Understanding the Singlet-Triplet Energy Splittings in Transition Metal-Capped Carbon Chains

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Electronic Supplementary Information

Complete Q-Chem and Gaussian Reference (reference 69 and 78).

Table S1. Relative energies, S^2 and number of unpaired electrons (Head-Gordon Index) using spin-flip DFT (SF-DFT) method (non-collinear SF-DFT with PBE0/ def2-SVP) of **RuCC**, **MnCC**, **W^{1}CC**, **IrCC** and **W^{2}CC**.

Table S2. Bond parameters of **RuC$_4$** from computation (this work) and experiment (with dppe and Cp* ligands).

Table S3. Zero-point vibration energy corrected electronic energy of odd and even Ru-capped carbon chains (**RuCC**) in singlet and triplet states.

Table S4. Zero-point vibration energy corrected electronic energy of odd and even Mn-capped carbon chains (**MnCC**) in singlet and triplet states.

Table S5. Zero-point vibration energy corrected electronic energy of odd and even W-capped carbon chains (**W^{1}CC**) with the terminus [W(CO)$_2$(dmpe)NO] in singlet and triplet states.

Table S6. Zero-point vibration energy corrected electronic energy of odd and even Ir-capped carbon chains (**IrCC**) in singlet and triplet states.

Table S7. Zero-point vibration energy corrected electronic energy of odd and even

W-capped carbon chains (**W^2CC**) with the terminus [$W(CO)_2$(dmpe)Cl] in singlet and triplet states.

Figure S1. The lowest unoccupied molecular orbitals (LUMO), the highest occupied molecular orbitals (HOMO) and the singly occupied molecular orbital (SOMO), SOMO−1, fragment's contribution to MO (metal/carbon chain/others, in percentage in the table), electron occupation and orbital energy (in eV, beside the electron occupation) from **RuC_5** to **RuC_{10}** in singlet and triplet states.

Figure S2. The LUMO, HOMO, SOMO, SOMO−1, fragment's contribution to MO (metal/carbon chain/others, in percentage in the table), electron occupation and orbital energy (in eV, beside the electron occupation) from **MnC_5** to **MnC_{10}** in singlet and triplet states.

Figure S3. The LUMO, HOMO, SOMO, SOMO−1, fragment's contribution to MO (metal/carbon chain/others, in percentage in the table), electron occupation and orbital energy (in eV, beside the electron occupation) from **W^1C_5** to **W^1C_{10}** in singlet and triplet states.

Figure S4. The LUMO, HOMO, SOMO, SOMO−1, fragment's contribution to MO (metal/carbon chain/others, in percentage in the table), electron occupation and orbital energy (in eV, beside the electron occupation) from **IrC_5** to **IrC_{10}** in singlet and triplet states.

Figure S5. The LUMO, HOMO, SOMO, SOMO−1, fragment's contribution to MO (metal/carbon chain/others, in percentage in the table), electron occupation and orbital energy (in eV, beside the electron occupation) from **W^2C_5** to **W^2C_{10}** in singlet and triplet states.

Figure S6. The LUMO, HOMO, SOMO, SOMO−1, electron occupation and orbital energy (in eV, beside the electron occupation) from uncapped carbon chain **C_5** to **C_{10}** in singlet and triplet states.

Figure S7. The various MO/LUMO energy gaps of **W^1CC** and HOMO/LUMO gap of **MnCC**, and the MOs and fragment's contribution to MO of **W^1C_7** in singlet.

Table S8. The Spin Densities on transition metals of the triplet metal-capped carbon chains.

Table S9. The bond distance (Å) of the single and triplet states Ru-capped carbon chains.

Table S10. The bond distance (Å) of the single and triplet states Mn-capped carbon chains.

Table S11. The bond distance (Å) of the single and triplet states W-capped carbon chains with the terminus [$W(CO)_2$(dmpe)NO].

Table S12. The bond distance (Å) of the single and triplet states Ir-capped carbon chains.

Table S13. The bond distance (Å) of the single and triplet states W-capped carbon chains with the terminus [$W(CO)_2$(dmpe)Cl].

Table S14. The W-N-O angle between tungsten and NO ligands in the **W^1CCs** with the terminus [$W(CO)_2$(dmpe)NO].

Theoretical Cartesian coordinates for all complexes. (see the txt ESI file)

Complete Q-Chem reference (reference 69)

Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kuś, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. D. Hanson-Heine, P. H. P. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyaev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, E. Neuscamman, C. M. Oana, R. Olivares-Amaya, D. P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A. J. W. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yeganeh, S. R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J.-D. Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. Van Voorhis, J. M. Herbert, A. I. Krylov, P. M. W. Gill and M. Head-Gordon, *Mol. Phys.*, 2015, **113**, 184-215.

Complete Gaussian reference (reference 78)

Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

Table S1. Relative energies, S^2 and number of unpaired electrons (Head-Gordon Index) using spin-flip DFT (SF-DFT) method (non-collinear SF-DFT with PBE0/ def2-SVP) of **RuCC**, **MnCC**, **W[1]CC**, **IrCC** and **W[2]CC**. [a]RuC_4 with dppe and Cp* ligands.

RuCC	E_ex, eV	$<S^2>$	$n_{u,nl}$	State
C1	0.00	0.13	0.03	singlet
	0.46	2.06	2.00	triplet
	0.58	0.45	2.00	open-shell singlet
C2	0.00	0.45	0.67	singlet
	0.03	1.63	1.88	triplet
	0.24	0.07	2.00	open-shell singlet
C3	0.00	1.13	1.95	open-shell singlet (spin-contaminated)
	0.16	0.94	0.85	singlet
	0.23	2.05	1.98	triplet
C4	0.00	2.20	2.03	triplet
	0.04	0.16	0.49	singlet
	0.20	0.50	2.12	open-shell singlet
C4 dppe-Cp*[a]	0.00	0.25	0.10	singlet
	0.15	2.27	2.04	triplet
	0.26	0.63	2.11	open-shell singlet
C5	0.00	0.48	0.82	singlet
	0.05	1.23	2.02	open-shell singlet (spin-contaminated)
	0.05	1.99	2.01	triplet
C6	0.00	0.70	0.49	singlet
	0.21	1.82	2.04	triplet
	0.24	1.67	2.14	open-shell singlet (spin-contaminated)

MnCC	E_ex, eV	$<S^2>$	$n_{u,nl}$	State
C1	0.00	0.23	0.68	singlet
	0.27	2.19	2.01	triplet
	0.74	1.05	2.05	open-shell singlet (spin-contaminated)

C2	0.00	2.37	2.03	triplet
	0.40	0.22	1.94	singlet
	0.42	0.23	2.02	open-shell singlet
C3	0.00	0.41	0.13	singlet
	1.44	1.56	2.10	triplet
	1.51	1.21	2.30	open-shell singlet (spin-contaminated)
C4	0.00	2.34	2.02	triplet
	0.29	0.22	1.90	singlet
	0.31	0.25	2.02	open-shell singlet
C5	0.00	0.34	0.12	singlet
	1.14	0.97	2.11	open-shell singlet (spin-contaminated)
	1.19	2.05	2.08	triplet

W^{1}CC	E_ex, eV	<S^2>	$n_{u,nl}$	State
C1	0.00	3.66	4.90	
	0.05	2.10	4.97	
	0.22	3.39	4.83	
C2	0.00	2.07	3.65	
	0.07	1.95	3.88	
	0.32	3.46	4.38	
C3	0.00	3.19	5.80	
	0.06	4.57	5.73	
	0.16	4.27	5.98	
C4	0.00	2.30	3.23	
	0.19	2.23	3.70	
	0.23	2.73	3.64	
C6	0.00	2.00	3.48	
	0.96	2.34	2.03	
	1.20	0.22	1.91	

IrCC	E_ex, eV	<S^2>	$n_{u,nl}$	State
C1	0.00	2.79	2.90	

	0.04	1.93	2.99	
	0.23	2.60	4.23	
C3	0.00	3.23	5.01	
	0.06	2.33	4.37	
	0.09	2.52	4.68	
C4	0.00	2.06	3.65	
	0.01	1.95	3.68	
	0.13	1.62	3.66	
C5	0.00	2.92	5.06	
	0.04	3.09	4.65	
	0.14	3.23	5.15	

W^2CC	E_ex, eV	$<S^2>$	$n_{u,nl}$	State
C1	0.00	2.21	4.14	
	0.06	4.48	4.26	
	0.19	1.96	2.91	
C2	0.00	1.62	3.28	
	0.00	1.63	3.29	
	0.25	4.32	3.79	
C3	0.00	3.91	6.50	
	0.10	3.92	6.54	
	0.14	3.58	6.15	
C4	0.00	2.23	3.74	
	0.27	2.19	4.31	
	0.43	3.86	4.71	
C5	0.00	3.12	5.85	
	0.18	6.54	6.33	
	0.21	3.12	6.24	

Table S2. Bond parameters of **RuC_4** from computation (this work) and experiment (with dppe and Cp* ligands).

	Ru1-C1	C1-C2	C2-C3	C3-C4	C4-Ru2
Exp.[a]	1.856	1.280	1.294	1.269	1.858
This work	1.863	1.282	1.310	1.282	1.863
	Ru-P1	Ru-P2	Ru-C(Cp)		
Exp.[a]	2.319, 2.312	2.311, 2.330	2.260-2.300 /2.262-2.309		
This work	2.328,2.331	2.328,2.331	2.265, 2.271, 2.296, 2.319, 2.326		
	Ru1-C1-C2	C1-C2-C3	C2-C3-C4		
Exp[a]	175.6/170.1	176.7	174.2		
This work	178.5	179.2	179.1		

[a]ref: M. I. Bruce, B. G. Ellis, P. J. Low, B. W. Skelton and A. H. White, *Organometallics*, 2003, **22**, 3184-3198.

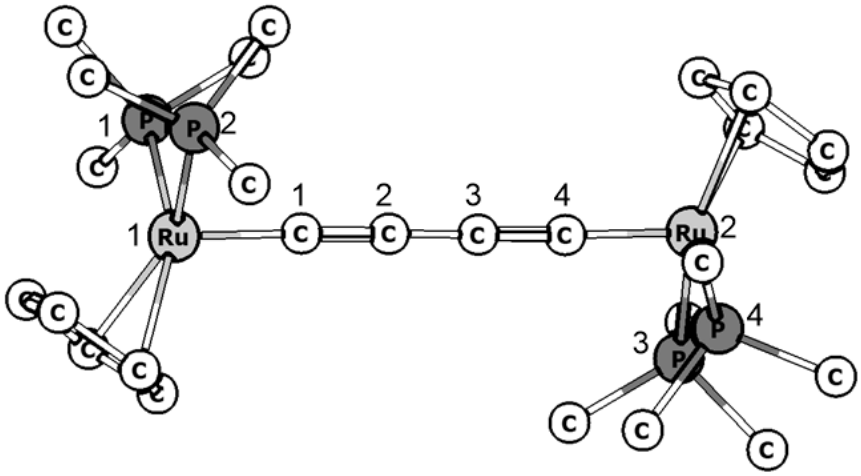


Table S3. Zero-point vibration energy corrected electronic energy of odd and even Ru-capped carbon chains (**RuCC**) in singlet and triplet states.

Odd carbon chain				Even carbon chain			
n_C*	E(S)/hartree	E(T)/hartree	ΔE(S-T) kcal·mol^{-1}	n_C*	E(S)/hartree	E(T)/hartree	ΔE(S-T) kcal·mol^{-1}
				4[#]	-2569.467937	-2569.463778	-2.61
				4	-2571.835985	-2571.836253	0.17
5	-2609.917345	-2609.867495	-31.28	6	-2647.946954	-2647.948070	0.70
7	-2686.020662	-2685.98251	-23.94	8	-2724.054628	-2724.055493	0.54
9	-2762.123430	-2762.093351	-18.87	10	-2800.159669	-2800.161260	1.00
11	-2838.225494	-2838.196558	-18.16	12	-2876.264165	-2876.265463	0.81
13	-2914.327151	-2914.302861	-15.24	14	-2952.367423	-2952.368706	0.81
15	-2990.428518	-2990.412545	-10.02	16	-3028.470053	-3028.471362	0.82
17	-3066.529644	-3066.516941	-7.97	18	-3104.572195	-3104.573541	0.84
19	-3142.630572	-3142.612762	-11.18	20	-3180.673960	-3180.675351	0.87

*number of carbon atoms in the chain; [#]RuC_4-dppe.

Table S4. Zero-point vibration energy corrected electronic energy of odd and even Mn-capped carbon chains (**MnCC**) in singlet and triplet states.

Odd carbon chain				Even carbon chain			
n_C*	E(S)/hartree	E(T)/hartree	ΔE(S-T) kcal·mol^{-1}	n_C*	E(S)/hartree	E(T)/hartree	ΔE(S-T) kcal·mol^{-1}
				4	-4974.083812	-4974.100446	10.44
5	-5012.172310	-5012.129669	-26.76	6	-5050.196371	-5050.210150	8.65
7	-5088.277595	-5088.243511	-21.39	8	-5126.306250	-5126.318096	7.43
9	-5164.382362	-5164.354764	-17.32	10	-5202.414223	-5202.424661	6.55
11	-5240.486563	-5240.463582	-14.42	12	-5278.520828	-5278.530195	5.88
13	-5316.590298	-5316.570872	-12.19	14	-5354.626479	-5354.634918	5.30
15	-5392.693635	-5392.676382	-10.83	16	-5430.731293	-5430.739041	4.86
17	-5468.796534	-5468.781237	-9.60	18	-5506.835467	-5506.842680	4.53
19	-5544.899113	-5544.885544	-8.51	20	-5582.939092	-5582.945918	4.28

*number of carbon atoms in the chain

Table S5. Zero-point vibration energy corrected electronic energy of odd and even W-capped carbon chains (**W^{1}CC**) with the terminus [W(CO)$_2$(dmpe)NO] in singlet and triplet states.

Odd carbon chain				Even carbon chain			
n_C*	E(S)/hartree	E(T)/hartree	ΔE(S-T) kcal·mol^{-1}	n_C*	E(S)/hartree	E(T)/hartree	ΔE(S-T) kcal·mol^{-1}
				4	-2839.819425	-2839.822331	1.82
5	-2877.882509	-2877.861066	-13.46	6	-2915.927746	-2915.931633	2.44
7	-2953.989549	-2953.971625	-11.25	8	-2992.034998	-2992.039408	2.77
9	-3030.096020	-3030.080260	-9.89	10	-3068.141127	-3068.145725	2.89
11	-3106.201726	-3106.187563	-8.89	12	-3144.245029	-3144.251032	3.77
13	-3182.306769	-3182.293960	-8.04	14	-3220.349467	-3220.355923	4.05
15	-3258.411254	-3258.399925	-7.11	16	-3296.454634	-3296.460584	3.73
17	-3334.515264	-3334.504522	-6.74				

*number of carbon atoms in the chain

Table S6. Zero-point vibration energy corrected electronic energy of odd and even Ir-capped carbon chains (**IrCC**) in singlet and triplet states.

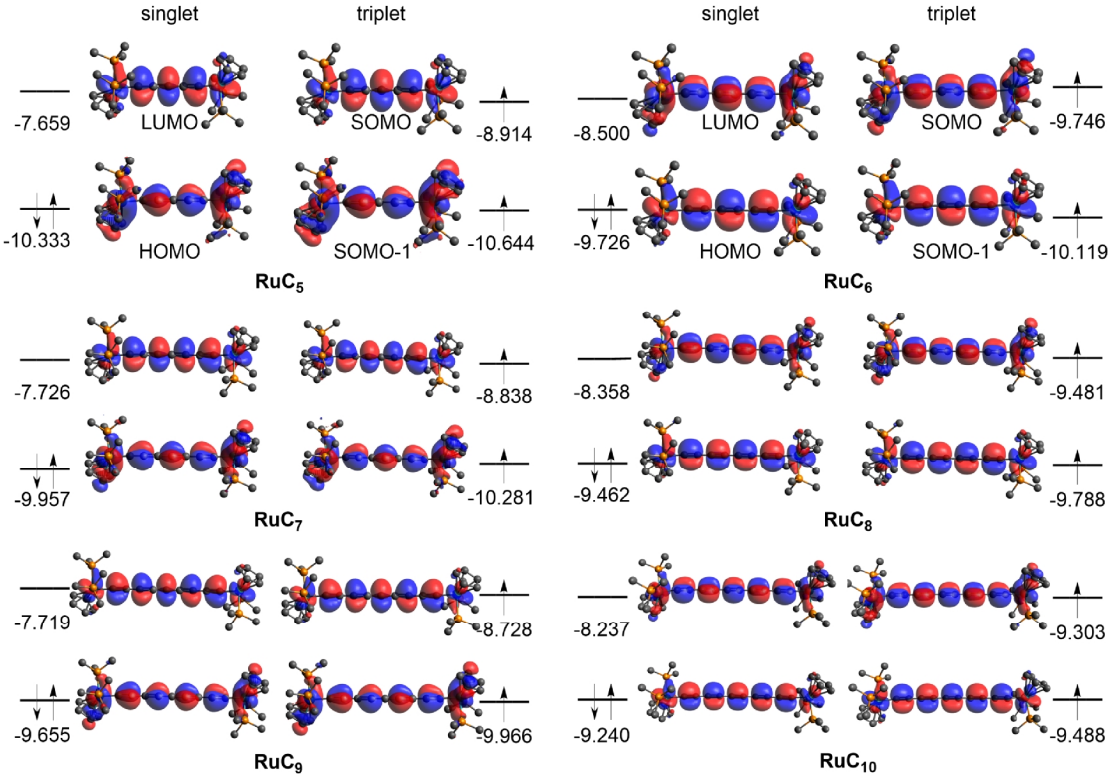
Odd carbon chain				Even carbon chain			
n_C*	E(S)/hartree	E(T)/hartree	ΔE(S-T) kcal·mol^{-1}	n_C*	E(S)/hartree	E(T)/hartree	ΔE(S-T) kcal·mol^{-1}
				4	-2428.180024	-2428.185132	3.21
5	-2466.265697	-2466.214180	-32.33	6	-2504.291416	-2504.296833	3.40
7	-2542.370086	-2542.331918	-23.95	8	-2580.400643	-2580.405750	3.20
9	-2618.474168	-2618.442519	-19.86	10	-2656.507998	-2656.512861	3.05
11	-2694.577857	-2694.551197	-16.73	12	-2732.614052	-2732.618728	2.93
13	-2770.681149	-2770.658738	-14.06	14	-2808.719141	-2808.723672	2.84
15	-2846.784083	-2846.764578	-12.24	16	-2884.823484	-2884.827902	2.77
17	-2922.886690	-2922.870073	-10.43	18	-2960.927233	-2960.931561	2.72
19	-2998.989006	-2998.976172	-8.05	20	-3037.030494	-3037.034753	2.67

*number of carbon atoms in the chain

Table S7. Zero-point vibration energy corrected electronic energy of odd and even W-capped carbon chains (**W^{2}CC**) with the terminus [W(CO)$_2$(dmpe)Cl] in singlet and triplet states.

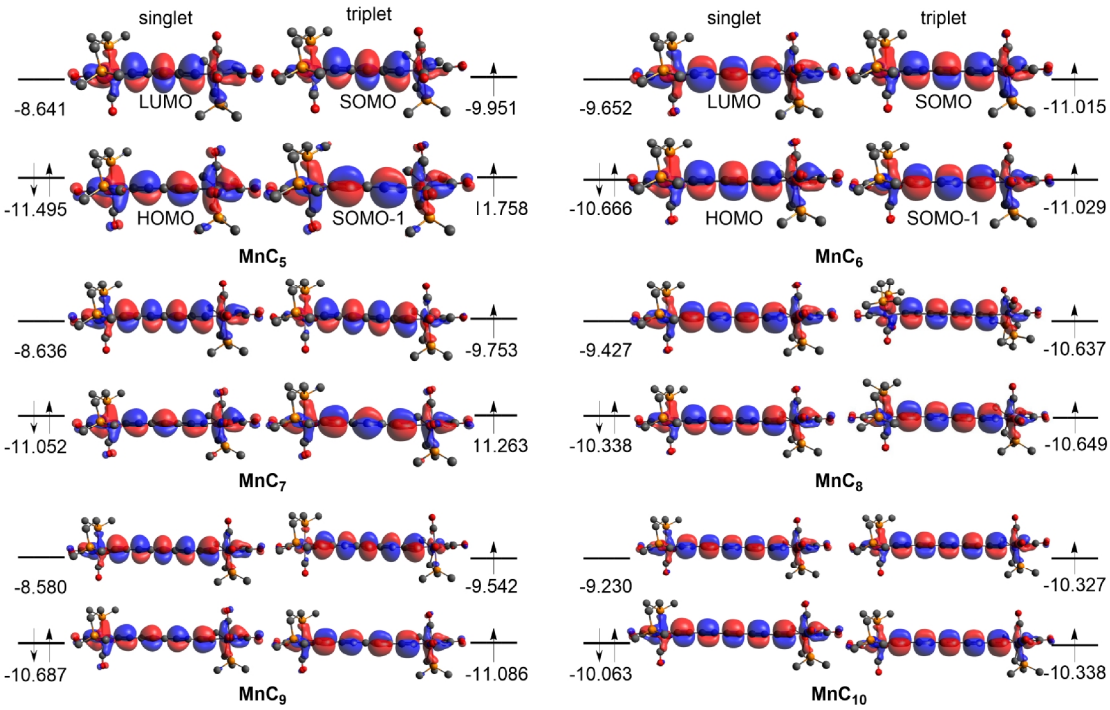
Odd carbon chain				Even carbon chain			
n_C*	E(S)/hartree	E(T)/hartree	ΔE(S-T) kcal·mol^{-1}	n_C*	E(S)/hartree	E(T)/hartree	ΔE(S-T) kcal·mol^{-1}
				4	-3500.347213	-3500.351076	2.42
5	-3538.413342	-3538.398888	-9.07	6	-3576.453238	-3576.460491	4.55
7	-3614.520797	-3614.507925	-8.08	8	-3652.560586	-3652.568710	5.10
9	-3690.627164	-3690.615574	-7.27	10	-3728.667927	-3728.675665	4.86
11	-3766.732649	-3766.722237	-6.53	12	-3804.774256	-3804.781680	4.66
13	-3842.837473	-3842.827968	-5.96	14	-3880.879786	-3880.887010	4.53
15	-3918.941694	-3918.933065	-5.41	16	-3956.984614	-3956.991636	4.41
17	-3995.045436	-3995.037236	-5.15	18	-4033.088924	-4033.095823	4.33
19	-4071.148675	-4071.141351	-4.60	20	-4109.192724	-4109.199563	4.29

*number of carbon atoms in the chain



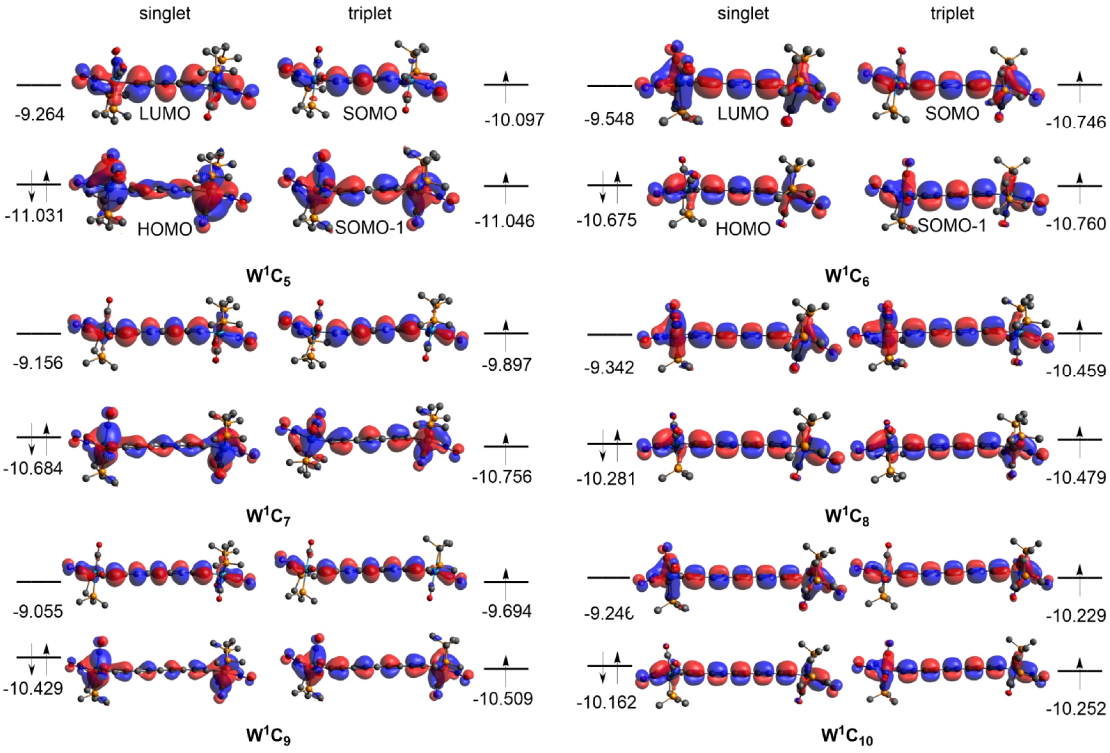
	S(LUMO, HOMO)	T(SOMO, SOMO-1)		S(LUMO, HOMO)	T(SOMO, SOMO-1)
			RuC$_4$	33.35/48.08/18.57 34.19/57.91/7.90	33.47/42.60/23.93 36.16/54.64/9.19
RuC$_5$	18.29/75.35/6.36 39.70/33.29/27.01	17.26/76.81/5.93 35.85/30.88/33.27	**RuC$_6$**	27.60/56.90/15.50 26.89/66.78/6.33	28.28/52.10/19.62 28.58/64.08/7.34
RuC$_7$	15.60/79.04/5.36 33.80/44.25/21.95	15.00/79.96/5.04 31.11/42.43/26.46	**RuC$_8$**	23.43/63.35/13.22 22.05/72.58/5.37	24.35/59.28/16.37 23.51/70.42/6.07
RuC$_9$	13.60/81.68/4.72 29.24/52.58/18.18	13.15/82.49/4.36 27.01/51.56/21.43	**RuC$_{10}$**	20.28/68.09/11.63 18.52/76.83/4.64	20.99/65.98/13.04 19.84/73.23/6.93

Figure S1. The lowest unoccupied molecular orbitals (LUMO), the highest occupied molecular orbitals (HOMO) and the singly occupied molecular orbital (SOMO), SOMO−1, fragment's contribution to MO (metal/carbon chain/others, in percentage in the table), electron occupation and orbital energy (in eV, beside the electron occupation) from **RuC$_5$** to **RuC$_{10}$** in singlet and triplet states. Contour values are 0.02.



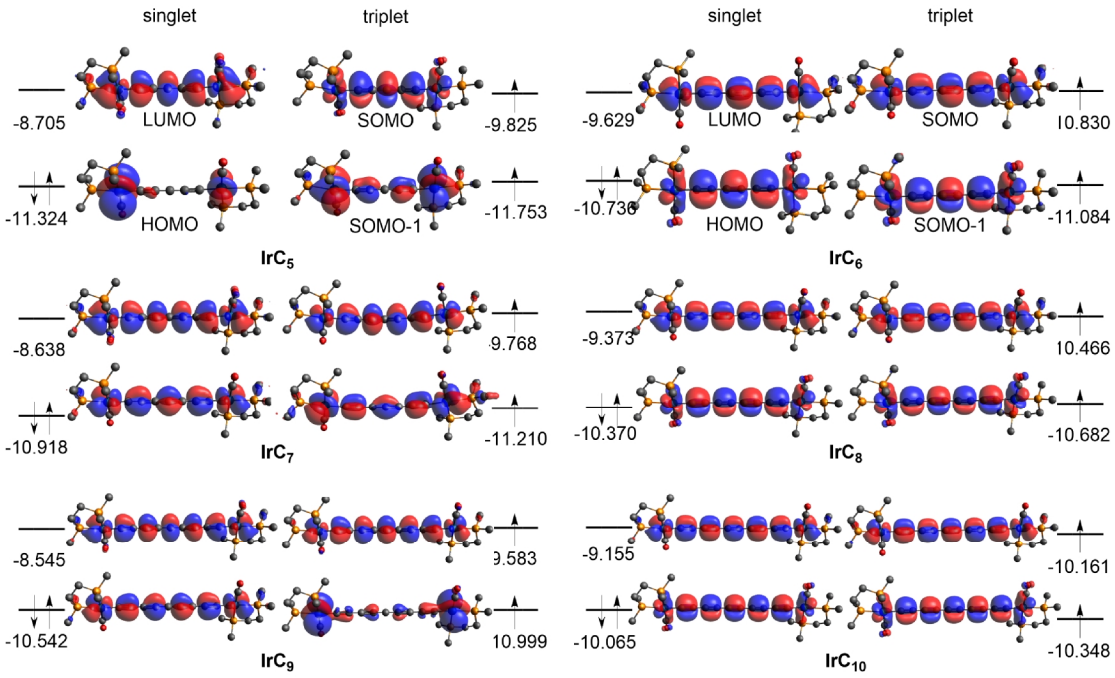
	S(LUMO, HOMO)	T(SOMO, SOMO-1)		S(LUMO, HOMO)	T(SOMO, SOMO-1)
MnC$_5$	16.36/71.79/11.85	13.82/78.58/7.60	**MnC$_6$**	30.03/57.78/12.19	26.16/64.75/9.09
	55.46/29.24/15.31	49.81/36.94/13.25		29.34/60.14/10.53	25.78/65.20/9.02
MnC$_7$	14.50/75.99/9.50	10.63/83.15/6.22	**MnC$_8$**	24.78/64.88/10.33	21.78/70.42/7.80
	45.92/40.77/13.32	38.29/51.08/10.63		24.32/66.61/9.07	21.43/70.86/7.71
MnC$_9$	12.76/79.22/8.02	9.76/84.95/5.29	**MnC$_{10}$**	20.88/70.19/8.93	18.72/74.37/6.91
	38.44/49.88/11.69	31.21/59.53/9.26		20.63/71.42/7.95	18.37/74.83/6.80

Figure S2. The LUMO, HOMO, SOMO, SOMO−1, fragment's contribution to MO (metal/carbon chain/others, in percentage in the table), electron occupation and orbital energy (in eV, beside the electron occupation) from **MnC$_5$** to **MnC$_{10}$** in singlet and triplet states. Contour values are 0.02.



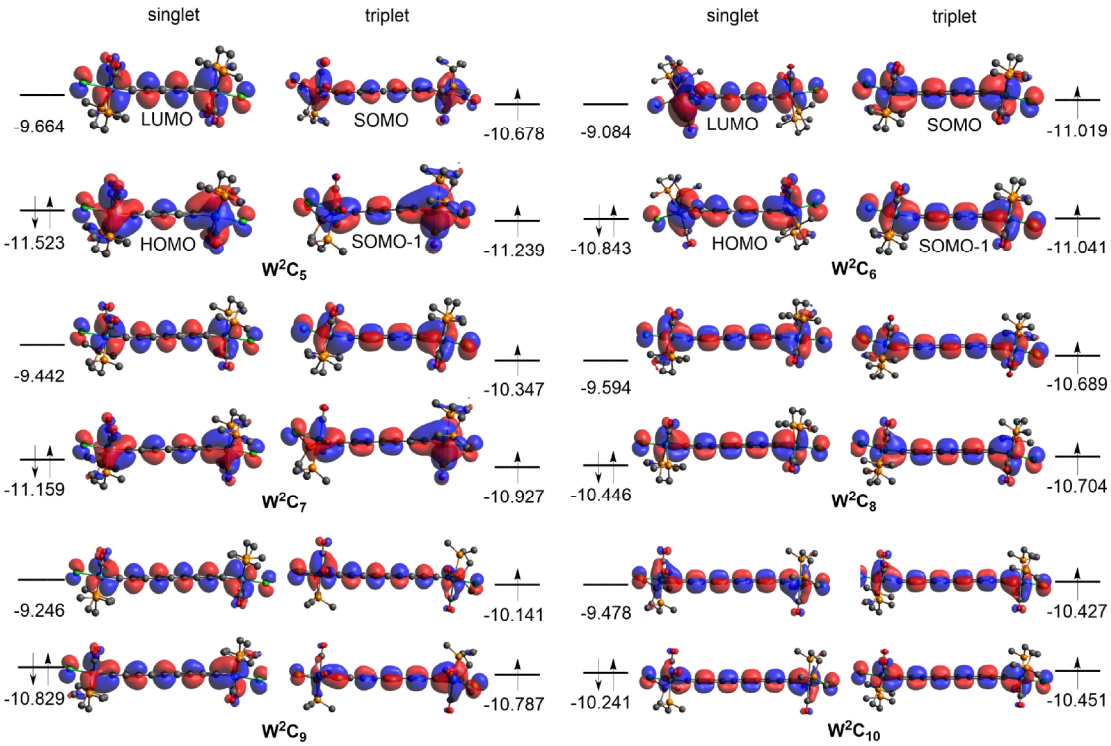
	S(LUMO, HOMO)	T(SOMO, SOMO-1)		S(LUMO, HOMO)	T(SOMO, SOMO-1)
W^1C_5	5.09/57.04/37.87	0.97/61.62/37.42	**W^1C_6**	27.98/38.95/33.07	18.65/51.26/30.10
	58.15/9.77 /32.08	52.56/17.62/29.83		16.87/50.44/32.69	19.94/50.12/29.93
W^1C_7	3.60/66.06/30.34	1.38/69.75/28.87	**W^1C_8**	25.12/45.37/29.51	15.63/58.50/25.87
	57.98/12.42/29.60	46.91/24.89/28.20		15.69/55.98/28.33	16.39/58.09/25.52
W^1C_9	2.95/71.74/25.31	1.53/75.08/23.39	**W^1C_{10}**	22.53/50.90/26.57	13.25/63.96/22.78
	57.35/13.86/28.79	41.81/31.60/26.59		12.39/62.63/24.98	13.66/63.81/22.52

Figure S3. The LUMO, HOMO, SOMO, SOMO−1, fragment's contribution to MO (metal/carbon chain/others, in percentage in the table), electron occupation and orbital energy (in eV, beside the electron occupation) from **W^1C_5** to **W^1C_{10}** in singlet and triplet states. Contour values are 0.02.



	S(LUMO, HOMO)	T(SOMO, SOMO-1)		S(LUMO, HOMO)	T(SOMO, SOMO-1)
IrC$_5$	27.37/64.24/8.40	10.40/82.44/7.17	**IrC$_6$**	35.21/60.95/3.84	39.80/56.64/3.56
	91.79/2.84 /5.38	76.96/17.59/5.46		16.92/74.76/8.32	20.91/68.33/10.76
IrC$_7$	23.52/70.12/6.36	18.03/77.56/4.41	**IrC$_8$**	14.86/78.19/6.94	33.80/62.94/3.26
	52.03/44.93/3.04	92.29/2.34 /5.36		40.17/56.54/3.30	16.50/74.91/8.59
IrC$_9$	20.49/74.26/5.25	9.36/84.53/6.11	**IrC$_{10}$**	25.31/71.43/3.25	29.35/67.60/3.05
	44.10/53.02/2.88	48.11/49.00/2.89		10.91/83.27/5.82	13.47/79.37/7.17

Figure S4. The LUMO, HOMO, SOMO, SOMO−1, fragment's contribution to MO (metal/carbon chain/others, in percentage in the table), electron occupation and orbital energy (in eV, beside the electron occupation) from **IrC$_5$** to **IrC$_{10}$** in singlet and triplet states. Contour values are 0.02.



	S(LUMO, HOMO)	T(SOMO, SOMO-1)		S(LUMO, HOMO)	T(SOMO, SOMO-1)
W²C₅	50.89/26.72/22.39	48.19/24.18/27.62	**W²C₆**	33.31/27.71/38.98	42.31/28.64/29.05
	53.07/15.68/31.26	51.30/16.82/31.89		41.34/30.62/28.04	43.10/28.92/27.98
W²C₇	44.68/35.30/20.02	43.20/32.13/24.67	**W²C₈**	37.06/34.70/28.25	38.64/35.71/25.66
	40.46/30.73/28.82	28.57/42.04/29.39		38.55/38.68/22.77	39.37/35.93/24.71
W²C₉	39.55/42.41/18.04	38.96/38.65/22.40	**W²C₁₀**	34.94/44.96/20.09	35.47/41.60/22.93
	31.07/43.95/24.97	26.83/48.65/24.52		34.48/43.91/21.61	36.09/41.67/22.24

Figure S5. The LUMO, HOMO, SOMO, SOMO−1, fragment's contribution to MO (metal/carbon chain/others, in percentage in the table), electron occupation and orbital energy (in eV, beside the electron occupation) from **W²C₅** to **W²C₁₀** in singlet and triplet states. Contour values are 0.02.

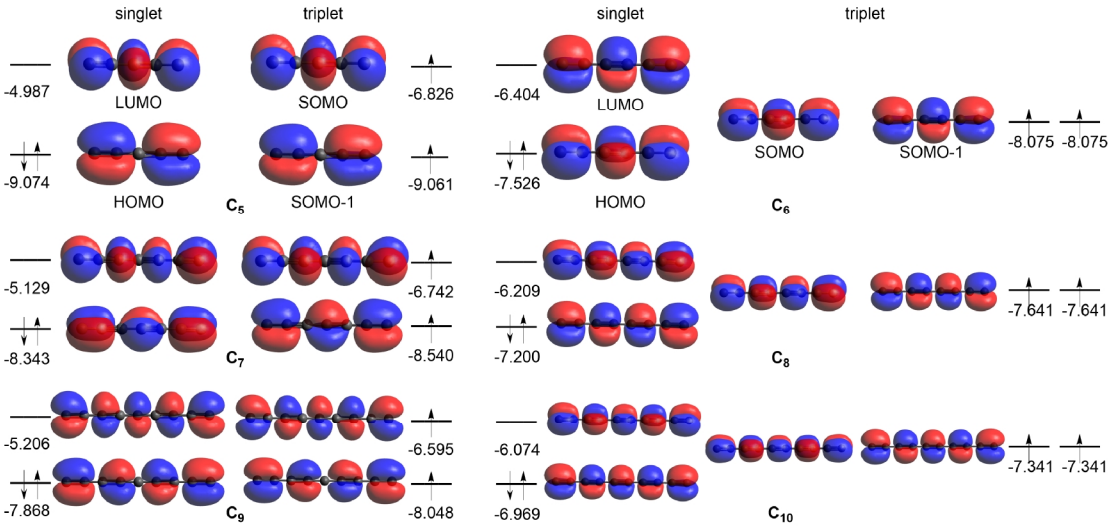


Figure S6. The LUMO, HOMO, SOMO, SOMO−1, electron occupation and orbital energy (in eV, beside the electron occupation) from uncapped carbon chain $\mathbf{C_5}$ to $\mathbf{C_{10}}$ in singlet and triplet states. Contour values are 0.02.

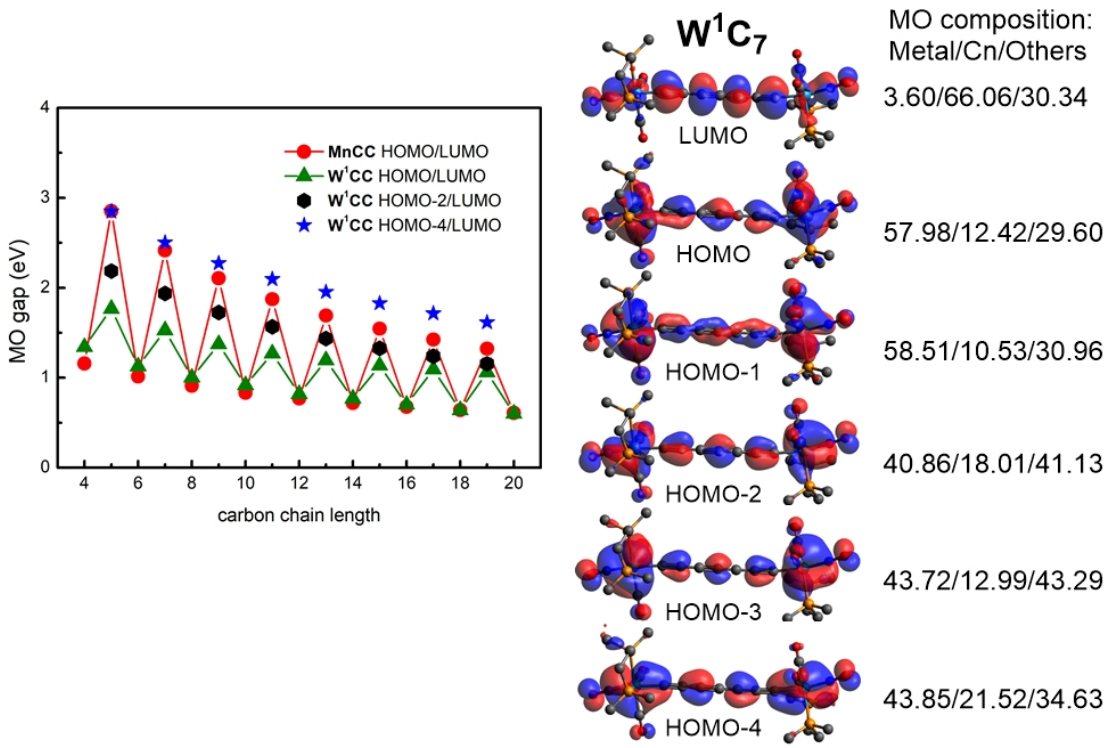


Figure S7. The various MO/LUMO energy gaps of **W^{1}CC** and HOMO/LUMO gap of **MnCC**, and the MOs and fragment's contribution to MO of **W^{1}C$_7$** in singlet. Contour values are 0.02.

Table S8. The Spin Densities on transition metals of the triplet metal-capped carbon chains.

	RuCC	MnCC	W^1CC	IrCC	W^2CC
4	0.476349	0.845001	0.440739	0.406567	0.716976
	0.476350	0.844995	0.385443	0.406569	0.716962
5	0.419352	0.591324	0.195140	0.489540	0.576356
	0.419356	0.928432	0.194640	0.489559	1.078506
6	0.400137	0.735665	0.394287	0.337537	0.690372
	0.400131	0.735676	0.430086	0.337528	0.689955
7	0.377027	0.506089	0.208730	0.416272	0.562090
	0.377043	0.906424	0.208699	0.497831	1.052217
8	0.348755	0.645859	0.360471	0.288686	0.667122
	0.348756	0.645854	0.398656	0.288686	0.667125
9	0.338319	0.747700	0.205683	0.391880	0.551541
	0.338319	0.733052	0.205421	0.391917	1.014794
10	0.314297	0.572100	0.357540	0.252046	0.646563
	0.314287	0.572102	0.318011	0.252044	0.646568
11	0.307729	0.683579	0.193698	0.347640	0.950240
	0.307725	0.682892	0.194010	0.347637	0.526645
12	0.277418	0.511098	0.282898	0.223613	0.629310
	0.277417	0.511099	0.309828	0.223613	0.629292
13	0.282736	0.577697	0.176324	0.307866	0.919053
	0.282746	0.672727	0.176639	0.304670	0.519120
14	0.252876	0.459804	0.238618	0.200886	0.613777
	0.252876	0.459808	0.280098	0.200886	0.613763
15	0.192425	0.571240	0.040397	0.282131	0.886427
	0.192434	0.572760	0.294860	0.282142	0.512276
16	0.233136	0.416121	0.202335	0.182350	0.599817
	0.233137	0.416126	0.218053	0.182351	0.600203
17	0.245109	0.519775	0.334612	0.257400	0.527587
	0.245103	0.523000	0.046878	0.257380	0.855073
18	0.216606	0.378830		0.166942	0.586889
	0.216607	0.378824		0.166944	0.587062
19	0.194012	0.477154		0.216662	0.527928
	0.122684	0.473826		0.216523	0.788335
20	0.202888	0.346860		0.153963	0.574904
	0.202889	0.346845		0.153963	0.574908

Table S9. The bond distance (Å) of the single and triplet states Ru-capped carbon chains.

RuC_4		**RuC_5**		**RuC_6**		**RuC_7**		**RuC_8**	
S	T	S	T	S	T	S	T	S	T
1.863	1.861	1.832	1.879	1.855	1.850	1.835	1.870	1.853	1.847
1.282	1.283	1.291	1.286	1.283	1.286	1.289	1.283	1.283	1.286
1.310	1.310	1.289	1.300	1.303	1.300	1.290	1.302	1.300	1.298
1.282	1.283	1.289	1.300	1.276	1.279	1.284	1.286	1.277	1.279
1.863	1.861	1.291	1.286	1.303	1.300	1.284	1.286	1.297	1.294
		1.832	1.879	1.283	1.286	1.290	1.302	1.277	1.279
				1.855	1.850	1.289	1.283	1.300	1.298
						1.835	1.870	1.283	1.286
								1.853	1.847
RuC_9		**RuC_{10}**		**RuC_{11}**		**RuC_{12}**		**RuC_{13}**	
S	T	S	T	S	T	S	T	S	T
1.837	1.863	1.852	1.849	1.840	1.860	1.851	1.847	1.843	1.859
1.288	1.282	1.283	1.284	1.286	1.281	1.283	1.284	1.285	1.280
1.292	1.303	1.299	1.299	1.293	1.303	1.299	1.297	1.295	1.303
1.283	1.281	1.277	1.278	1.281	1.278	1.277	1.279	1.280	1.276
1.286	1.291	1.295	1.294	1.287	1.293	1.294	1.292	1.289	1.295
1.286	1.291	1.278	1.279	1.284	1.285	1.279	1.281	1.283	1.282
1.283	1.281	1.295	1.294	1.284	1.285	1.293	1.291	1.286	1.288
1.292	1.303	1.277	1.278	1.287	1.293	1.279	1.281	1.286	1.288
1.288	1.282	1.299	1.299	1.281	1.278	1.294	1.292	1.283	1.282
1.837	1.863	1.283	1.284	1.293	1.303	1.277	1.279	1.289	1.295
		1.852	1.849	1.286	1.281	1.299	1.297	1.280	1.276
				1.840	1.860	1.283	1.284	1.295	1.303
						1.851	1.847	1.285	1.280
								1.843	1.859
RuC_{14}		**RuC_{15}**		**RuC_{16}**		**RuC_{17}**		**RuC_{18}**	
S	T	S	T	S	T	S	T	S	T
1.852	1.849	1.846	1.859	1.853	1.850	1.848	1.859	1.854	1.852
1.282	1.284	1.284	1.280	1.281	1.283	1.283	1.280	1.281	1.282
1.300	1.298	1.296	1.302	1.300	1.298	1.297	1.303	1.301	1.299
1.277	1.279	1.279	1.277	1.276	1.278	1.278	1.276	1.276	1.277
1.294	1.292	1.290	1.295	1.294	1.292	1.291	1.296	1.295	1.293
1.279	1.280	1.282	1.281	1.278	1.280	1.281	1.280	1.278	1.280
1.292	1.290	1.287	1.290	1.292	1.290	1.288	1.291	1.293	1.291
1.279	1.281	1.284	1.285	1.279	1.281	1.283	1.283	1.279	1.281
1.292	1.290	1.284	1.285	1.292	1.290	1.285	1.287	1.292	1.289
1.279	1.280	1.287	1.290	1.279	1.281	1.285	1.287	1.279	1.281
1.294	1.292	1.282	1.281	1.292	1.290	1.283	1.283	1.292	1.289

1.277	1.279	1.290	1.295	1.278	1.280	1.288	1.291	1.279	1.281
1.300	1.298	1.279	1.277	1.294	1.292	1.281	1.280	1.293	1.291
1.282	1.284	1.296	1.303	1.276	1.278	1.291	1.296	1.278	1.280
1.852	1.849	1.284	1.280	1.300	1.298	1.278	1.276	1.295	1.293
		1.846	1.859	1.281	1.283	1.297	1.303	1.276	1.277
				1.853	1.850	1.283	1.280	1.301	1.299
						1.848	1.859	1.281	1.282
								1.854	1.852

RuC_{19}		**RuC_{20}**	
S	T	S	T
1.851	1.853	1.856	1.854
1.282	1.282	1.280	1.281
1.298	1.301	1.301	1.300
1.277	1.276	1.275	1.277
1.292	1.297	1.295	1.294
1.280	1.276	1.277	1.279
1.289	1.297	1.293	1.291
1.282	1.275	1.278	1.280
1.287	1.298	1.292	1.290
1.284	1.274	1.279	1.281
1.284	1.298	1.291	1.289
1.287	1.275	1.279	1.281
1.282	1.296	1.292	1.290
1.289	1.278	1.278	1.280
1.280	1.291	1.293	1.291
1.292	1.284	1.277	1.279
1.277	1.285	1.295	1.294
1.298	1.295	1.275	1.277
1.282	1.285	1.301	1.300
1.851	1.851	1.280	1.281
		1.856	1.854

Table S10. The bond distance (Å) of the single and triplet states Mn-capped carbon chains.

MnC_4		**MnC_5**		**MnC_6**		**MnC_7**		**MnC_8**	
S	T	S	T	S	T	S	T	S	T
1.828	1.832	1.803	1.843	1.826	1.829	1.810	1.838	1.826	1.829
1.279	1.276	1.286	1.288	1.280	1.277	1.284	1.284	1.279	1.278
1.312	1.314	1.289	1.29	1.305	1.306	1.293	1.294	1.303	1.304
1.279	1.276	1.289	1.31	1.274	1.272	1.283	1.296	1.275	1.274
1.828	1.832	1.286	1.27	1.305	1.306	1.283	1.271	1.297	1.298
		1.803	1.885	1.280	1.277	1.293	1.319	1.275	1.274
				1.826	1.829	1.284	1.264	1.303	1.304
						1.810	1.882	1.279	1.278
								1.826	1.829
MnC_9		**MnC_{10}**		**MnC_{11}**		**MnC_{12}**		**MnC_{13}**	
S	T	S	T	S	T	S	T	S	T
1.817	1.863	1.829	1.832	1.824	1.857	1.833	1.835	1.830	1.851
1.281	1.282	1.278	1.277	1.279	1.270	1.277	1.276	1.277	1.272
1.295	1.303	1.302	1.303	1.298	1.311	1.303	1.303	1.300	1.308
1.280	1.281	1.275	1.274	1.278	1.273	1.275	1.274	1.276	1.274
1.286	1.291	1.296	1.296	1.289	1.296	1.295	1.295	1.291	1.295
1.286	1.291	1.277	1.276	1.283	1.284	1.277	1.277	1.281	1.284
1.280	1.281	1.296	1.296	1.283	1.284	1.294	1.294	1.286	1.285
1.295	1.303	1.275	1.274	1.289	1.296	1.277	1.277	1.286	1.293
1.281	1.282	1.302	1.303	1.278	1.273	1.295	1.295	1.281	1.276
1.817	1.863	1.278	1.277	1.298	1.311	1.275	1.274	1.291	1.302
		1.829	1.832	1.279	1.270	1.303	1.303	1.276	1.268
				1.824	1.856	1.277	1.276	1.300	1.314
						1.833	1.835	1.277	1.268
								1.830	1.859
MnC_{14}		**MnC_{15}**		**MnC_{16}**		**MnC_{17}**		**MnC_{18}**	
S	T	S	T	S	T	S	T	S	T
1.837	1.838	1.835	1.854	1.841	1.842	1.841	1.855	1.845	1.846
1.275	1.275	1.275	1.270	1.274	1.274	1.274	1.270	1.273	1.273
1.304	1.304	1.302	1.311	1.305	1.305	1.304	1.311	1.306	1.306
1.274	1.274	1.274	1.270	1.273	1.273	1.273	1.269	1.272	1.272
1.296	1.295	1.293	1.300	1.296	1.296	1.294	1.300	1.297	1.297
1.277	1.277	1.279	1.277	1.276	1.277	1.278	1.276	1.275	1.276
1.293	1.293	1.288	1.292	1.293	1.293	1.290	1.294	1.294	1.293
1.278	1.278	1.283	1.284	1.278	1.278	1.282	1.282	1.278	1.278
1.293	1.293	1.283	1.284	1.292	1.292	1.285	1.287	1.292	1.291
1.277	1.277	1.288	1.292	1.278	1.278	1.285	1.288	1.278	1.279
1.296	1.295	1.279	1.277	1.293	1.293	1.282	1.281	1.292	1.291

1.274	1.274	1.293	1.300	1.276	1.277	1.290	1.294	1.278	1.278
1.304	1.304	1.274	1.270	1.296	1.296	1.278	1.275	1.294	1.293
1.275	1.275	1.302	1.311	1.273	1.273	1.294	1.301	1.275	1.276
1.837	1.838	1.275	1.270	1.305	1.305	1.273	1.269	1.297	1.297
		1.835	1.854	1.274	1.274	1.304	1.311	1.272	1.272
				1.841	1.842	1.274	1.270	1.306	1.306
						1.841	1.855	1.273	1.273
								1.845	1.846

MnC_{19}		**MnC_{20}**	
S	T	S	T
1.845	1.856	1.849	1.850
1.273	1.270	1.272	1.272
1.305	1.311	1.307	1.307
1.271	1.269	1.271	1.271
1.296	1.301	1.298	1.298
1.276	1.274	1.274	1.275
1.291	1.295	1.295	1.294
1.280	1.279	1.277	1.278
1.287	1.290	1.293	1.291
1.284	1.284	1.278	1.279
1.284	1.285	1.292	1.291
1.287	1.29	1.278	1.279
1.280	1.28	1.293	1.291
1.291	1.295	1.277	1.278
1.276	1.274	1.295	1.294
1.296	1.301	1.274	1.275
1.271	1.269	1.298	1.298
1.305	1.311	1.271	1.271
1.273	1.27	1.307	1.307
1.845	1.856	1.272	1.272
		1.849	1.850

Table S11. The bond distance (Å) of the single and triplet states W-capped carbon chains with the terminus [$W(CO)_2$(dmpe)NO].

W^1C_4		W^1C_5		W^1C_6		W^1C_7		W^1C_8	
S	T	S	T	S	T	S	T	S	T
2.100	2.064	2.054	2.058	2.063	2.103	2.067	2.071	2.066	2.100
1.259	1.272	1.284	1.284	1.272	1.259	1.280	1.277	1.272	1.260
1.336	1.318	1.291	1.296	1.314	1.331	1.296	1.304	1.312	1.328
1.259	1.272	1.291	1.296	1.265	1.251	1.282	1.283	1.266	1.253
2.099	2.064	1.284	1.284	1.313	1.331	1.282	1.283	1.307	1.323
		2.054	2.058	1.272	1.259	1.296	1.304	1.266	1.253
				2.063	2.101	1.280	1.277	1.312	1.329
						2.067	2.071	1.272	1.260
								2.066	2.100
W^1C_9		W^1C_{10}		W^1C_{11}		W^1C_{12}		W^1C_{13}	
S	T	S	T	S	T	S	T	S	T
2.075	2.079	2.070	2.098	2.082	2.085	2.081	2.099	2.088	2.089
1.277	1.273	1.271	1.261	1.274	1.270	1.270	1.261	1.273	1.269
1.300	1.308	1.312	1.327	1.303	1.311	1.312	1.325	1.305	1.313
1.278	1.276	1.267	1.254	1.275	1.272	1.266	1.256	1.273	1.269
1.287	1.290	1.305	1.321	1.290	1.295	1.304	1.319	1.293	1.299
1.287	1.290	1.268	1.255	1.283	1.283	1.269	1.256	1.28	1.279
1.278	1.276	1.305	1.321	1.283	1.283	1.302	1.318	1.286	1.289
1.300	1.308	1.267	1.254	1.290	1.295	1.269	1.256	1.286	1.289
1.277	1.273	1.312	1.326	1.275	1.272	1.304	1.319	1.28	1.279
2.075	2.079	1.271	1.261	1.303	1.311	1.266	1.256	1.293	1.299
		2.070	2.101	1.274	1.270	1.312	1.325	1.273	1.269
				2.082	2.085	1.270	1.261	1.305	1.313
						2.081	2.099	1.273	1.269
								2.088	2.089
W^1C_{14}		W^1C_{15}		W^1C_{16}		W^1C_{17}		W^1C_{18}	
S	T	S	T	S	T	S	T	S	T
2.086	2.101	2.094	2.088	2.083	2.102	2.099	2.106	1.854	1.852
1.269	1.262	1.271	1.271	1.269	1.262	1.269	1.260	1.281	1.282
1.312	1.324	1.307	1.309	1.313	1.323	1.309	1.327	1.301	1.299
1.266	1.256	1.271	1.274	1.265	1.257	1.269	1.255	1.276	1.277
1.304	1.318	1.295	1.293	1.304	1.316	1.297	1.318	1.295	1.293
1.269	1.257	1.277	1.284	1.269	1.258	1.275	1.259	1.278	1.280
1.301	1.316	1.289	1.283	1.301	1.315	1.291	1.313	1.293	1.291
1.270	1.257	1.283	1.294	1.270	1.259	1.281	1.264	1.279	1.281
1.301	1.317	1.283	1.273	1.300	1.314	1.286	1.306	1.292	1.289
1.269	1.257	1.289	1.303	1.270	1.259	1.286	1.270	1.279	1.281

1.304	1.318	1.277	1.266	1.301	1.315	1.281	1.298	1.292	1.289
1.266	1.255	1.295	1.311	1.269	1.258	1.291	1.279	1.279	1.281
1.312	1.325	1.271	1.259	1.304	1.316	1.275	1.288	1.293	1.291
1.269	1.261	1.307	1.323	1.265	1.256	1.297	1.290	1.278	1.280
2.086	2.099	1.271	1.262	1.314	1.324	1.269	1.276	1.295	1.293
		2.094	2.103	1.268	1.262	1.309	1.306	1.276	1.277
				2.093	2.101	1.269	1.273	1.301	1.299
						2.099	2.088	1.281	1.282
								1.854	1.852

Table S12. The bond distance (Å) of the single and triplet states Ir-capped carbon chains.

IrC_4		**IrC_5**		**IrC_6**		**IrC_7**		**IrC_8**	
S	T	S	T	S	T	S	T	S	T
1.903	1.893	1.879	1.933	1.900	1.893	1.886	1.905	1.901	1.896
1.279	1.286	1.285	1.280	1.279	1.284	1.282	1.283	1.278	1.282
1.311	1.302	1.288	1.300	1.303	1.298	1.292	1.297	1.303	1.298
1.279	1.286	1.288	1.300	1.274	1.279	1.282	1.287	1.275	1.279
1.903	1.893	1.285	1.280	1.303	1.298	1.282	1.281	1.297	1.293
		1.879	1.933	1.279	1.284	1.292	1.304	1.275	1.279
				1.900	1.893	1.282	1.278	1.303	1.298
						1.886	1.918	1.278	1.282
								1.901	1.896
IrC_9		**IrC_{10}**		**IrC_{11}**		**IrC_{12}**		**IrC_{13}**	
S	T	S	T	S	T	S	T	S	T
1.891	1.907	1.903	1.899	1.896	1.908	1.906	1.902	1.901	1.910
1.280	1.279	1.276	1.280	1.278	1.277	1.275	1.278	1.276	1.275
1.295	1.302	1.303	1.299	1.297	1.303	1.304	1.300	1.300	1.305
1.280	1.280	1.274	1.278	1.277	1.277	1.274	1.277	1.276	1.275
1.286	1.289	1.296	1.292	1.288	1.292	1.296	1.292	1.290	1.294
1.286	1.289	1.276	1.280	1.283	1.284	1.276	1.280	1.281	1.281
1.280	1.280	1.296	1.292	1.283	1.284	1.294	1.290	1.285	1.288
1.295	1.302	1.274	1.278	1.288	1.292	1.276	1.280	1.285	1.287
1.280	1.279	1.303	1.299	1.277	1.277	1.296	1.292	1.281	1.282
1.891	1.907	1.276	1.280	1.297	1.303	1.274	1.277	1.290	1.294
		1.903	1.899	1.278	1.277	1.304	1.300	1.276	1.275
				1.896	1.908	1.275	1.278	1.300	1.304
						1.906	1.902	1.276	1.275
								1.901	1.910
IrC_{14}		**IrC_{15}**		**IrC_{16}**		**IrC_{17}**		**IrC_{18}**	
S	T	S	T	S	T	S	T	S	T
1.909	1.906	1.905	1.911	1.911	1.909	1.908	1.913	1.914	1.912
1.274	1.277	1.275	1.274	1.272	1.275	1.273	1.273	1.271	1.274
1.305	1.301	1.302	1.305	1.306	1.303	1.303	1.306	1.307	1.304
1.273	1.276	1.274	1.274	1.272	1.274	1.273	1.272	1.271	1.273
1.296	1.293	1.292	1.295	1.297	1.294	1.294	1.296	1.298	1.295
1.276	1.279	1.279	1.279	1.275	1.279	1.278	1.278	1.274	1.278
1.294	1.290	1.288	1.290	1.294	1.290	1.289	1.291	1.295	1.291
1.277	1.280	1.283	1.284	1.277	1.280	1.282	1.282	1.277	1.280
1.294	1.290	1.283	1.284	1.293	1.289	1.285	1.287	1.293	1.289
1.276	1.279	1.288	1.290	1.277	1.280	1.285	1.287	1.277	1.281
1.296	1.293	1.279	1.279	1.294	1.290	1.282	1.282	1.293	1.289

1.273	1.276	1.292	1.295	1.275	1.279	1.289	1.291	1.277	1.280
1.305	1.301	1.274	1.274	1.297	1.294	1.278	1.278	1.295	1.291
1.274	1.277	1.302	1.305	1.272	1.274	1.294	1.296	1.274	1.278
1.909	1.906	1.275	1.274	1.306	1.303	1.273	1.272	1.298	1.295
		1.905	1.911	1.272	1.275	1.303	1.306	1.271	1.273
				1.911	1.909	1.273	1.273	1.307	1.304
						1.908	1.913	1.271	1.274
								1.914	1.912

IrC_{19}		**IrC_{20}**	
S	T	S	T
1.911	1.918	1.916	1.914
1.272	1.271	1.270	1.272
1.305	1.309	1.308	1.305
1.271	1.271	1.270	1.272
1.296	1.299	1.299	1.296
1.276	1.276	1.274	1.277
1.291	1.294	1.296	1.292
1.280	1.280	1.276	1.279
1.287	1.289	1.294	1.290
1.284	1.285	1.277	1.281
1.284	1.285	1.293	1.289
1.287	1.289	1.277	1.281
1.280	1.28	1.294	1.290
1.291	1.294	1.276	1.279
1.276	1.276	1.296	1.292
1.296	1.299	1.274	1.277
1.271	1.271	1.299	1.296
1.305	1.309	1.270	1.272
1.272	1.271	1.308	1.305
1.911	1.918	1.270	1.272
		1.916	1.914

Table S13. The bond distance (Å) of the single and triplet states W-capped carbon chains with the terminus [$W(CO)_2$(dmpe)Cl].

W^2C_4		W^2C_5		W^2C_6		W^2C_7		W^2C_8	
S	T	S	T	S	T	S	T	S	T
1.916	1.974	1.931	1.998	1.917	1.965	1.929	1.992	1.957	1.958
1.306	1.287	1.300	1.275	1.306	1.290	1.301	1.276	1.293	1.292
1.286	1.301	1.287	1.316	1.282	1.296	1.286	1.315	1.292	1.294
1.293	1.287	1.287	1.263	1.289	1.278	1.285	1.260	1.282	1.280
1.974	1.974	1.300	1.330	1.286	1.296	1.285	1.317	1.289	1.291
		1.931	1.892	1.291	1.290	1.286	1.260	1.282	1.280
				1.981	1.965	1.301	1.333	1.292	1.294
						1.929	1.888	1.293	1.292
								1.958	1.958
W^2C_9		W^2C_{10}		W^2C_{11}		W^2C_{12}		W^2C_{13}	
S	T	S	T	S	T	S	T	S	T
1.926	1.863	1.947	1.952	1.923	1.883	1.941	1.947	1.920	1.882
1.302	1.282	1.295	1.294	1.304	1.335	1.298	1.296	1.305	1.336
1.285	1.303	1.290	1.292	1.283	1.257	1.288	1.290	1.282	1.256
1.286	1.281	1.283	1.281	1.288	1.321	1.284	1.282	1.289	1.323
1.284	1.291	1.288	1.289	1.283	1.255	1.286	1.288	1.281	1.253
1.284	1.291	1.283	1.281	1.285	1.319	1.284	1.282	1.287	1.322
1.286	1.281	1.288	1.289	1.285	1.258	1.286	1.288	1.284	1.255
1.285	1.303	1.283	1.281	1.283	1.315	1.284	1.282	1.284	1.318
1.302	1.282	1.290	1.292	1.288	1.262	1.286	1.288	1.287	1.258
1.926	1.863	1.295	1.294	1.283	1.312	1.284	1.282	1.281	1.314
		1.948	1.952	1.303	1.279	1.288	1.290	1.289	1.263
				1.923	1.980	1.298	1.296	1.282	1.311
						1.941	1.947	1.305	1.280
								1.920	1.975
W^2C_{14}		W^2C_{15}		W^2C_{16}		W^2C_{17}		W^2C_{18}	
S	T	S	T	S	T	S	T	S	T
1.936	1.942	1.918	1.882	1.931	1.938	1.915	1.970	1.927	1.934
1.300	1.297	1.306	1.336	1.302	1.299	1.308	1.281	1.303	1.300
1.286	1.289	1.281	1.255	1.285	1.287	1.279	1.309	1.283	1.286
1.286	1.284	1.290	1.324	1.288	1.285	1.292	1.264	1.289	1.286
1.285	1.287	1.280	1.252	1.283	1.286	1.279	1.313	1.282	1.284
1.285	1.283	1.288	1.324	1.287	1.284	1.289	1.258	1.288	1.285
1.285	1.287	1.282	1.253	1.284	1.286	1.281	1.318	1.282	1.285
1.285	1.283	1.285	1.321	1.286	1.283	1.287	1.254	1.287	1.284
1.285	1.287	1.285	1.255	1.284	1.286	1.284	1.323	1.283	1.286
1.285	1.283	1.282	1.318	1.286	1.283	1.284	1.251	1.287	1.284
1.285	1.287	1.288	1.259	1.284	1.286	1.287	1.325	1.283	1.286

1.286	1.284	1.280	1.313	1.287	1.284	1.281	1.250	1.287	1.284
1.287	1.289	1.290	1.264	1.283	1.286	1.289	1.326	1.282	1.285
1.300	1.297	1.281	1.309	1.288	1.285	1.279	1.250	1.288	1.285
1.936	1.942	1.306	1.281	1.285	1.287	1.292	1.326	1.281	1.284
		1.918	1.971	1.302	1.299	1.279	1.254	1.289	1.286
				1.931	1.938	1.308	1.337	1.283	1.286
						1.915	1.885	1.303	1.300
								1.927	1.934

W^2C_{19}		W^2C_{20}	
S	T	S	T
1.913	1.967	1.923	1.931
1.309	1.282	1.305	1.302
1.278	1.308	1.282	1.285
1.293	1.264	1.291	1.287
1.277	1.312	1.280	1.283
1.291	1.259	1.289	1.286
1.280	1.318	1.281	1.284
1.288	1.255	1.288	1.285
1.282	1.322	1.282	1.285
1.285	1.251	1.288	1.284
1.285	1.325	1.282	1.285
1.282	1.25	1.288	1.284
1.288	1.327	1.282	1.285
1.280	1.249	1.288	1.285
1.291	1.327	1.281	1.284
1.277	1.25	1.289	1.286
1.293	1.325	1.280	1.283
1.278	1.254	1.291	1.287
1.309	1.336	1.282	1.285
1.913	1.887	1.305	1.302
		1.923	1.931

Table S14. The W-N-O angle between tungsten and NO ligands in the **W^{1}CCs** with the terminus [W(CO)$_2$(dmpe)NO].

n_C	W–N–O angle	
	singlet	triplet
4	171.9	174.40
5	173.4	173.60
6	171.5	173.30
7	175.2	173.90
8	171.8	175.05
9	176.4	174.20
10	171.9	175.60
11	177.3	174.50
12	174.0	173.40
13	178.2	174.90
14	174.3	173.30
15	179.1	175.90
16	175.8	174.30
17	179.6	177.00