E:1941.96; 1955.15 A:1992.35	E:1893; 1908 A:1971	E:1932.24; 1948.37 A:1990.95	E:1859; 1883 A:1960	E:1936.92; 1951.12 A:1992.10	E:1856; 1879 A:1956

* Oprunenko Yu.F., Doctor of science thesis (Habilitation), Department of Chemistry, M.V. Lomonosov Moscow State University, **1999**, Moscow, 350c; ** R.S. Armstrong, M.J. Aroney, C.M. Barnes, K.W. Nugent, *Appl. Organomet. Chem.*, 1990, **4**, 569.

Table S12. Computed bond lengths (\AA) in model graphene **III**.

C1-C2	1.422
C2-C3	1.424
C3-C4	1.427
C4-C5	1.423
C5-C6	1.439
C6-C7	1.394
C6-C8	1.440
C8-C9	1.364
C8-H	1.094