Zinc (0) Chemistry: Does the missing 18-electron zinc tricarbonyl really exist?

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Supporting Information

Table S1: Total energies (atomic units) of $Zn(CO)_3$ and transition state.

Methods	$Zn(CO)_3$ (D_{3h})	TS(C_{3v})	$Zn(CO)_3$ (D_{3h}) in Ar
BP86/6-311+G(3df)	-2119.616834	-2119.616476	-2119.617808
B3PW91/6-311+G(3df)	-2119.191851	-2119.191762	-2119.192856
BPW91/6-311+G(3df)	-2119.508574	-2119.508157	-2119.509534
PBEPBE/6-311+G(3df)	-2118.71872	-2118.718134	-2118.719686
BH&HLYP/6-311+G(3df)	-2119.084838		-2119.086064
B3LYP/6-311+G(3df)	-2119.381275		-2119.382413
MP2/6-311+G(3df)	-2117.584458	-2117.583886	-2117.584976
MP4SDQ/6-311+G(3df)	-2117.5368996		-2117.722378**
QCISD/6-311+G(3df)	-2117.521651		-2117.70721**
CCSD/6-311+G(3df)	-2117.511513		-2117.697063**
CASPT2(12,12)/6-31+G(d)	-2116.851367	-2116.85325	
CCSD(T)/aug-cc-pVTZ //QCISD/6-311+G(3df)	-2117.782795		

** the single-point energies obtained at MP4SDQ/aug-cc-pVTZ// MP4SDQ/6-311+G(3df), QCISD/aug-cc-pVTZ// QCISD/6-311+G(3df) and CCSD/aug-cc-pVTZ// CCSD/6-311+G(3df) levels.

Table S2: Total H and G (atomic units) of $Zn(CO)_3$ at 7K.

Methods	H	G
BP86/6-311+G(3df)	-2119.595473	-2119.595882
B3PW91/6-311+G(3df)	-2119.169728	-2119.170137
BPW91/6-311+G(3df)	-2119.487192	-2119.487601
PBEPBE/6-311+G(3df)	-2118.697312	-2118.697721
BH&HLYP/6-311+G(3df)	-2119.062157	-2119.062566

B3LYP/6-311+G(3df)	-2119.359529	-2119.359939
MP2/6-311+G(3df)	-2117.562793	-2117.563201
MP4SDQ/6-311+G(3df)	-2117.515216	-2117.515625

Table S3: Total energies (atomic units) of the ^{3}(CO)ZnZn.

Methods	E
BP86/6-311+G(3df)	-3672.429758
B3PW91/6-311+G(3df)	-3671.862867
BPW91/6-311+G(3df)	-3672.270993
PBEPBE/6-311+G(3df)	-3671.247542
BH&HLYP/6-311+G(3df)	-3671.732852
B3LYP/6-311+G(3df)	-3671.99516
MP2/6-311+G(3df)	-3669.486509
MP4SDQ/6-311+G(3df)	-3669.416636
QCISD/6-31+G(3df)	-3669.400672
CCSD/6-311+G(3df)	-3669.393733

Table S4: Total energies (atomic units) of the $^3(CO)_2$ZnZn.

Methods	E
BP86/6-311+G(3df)	-3785.814631
B3PW91/6-311+G(3df)	-3785.19024
BPW91/6-311+G(3df)	-3785.64378
PBEPBE/6-311+G(3df)	-3784.509515
BH&HLYP/6-311+G(3df)	-3785.044985
B3LYP/6-311+G(3df)	-3785.372186
MP2/6-311+G(3df)	-3782.645815
MP4SDQ/6-311+G(3df)	-3782.574111
QCISD/6-311+G(3df)	-3782.555313
CCSD/6-311+G(3df)	-3782.546157

Table S5: Total energies (atomic units) of the $^3Zn(CO)_3$. The dissociated energies of E_1 and E_2 mean the energies of $^3Zn(CO)_3 \rightarrow {}^3Zn+3CO$ and $^3Zn(CO)_3 \rightarrow {}^3Zn(CO)_2+CO$, respectively

Methods	E	E_1	E_2
BP86/6-311+G(3df)	-2119.599197	78.85	10.26
B3PW91/6-311+G(3df)	-2119.177683	61.71	6.97
BPW91/6-311+G(3df)	-2119.492108	73.84	9.12

PBEPBE/6-311+G(3df)	-2118.701009	82.29	11.45
BH&HLYP/6-311+G(3df)	-2119.075767	42.09	0.48
B3LYP/6-311+G(3df)	-2119.366804	58.90	5.98
MP2/6-311+G(3df)	-2117.551996	43.97	-0.52
MP4SDQ/6-311+G(3df)	-2117.521758	37.78	-1.76
QCISD/6-311+G(d)	-2117.233118	31.02	-1.13
CCSD/6-311+G(d)	-2117.222903	30.33	-1.14

Table S6: The dissociated energies of E_1, E_2, and E_3 mean the energies of ^{3}(CO)ZnZn → ^{3}Zn+^{1}Zn+CO, ^{3}(CO)ZnZn→ ^{3}Zn-Zn+CO, and ^{3}(CO)ZnZn → ^{3}ZnCO+^{1}Zn, respectively.

Methods	E_1	E_2	E_3
BP86/6-311+G(3df)	61.56	22.99	17.09
B3PW91/6-311+G(3df)	53.48	19.27	14.93
BPW91/6-311+G(3df)	58.21	21.77	15.84
PBEPBE/6-311+G(3df)	63.49	24.19	18.17
BH&HLYP/6-311+G(3df)	44.68	15.08	12.31
B3LYP/6-311+G(3df)	51.63	18.19	13.24
MP2/6-311+G(3df)	44.09	15.12	13.09
MP4SDQ/6-311+G(3df)	40.96	12.59	11.46
QCISD/6-311+G(3df)	39.85	11.78	10.70
CCSD/6-311+G(3df)	39.03	11.28	10.41

Table S7: The dissociated energies of E_1, E_2, E_3 and E_4 mean the energies of ^{3}(CO)$_2$ZnZn → ^{3}Zn+^{1}Zn+2CO, ^{3}(CO)$_2$ZnZn → ^{3}Zn-Zn+2CO, ^{3}(CO)$_2$ZnZn → ^{3}Zn(CO)$_2$+^{1}Zn, and ^{3}(CO)$_2$ZnZn → ^{3}(CO)ZnZn +CO respectively.

Methods	E_1	E_2	E_3	E_4
BP86/6-311+G(3df)	81.30	42.73	12.72	19.74
B3PW91/6-311+G(3df)	67.98	33.77	13.25	14.50
BPW91/6-311+G(3df)	76.64	40.19	11.92	18.43
PBEPBE/6-311+G(3df)	84.48	45.18	13.64	20.99
BH&HLYP/6-311+G(3df)	52.82	23.23	11.22	8.15
B3LYP/6-311+G(3df)	64.33	30.88	11.40	12.70
MP2/6-311+G(3df)	58.25	29.28	13.76	14.16
MP4SDQ/6-311+G(3df)	50.66	22.29	11.13	9.69
QCISD/6-311+G(3df)	48.10	20.03	10.08	8.25
CCSD(/6-311+G(3df)	47.14	19.39	9.82	8.11

Table S8: The total and dissociated energies of $^3(CO)_2ZnZnZn$. E_1, E_2, E_3 and E_4 mean the energies of $^3(CO)_2ZnZnZn \rightarrow {}^3Zn+2{}^1Zn+2CO$, $^3(CO)_2ZnZnZn \rightarrow {}^3Zn\text{-}Zn\text{-}Zn+2CO$, $^3(CO)_2ZnZnZn \rightarrow {}^3Zn(CO)_2+{}^3Zn\text{-}Zn$, and $^3(CO)_2ZnZnZn \rightarrow {}^3(CO)_2ZnZn + {}^1Zn$, respectively.

Methods	E	E_1	E_2	E_3	E_4
BP86/6-311+G(3df)	-5565.390763	88.33	31.70	76.32	7.02
B3PW91/6-311+G(3df)	-5564.507365	74.45	24.86	73.51	6.47
BPW91/6-311+G(3df)	-5565.144781	83.15	29.86	73.88	6.51
PBEPBE/6-311+G(3df)	-5563.555987	92.60	34.38	76.09	8.12
BH&HLYP/6-311+G(3df)	-5564.302793	56.93	15.63	73.59	4.11
B3LYP/6-311+G(3df)	-5564.732419	68.53	21.07	76.90	4.20
MP2/6-311+G(2df)	-5560.753185	63.11	23.62	18.23	5.86
MP4SDQ/6-311+G(2df)	-5560.657843	53.70	16.18	14.23	3.96
QCISD/6-311+G(2df)	-5560.629562	50.15	13.08	12.39	3.03
CCSD/6-311+G(2df)	-5560.617342	48.99	12.52	11.98	2.90

Table S9: Total energies (atomic units) and relative energies (in parentheses) of $^1[ZnH_2]$ and $^3[ZnH_2]$ systems.

Species	B3LYP/6-311++G(3df,3pd)
$^1Zn+H_2$	-1780.533568(0.00)
^1TS	-1780.369496(102.96)
^1HZnH	-1780.522362(7.03)
$^3Zn+H_2$	-1780.382591(94.74)
^3TS	-1780.401842(82.66)
$^3Zn\ldots H_2$	-1780.408101(78.73)
^3HZnH	-1780.401928(82.61)

$^1Zn(CO)_3$ (D_{3h})

BP86/6-311+G(3df)

30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.888341	0.000000
8	0	0.000000	3.044222	0.000000
6	0	1.635351	-0.944170	0.000000
8	0	2.636373	-1.522111	0.000000
6	0	-1.635351	-0.944170	0.000000
8	0	-2.636373	-1.522111	0.000000

B3PW91/6-311+G(3df)

30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.894496	0.000000
6	0	1.640682	-0.947248	0.000000
6	0	-1.640682	-0.947248	0.000000
8	0	0.000000	3.035257	0.000000
8	0	2.628610	-1.517628	0.000000
8	0	-2.628610	-1.517628	0.000000
BPW91/6-311+G(3df)				
30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.889268	0.000000
6	0	1.636154	-0.944634	0.000000
6	0	-1.636154	-0.944634	0.000000
8	0	0.000000	3.044344	0.000000
8	0	2.636479	-1.522172	0.000000
8	0	-2.636479	-1.522172	0.000000
PBEPBE/6-311+G(3df)				
30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.888368	0.000000
6	0	1.635374	-0.944184	0.000000
6	0	-1.635374	-0.944184	0.000000
8	0	0.000000	3.043706	0.000000
8	0	2.635927	-1.521853	0.000000
8	0	-2.635927	-1.521853	0.000000
BHandHLYP/6-311+G(3df)				
30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.920420	0.000000
6	0	1.663132	-0.960210	0.000000
6	0	-1.663132	-0.960210	0.000000
8	0	0.000000	3.044815	0.000000
8	0	2.636887	-1.522407	0.000000
8	0	-2.636887	-1.522407	0.000000
B3LYP/6-311+G(3df)				
30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.907768	0.000000
8	0	0.000000	3.049188	0.000000
6	0	1.652176	-0.953884	0.000000
8	0	2.640674	-1.524594	0.000000
6	0	-1.652176	-0.953884	0.000000
8	0	-2.640674	-1.524594	0.000000
MP2/6-311+G(3df)				
30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.864157	0.000000
8	0	0.000000	3.016620	0.000000
6	0	1.614408	-0.932079	0.000000
8	0	2.612470	-1.508310	0.000000
6	0	-1.614408	-0.932079	0.000000
8	0	-2.612470	-1.508310	0.000000
MP4SDQ/6-311+G(3df)				
30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.892133	0.000000

8	0	0.000000	3.034101	0.000000
6	0	1.638636	-0.946067	0.000000
8	0	2.627609	-1.517051	0.000000
6	0	-1.638636	-0.946067	0.000000
8	0	-2.627609	-1.517051	0.000000
QCISD/6-311+G(3df)				
30	0	0.000000	0.000000	0.000000
6	0	0.000000	0.000000	1.909321
8	0	0.000000	0.000000	3.048864
6	0	1.653520	0.000000	-0.954660
8	0	2.640394	0.000000	-1.524432
6	0	-1.653520	0.000000	-0.954660
8	0	-2.640394	0.000000	-1.524432
CCSD/6-311+G(3df)				
30	0	0.000000	0.000000	0.000000
6	0	1.912775	0.000000	0.000000
8	0	3.049568	0.000000	0.000000
6	0	-0.956388	-1.656512	0.000000
8	0	-1.524784	-2.641003	0.000000
6	0	-0.956388	1.656512	0.000000
8	0	-1.524784	2.641003	0.000000
CASSCF(12, 12)/6-31+G(d)				
30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.956833	0.000000
6	0	1.694667	-0.978416	0.000000
6	0	-1.694667	-0.978416	0.000000
8	0	0.000000	3.076564	0.000000
8	0	2.664383	-1.538282	0.000000
8	0	-2.664383	-1.538282	0.000000

$^1Zn(CO)_3$ (D_{3h}) in Ar solvent

BP86/6-311+G(3df)				
30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.889013	0.000000
8	0	0.000000	3.045075	0.000000
6	0	1.635933	-0.944506	0.000000
8	0	2.637112	-1.522537	0.000000
6	0	-1.635933	-0.944506	0.000000
8	0	-2.637112	-1.522537	0.000000
B3PW91/6-311+G(3df)				
30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.895614	0.000000
6	0	1.641650	-0.947807	0.000000
6	0	-1.641650	-0.947807	0.000000
8	0	-0.000216	3.036609	0.000000
8	0	2.629888	-1.518118	0.000000
8	0	-2.629673	-1.518491	0.000000
BPW91/6-311+G(3df)				
30	0	0.000000	0.000000	0.000000

6	0	0.000000	1.889408	0.000000
6	0	1.636276	-0.944704	0.000000
6	0	-1.636276	-0.944704	0.000000
8	0	0.000000	3.044848	0.000000
8	0	2.636916	-1.522424	0.000000
8	0	-2.636916	-1.522424	0.000000

PBEPBE/6-311+G(3df)

30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.889113	0.000000
6	0	1.636020	-0.944556	0.000000
6	0	-1.636020	-0.944556	0.000000
8	0	0.000000	3.044748	0.000000
8	0	2.636830	-1.522374	0.000000
8	0	-2.636830	-1.522374	0.000000

BHandHLYP/6-311+G(3df)

30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.921694	0.000000
6	0	1.664236	-0.960847	0.000000
6	0	-1.664236	-0.960847	0.000000
8	0	0.000000	3.046418	0.000000
8	0	2.638276	-1.523209	0.000000
8	0	-2.638276	-1.523209	0.000000

B3LYP/6-311+G(3df)

30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.909208	0.000000
6	0	1.653423	-0.954604	0.000000
6	0	-1.653423	-0.954604	0.000000
8	0	-0.000385	3.051018	0.000000
8	0	2.642451	-1.525175	0.000000
8	0	-2.642066	-1.525843	0.000000

MP2/6-311+G(3df)

30	0	0.000000	0.000000	0.000000
6	0	0.000000	1.864157	0.000000
8	0	0.000000	3.016620	0.000000
6	0	1.614407	-0.932079	0.000000
8	0	2.612470	-1.508310	0.000000
6	0	-1.614407	-0.932079	0.000000
8	0	-2.612470	-1.508310	0.000000

$^1Zn(CO)_3Ne(C_s)$

BP86/6-31+G(d)

30	0	0.000000	0.693029	0.000000
6	0	1.654576	-0.217822	0.000000
6	0	-0.040197	2.581223	0.000000
6	0	-1.614965	-0.286706	0.000000
8	0	-0.065072	3.748912	0.000000
8	0	2.677784	-0.780943	0.000000
8	0	-2.613679	-0.892190	0.000000
10	0	0.001126	-4.985728	0.000000

TS (C_{3v})

BP86/6-311+G(3df)				
30	0	-0.000128	-0.000097	0.203343
6	0	-1.878115	-0.155652	-0.156733
6	0	0.804142	1.704321	-0.156592
6	0	1.074158	-1.548344	-0.156496
8	0	-3.028849	-0.251270	-0.137101
8	0	1.296975	2.748557	-0.136895
8	0	1.732215	-2.497168	-0.136172
B3PW91/6-311+G(3df)				
30	0	-.001243	-.000051	.147066
6	0	-1.889105	-.104765	-.094899
6	0	0.854278	1.686198	-.094692
6	0	1.035730	-1.581713	-.094355
8	0	-3.027443	-.168407	-.113200
8	0	1.369497	2.703256	-.112892
8	0	1.661928	-2.534448	-.112447
BPW91/6-311+G(3df)				
30	0	.000199	-.000026	.211301
6	0	1.815259	-.510876	-.165780
6	0	-1.350189	-1.316676	-.165165
6	0	-.465360	1.827437	-.165617
8	0	2.925726	-.823645	-.140285
8	0	-2.176568	-2.121686	-.139896
8	0	-.749687	2.945513	-.139777
PBEPBE/6-311+G(3df)				
30	0	0.000416	-0.000377	0.242059
6	0	-0.400732	1.838064	-0.184811
6	0	1.792808	-0.571775	-0.185125
6	0	-1.392323	-1.265794	-0.184807
8	0	-0.647664	2.965149	-0.163763
8	0	2.892201	-0.921983	-0.164101
8	0	-2.245912	-2.042123	-0.163798
MP2/6-311+G(3df)				
30	0	-0.000098	-0.000082	0.274480
6	0	0.528804	1.768693	-0.147015
6	0	1.267467	-1.342303	-0.147028
6	0	-1.796333	-0.426442	-0.147044
8	0	0.857912	2.868340	-0.232788
8	0	2.055697	-2.176703	-0.232825
8	0	-2.913195	-0.691289	-0.232870
CASSCF(12,12)/6-31+G(d)				
30	0	0.000000	0.000000	0.004006
6	0	0.000000	1.995246	-0.002960
6	0	1.727934	-0.997623	-0.002960
6	0	-1.727934	-0.997623	-0.002960
8	0	0.000000	3.127588	-0.002788
8	0	2.708571	-1.563794	-0.002788

8	0	-2.708571	-1.563794	-0.002788

^{3}(CO)ZnZn ($C_{\infty v}$)

BP86/6-311+G(3df)				
30	0	-0.497286	-0.141846	0.002499
30	0	1.939934	0.069289	-0.002165
6	0	-2.429572	0.239000	0.018318
8	0	-3.587751	0.092838	-0.014992
B3PW91/6-311+G(3df)				
30	0	-0.007105	-1.976006	0.000000
30	0	0.000000	0.509864	0.000000
6	0	0.012141	2.482132	0.000000
8	0	0.017539	3.636431	0.000000
BPW91/6-311+G(3df)				
30	0	-0.008183	-1.973577	0.000000
30	0	0.000000	0.502442	0.000000
6	0	0.014552	2.486289	0.000000
8	0	0.019771	3.652037	0.000000
PBEPBE/6-311+G(3df)				
30	0	-0.008292	-1.973317	0.000000
30	0	0.000000	0.503060	0.000000
6	0	0.014825	2.484284	0.000000
8	0	0.019976	3.650251	0.000000
BHandHLYP/6-311+G(3df)				
30	0	0.000000	0.000000	2.003901
30	0	0.000000	0.000000	-0.529103
6	0	0.000000	0.000000	-2.506698
8	0	0.000000	0.000000	-3.650470
B3LYP/6-311+G(3df)				
30	0	0.000000	0.000000	1.997144
30	0	0.000000	0.000000	-0.518143
6	0	0.000000	0.000000	-2.508641
8	0	0.000000	0.000000	-3.664774
MP2/6-311+G(3df)				
30	0	0.000000	0.000000	1.928892
30	0	0.000000	0.000000	-0.487175
6	0	0.000000	0.000000	-2.428846
8	0	0.000000	0.000000	-3.584806
MP4SDQ/6-311+G(3df)				
30	0	0.000000	0.000000	1.961344
30	0	0.000000	0.000000	-0.505637
6	0	0.000000	0.000000	-2.459115
8	0	0.000000	0.000000	-3.614567
QCISD/6-311+G(3df)				
30	0	0.000000	0.000000	1.981863
30	0	0.000000	0.000000	-0.515944
6	0	0.000000	0.000000	-2.479178
8	0	0.000000	0.000000	-3.637814
CCSD/6-311+G(3df)				

30	0	0.000000	0.000000	1.985369
30	0	0.000000	0.000000	-0.517986
6	0	0.000000	0.000000	-2.484435
8	0	0.000000	0.000000	-3.639359

$^3(CO)_2ZnZn$ (C_{2v})

BP86/6-311+G(3df)				
30	0	0.409546	-0.000004	0.000037
6	0	1.565327	1.584739	0.000073
6	0	1.565530	-1.584596	0.000074
8	0	1.981405	2.664912	0.000199
8	0	1.981748	-2.664715	0.000200
30	0	-2.092558	-0.000077	-0.000172
B3PW91/6-311+G(3df)				
30	0	0.335748	-0.000030	0.000050
6	0	1.648164	1.505170	0.000053
6	0	1.648416	-1.505002	0.000055
8	0	2.198820	2.503950	0.000223
8	0	2.199253	-2.503682	0.000224
30	0	-2.167883	-0.000075	-0.000191
BPW91/6-311+G(3df)				
30	0	0.408714	-0.000005	0.000025
6	0	1.567966	1.584661	0.000068
6	0	1.568177	-1.584513	0.000069
8	0	1.987415	2.662492	0.000210
8	0	1.987773	-2.662287	0.000212
30	0	-2.095992	-0.000080	-0.000165
PBEPBE/6-311+G(3df)				
30	0	0.414280	-0.000004	0.000018
6	0	1.559030	1.588331	0.000072
6	0	1.559260	-1.588169	0.000073
8	0	1.970727	2.669743	0.000212
8	0	1.971118	-2.669520	0.000213
30	0	-2.089097	-0.000088	-0.000160
BHandHLYP/6-311+G(3df)				
30	0	0.285858	-0.000068	0.000143
6	0	1.739643	1.467711	0.000056
6	0	1.739941	-1.467516	0.000059
8	0	2.389677	2.383977	0.000199
8	0	2.390206	-2.383620	0.000199
30	0	-2.256411	-0.000066	-0.000272
B3LYP/6-311+G(3df)				
30	0	0.344436	-0.000041	0.000124
6	0	1.676082	1.520440	0.000004
6	0	1.676431	-1.520211	0.000014
8	0	2.209400	2.529690	0.000204
8	0	2.209994	-2.529321	0.000204
30	0	-2.193444	-0.000103	-0.000236
MP2/6-311+G(3df)				

30	0	0.000000	0.000000	2.143402
30	0	0.000000	0.000000	-0.279260
6	0	0.000000	1.460662	-1.629054
8	0	0.000000	2.409140	-2.273476
6	0	0.000000	-1.460662	-1.629054
8	0	0.000000	-2.409140	-2.273476
MP4SDQ/6-311+G(3df)				
30	0	0.000000	0.000000	2.202909
30	0	0.000000	0.000000	-0.267102
6	0	0.000000	1.461083	-1.687769
8	0	0.000000	2.377869	-2.363811
6	0	0.000000	-1.461083	-1.687769
8	0	0.000000	-2.377869	-2.363811
QCISD/6-311+G(3df)				
30	0	0.000000	0.000000	2.232011
30	0	0.000000	0.000000	-0.269592
6	0	0.000000	1.462505	-1.717507
8	0	0.000000	2.377727	-2.391407
6	0	0.000000	-1.462505	-1.717507
8	0	0.000000	-2.377727	-2.391407
CCSD/6-311+G(3df)				
30	0	0.000000	0.000000	2.239707
30	0	0.000000	0.000000	-0.266717
6	0	0.000000	1.461819	-1.725455
8	0	0.000000	2.369100	-2.405266
6	0	0.000000	-1.461819	-1.725455
8	0	0.000000	-2.369100	-2.405266

[ZnH_2] system

^{1}HZnH ($C_{\infty v}$)

30	0	0.000000	0.000000	0.000000
1	0	0.000000	0.000000	1.541711
1	0	0.000000	0.000000	-1.541711

^{1}TS (C_s)

30	0	0.000000	0.094262	0.000000
1	0	0.829534	-1.175160	0.000000
1	0	-0.829534	-1.652713	0.000000

^{3}HZnH (C_{2v})

30	0	0.000000	0.090983	0.000000
1	0	-0.911409	-1.364740	0.000000
1	0	0.911409	-1.364740	0.000000

^{3}TS (C_s)

30	0	0.000000	0.103793	0.000000
1	0	0.513213	-1.556825	0.000000
1	0	-0.513213	-1.556955	0.000000

^{3}Zn···H_2 (C_{2v})

30	0	0.000000	0.000000	0.106901
1	0	0.000000	0.466466	-1.603522
1	0	0.000000	-0.466466	-1.603522

Chemical bonding analysis

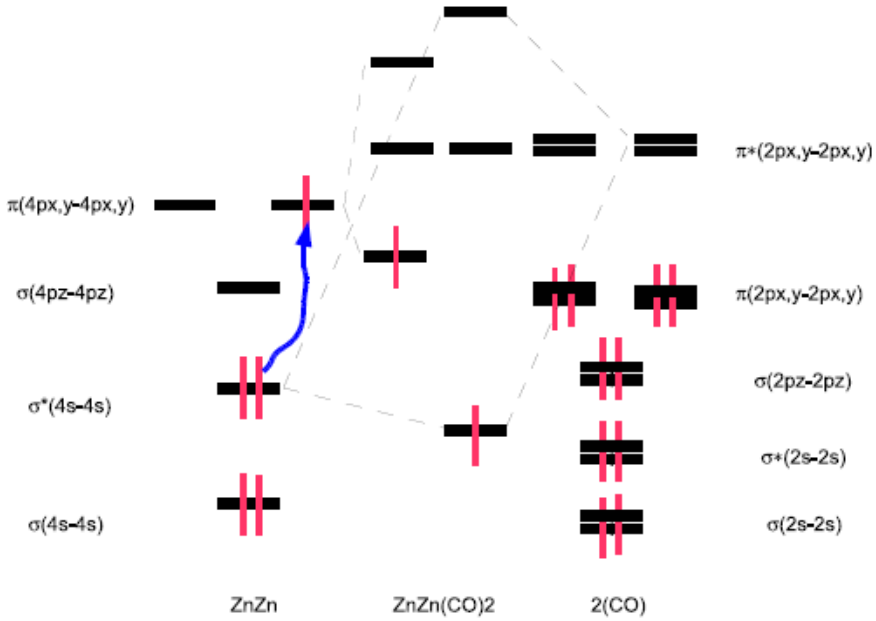

Figure S1: Schematic representation of the valence molecular orbitals of the $^3B_1$ ground state of $^3(CO)_2ZnZn$.

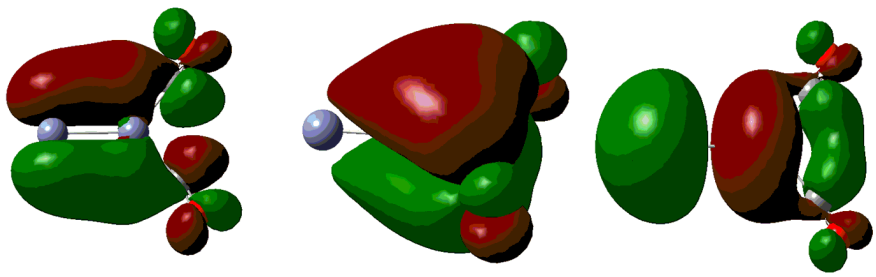

Figure S2: The pictures of characteristic orbitals of ground state of $^3(CO)_2ZnZn$.

As shown in **Figure S1**, the fragments selected are the zinc dimer, Zn_2, and the two carbonyl ligands. Bonding is then depicted as arising from an excitation of one of the electrons of the antibonding _(4s − 4s) orbitals of the zinc dimer to one the excited _(4py − 4py) bonding orbitals, being the y-axis the one perpendicular to the molecular plane of $^3(CO)_2ZnZn$. Then, this orbital and the _(4s−4s) orbitals mix with the _(2py−2py) of the carbonyls to form the singly occupied molecular orbitals that give raise to the triplet $^3B_1$ ground state of $^3(CO)_2ZnZn$. The singly occupied orbitals are shown in Figure **S2**.