JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
J. Am. Chem. Soc., 1996, 118(11), 2699-2707, DOI:10.1021/ja9529089

SUPPLEMENTARY MATERIAL

Nanocrystal $[Ti_{14}C_{13}]$ to Metallocarbohedrene $[Ti_8C_{13}]$: Structural Principles and Mechanism

Ian Dance

DENSITY FUNCTIONAL CALCULATIONS

Program DMol v2.3 and v2.35 (Biosym Technologies, Inc. San Diego, California.). Expressions capitalised in the following represent the values of the control parameters.

Basis sets Double numerical with d polarisation functions (DND). These are comparable to the Gaussian 6-31G* basis sets. Core orbitals are frozen (FROZEN =1).

n	L	occupancy in atomic calculation	energy in eV
		Carbon	
n=1	L=0	2.00	-270.6913 frozen
n=2	L=0	2.00	-13.6293
n=2	L=1	2.00	-5.4201
n=2	L=0	0.00	-40.1559
n=2	L=1	0.00	-31.8532
n=3	L=2	0.00	-37.7936
n=2	L=1	0.00	-85.0356 eliminated
n=1	L=0	0.00	-340.1425 eliminated
n=3	L=2	0.00	-74.0755 eliminated
n=2	L=1	0.00	-166.6698 eliminated
		Titanium	
n=1	L=0	2.00	-4823.9450 frozen
n=2	L=0	2.00	-529.4766 frozen
n=2	L=1	6.00	-443.1468 frozen
n=3	L=0	2.00	-61.4435
n=3	L=1	6.00	-38.7204
n=3	L=2	2.00	-4.6262
n=4	L=0	2.00	-4.5472
n=3	L=2	0.00	-25.3153
n=4	L=0	0.00	-19.1536
n=4	L=1	0.00	-14.3669

ATOMIC COORDINATES FOR SELECTED OPTIMISED STRUCTURES

Orthogonal coordinates, in Å. Note that the atom labels in these listings do not correspond with the atom labels in the Figures

$[Ti_{14}C_{13}]^0$, lyp/b88e optimisation

C1	0.0000	0.0000	0.0000
C2	2.1798	-0.0043	2.1789
C3	-2.1798	0.0043	2.1789
C4	2.1798	0.0043	-2.1789
C5	-2.1798	-0.0043	-2.1789
C6	-0.0012	-2.1818	2.1796
C7	0.0012	2.1818	2.1796
C8	-0.0012	2.1818	-2.1796
C9	0.0012	-2.1818	-2.1796
C10	2.1781	-2.1869	-0.0012
C11	-2.1781	2.1869	-0.0012
C12	2.1781	2.1869	0.0012
C13	-2.1781	-2.1869	0.0012
Ti1	0.0000	0.0000	2.1233
Ti2	0.0000	0.0000	-2.1233
Ti3	2.1245	0.0000	0.0000
Ti4	-2.1245	0.0000	0.0000
Ti5	0.0000	-2.1235	0.0000
Ti6	0.0000	2.1235	0.0000
Ti7	2.0371	-2.0419	2.0367
Ti8	-2.0371	2.0419	2.0367
Ti9	2.0371	2.0419	-2.0367
Ti10	-2.0371	-2.0419	-2.0367
Ti11	-2.0390	2.0355	-2.0385
Ti12	2.0390	-2.0355	-2.0385
Ti13	-2.0390	-2.0355	2.0385
Ti14	2.0390	2.0355	2.0385

$[Ti_{14}C_{13}]^+$, lyp/b88e optimisation

C1	0.0000	0.0000	0.0000
C2	2.1653	-0.0009	2.1652
C3	-2.1653	0.0009	2.1652
C4	2.1653	0.0009	-2.1652
C5	-2.1653	-0.0009	-2.1652
C6	-0.0005	-2.1657	2.1654
C7	0.0005	2.1657	2.1654
C8	-0.0005	2.1657	-2.1654
C9	0.0005	-2.1657	-2.1654
C10	2.1653	-2.1658	-0.0005
C11	-2.1653	2.1658	-0.0005
C12	2.1653	2.1658	0.0005
C13	-2.1653	-2.1658	0.0005
Ti1	0.0000	0.0000	2.1285
Ti2	0.0000	0.0000	-2.1285
Ti3	2.1286	0.0000	0.0000
Ti4	-2.1286	0.0000	0.0000
Ti5	0.0000	-2.1284	0.0000
Ti6	0.0000	2.1284	0.0000

Ti7	2.0432	-2.0442	2.0432
Ti8	-2.0432	2.0442	2.0432
Ti9	2.0432	2.0442	-2.0432
Ti10	-2.0432	-2.0442	-2.0432
Ti11	-2.0440	2.0426	-2.0439
Ti12	2.0440	-2.0426	-2.0439
Ti13	-2.0440	-2.0426	2.0439
Ti14	2.0440	2.0426	2.0439

$[Ti_8C_{13}]^0$, lyp/b88e optimisation

Ti1	-1.0868	-1.0868	1.0872
Ti2	1.0868	1.0868	1.0872
Ti3	-1.0868	1.0868	-1.0872
Ti4	1.0868	-1.0868	-1.0872
Ti5	1.7713	-1.7705	1.7696
Ti6	-1.7713	1.7705	1.7696
Ti7	1.7713	1.7705	-1.7696
Ti8	-1.7713	-1.7705	-1.7696
C1	0.0000	0.0000	0.0000
C2	0.4797	-2.6677	0.4788
C3	-0.4797	2.6677	0.4788
C4	0.4797	2.6677	-0.4788
C5	-0.4797	-2.6677	-0.4788
C6	2.6681	-0.4788	0.4796
C7	-2.6681	0.4788	0.4796
C8	2.6681	0.4788	-0.4796
C9	-2.6681	-0.4788	-0.4796
C10	0.4790	-0.4796	2.6671
C11	-0.4790	0.4796	2.6671
C12	0.4790	0.4796	-2.6671
C13	-0.4790	-0.4796	-2.6671

$[Ti_8C_{13}]^+$, lyp/b88e optimisation

Ti1	-1.0963	-1.0962	1.0964
Ti2	1.0963	1.0962	1.0964
Ti3	-1.0963	1.0962	-1.0964
Ti4	1.0963	-1.0962	-1.0964
Ti5	1.7725	-1.7720	1.7716
Ti6	-1.7725	1.7720	1.7716
Ti7	1.7725	1.7720	-1.7716
Ti8	-1.7725	-1.7720	-1.7716
C1	0.0000	0.0000	0.0000
C2	0.4758	-2.6646	0.4750
C3	-0.4758	2.6646	0.4750
C4	0.4758	2.6646	-0.4750
C5	-0.4758	-2.6646	-0.4750
C6	2.6650	-0.4752	0.4756
C7	-2.6650	0.4752	0.4756
C8	2.6650	0.4752	-0.4756
C9	-2.6650	-0.4752	-0.4756
C10	0.4753	-0.4756	2.6641
C11	-0.4753	0.4756	2.6641
C12	0.4753	0.4756	-2.6641
C13	-0.4753	-0.4756	-2.6641

$[Ti_{13}C_{13}]^0$, lyp/b88e optimisation

Ti1	0.0000	0.0000	-2.1039
Ti2	-0.0091	2.0932	-0.0361
Ti3	0.0091	-2.0932	-0.0361
Ti4	2.1983	-0.0333	-0.0684
Ti5	-2.1983	0.0333	-0.0684
Ti6	1.4796	1.2344	2.1599
Ti7	-1.4796	-1.2344	2.1599
Ti8	1.9276	-1.6766	2.2157
Ti9	-1.9276	1.6766	2.2157
Ti10	2.0456	2.0392	-1.9794
Ti11	-2.0456	-2.0392	-1.9794
Ti12	-2.0340	2.0681	-2.0105
Ti13	2.0340	-2.0681	-2.0105
C1	0.0000	0.0000	0.1357
C2	0.4208	-0.5375	3.0914
C3	-0.4208	0.5375	3.0914
C4	0.0008	-2.1675	-2.1613
C5	-0.0008	2.1675	-2.1613
C6	2.9239	-0.0633	1.9352
C7	-2.9239	0.0633	1.9352
C8	2.1398	-0.0336	-2.2297
C9	-2.1398	0.0336	-2.2297
C10	-2.0314	-2.1408	0.0239
C11	2.0314	2.1408	0.0239
C12	-2.0705	2.1663	0.0432
C13	2.0705	-2.1663	0.0432

$[Ti_{12}C_{13}]^0$, lyp/b88e optimisation

Ti1	-1.4506	0.2948	-1.2298
Ti2	0.1437	2.7001	-0.2660
Ti3	-0.0994	-2.3900	-0.5775
Ti4	1.3442	0.0419	-2.1949
Ti5	2.5270	1.2757	-0.0310
Ti6	-0.2578	-2.1390	2.5397
Ti7	-2.4451	2.0962	0.8572
Ti8	-0.7479	-1.7053	-3.2029
Ti9	-2.5349	-1.9881	0.6907
Ti10	-0.3371	2.2976	-2.9785
Ti11	2.3215	-1.3996	0.0877
Ti12	-0.1355	0.5998	1.6570
C1	0.4680	0.1293	-0.3033
C2	2.1382	0.0598	1.7253
C3	1.4970	-0.9765	2.2884
C4	-1.5687	2.3575	-1.2744
C5	-1.8575	-1.7447	-1.3565
C6	3.2956	-0.1672	-1.0615
C7	-1.7303	-0.7921	2.2918
C8	-2.3398	0.2026	1.5481
C9	-0.5495	0.2909	-3.2037
C10	1.3373	2.2543	-1.8829
C11	-1.0594	-3.2068	1.0448
C12	-0.7128	2.6017	1.5498
C13	0.9721	-2.0443	-2.2700

$[Ti_{11}C_{13}]^0$, lyp/b88e optimisation

Ti1	-2.7027	1.5992	-0.7773
Ti2	-1.6482	-2.1473	-1.7689
Ti3	0.5487	0.9527	-3.0393
Ti4	3.1792	0.8795	-0.1622
Ti5	0.3782	-2.9381	1.4672
Ti6	-0.8768	1.7858	2.6538
Ti7	-2.0112	0.2091	-2.9637
Ti8	-1.5764	-0.6527	0.7881
Ti9	0.2013	1.8540	-0.2326
Ti10	1.0526	-1.1672	-1.0162
Ti11	1.2056	-0.1221	1.7949
C1	0.0783	-0.0047	0.1274
C2	2.8289	-0.9899	0.4651
C3	2.0697	-2.0232	0.9205
C4	-1.8458	1.7216	0.9378
C5	-2.7051	-0.4560	-1.1575
C6	1.8830	0.9434	-1.6544
C7	-0.4003	-1.4849	2.6158
C8	-0.7330	-0.1981	2.9338
C9	-1.0960	1.8173	-2.0866
C10	2.0716	1.8875	1.1748
C11	-0.6398	-2.5993	-0.1952
C12	0.9774	2.1295	1.9491
C13	-0.3210	-0.9263	-2.8110

DIMENSIONS OF CLUSTERS

Table Supp 4 Dimensions (Å) of the optimised structure, **13/13**, of $[Ti_{13}C_{13}]$ and $[Ti_{13}C_{13}]^+$, in symmetry C_2.

Bond antecedents in $Ti_{14}C_{13}$	Bond [a]	$[Ti_{13}C_{13}]^0$	$[Ti_{13}C_{13}]^+$
		lyp/b88e	vwn/b88e
$C^6 - Ti^5$	C^c–Ti11	2.10	2.09
$C^6 - Ti^5$	C^c–Ti10	2.21	2.25
$C^6 - Ti^5$	C^c–Ti12	2.24	2.33
$C^6 - Ti^3$	C^c–Ti1	2.80	2.81
$C^6 - Ti^3$	C^c–Ti2	3.29	3.30
$Ti^3 - Ti^3$	Ti1–Ti4	3.44	3.44
$Ti^3 - Ti^3$	Ti1–Ti2	2.95	2.98
$Ti^3 - Ti^3$	Ti1–Ti3	3.85	3.91
none	C132–C134	1.37	1.36
$Ti^3 - C^4$	Ti1–C134	2.23	2.24
$Ti^3 - C^4$	Ti1–C132	2.27	2.31
$Ti^3 - C^4$	Ti2–C132	2.08	2.10
$Ti^3 - C^4$	Ti1–C12	1.96	1.95
$Ti^3 - C^4$	Ti2–C12	1.92	1.90
$Ti^3 - C^4$	Ti1–C16	2.39	2.36
$Ti^3 - C^4$	Ti5 – C25	2.06	2.04
$Ti^3 - C^4$	Ti5 – C56	2.05	2.07
$Ti^3 - C^4$	Ti5 – C58	2.04	2.05
$Ti^3 - C^4$	Ti6 – C16	2.01	2.01
$Ti^3 - C^4$	Ti6 – C56	2.09	2.09
$Ti^3 - C^4$	Ti6 – C67	2.06	2.06
$Ti^5 - C^4$	Ti10–C12	2.13	2.11
$Ti^5 - C^4$	Ti10–C56	2.16	2.14
$Ti^5 - C^4$	Ti10–C25	2.14	2.14
$Ti^5 - C^4$	Ti10–C16	2.18	2.17
$Ti^5 - C^4$	Ti11–C16	2.04	2.06
$Ti^5 - C^4$	Ti11–C47	2.06	2.06
$Ti^5 - C^4$	Ti11–C67	2.13	2.11
$Ti^5 - C^4$	Ti12–C56	2.14	2.14
$Ti^5 - C^4$	Ti12–C67	2.17	2.14
Ti^5–Ti^3	Ti11–Ti1	2.79	2.80
Ti^5–Ti^3	Ti11–Ti4	2.99	2.99
Ti^5–Ti^3	Ti10–Ti1	2.66	2.70
Ti^5–Ti^3	Ti10–Ti2	2.83	2.85

[a] Symmetry independent values are recorded.

Table Supp 5 Interatomic distances (Å) for the optimised structure, **12/13**, of $[Ti_{12}C_{13}]^0$, symmetry C_1.

Bond antecedent in $Ti_{14}C_{13}$	Interaction in subsequent structures (in Ti_8C_{13})	Bond in $Ti_{12}C_{13}$	$[Ti_{12}C_{13}]^0$ lyp/b88e
$C^6 - Ti^5$	—	C^c–Ti13	2.09
$C^6 - Ti^5$	—	C^c–Ti12	2.14
$C^6 - Ti^5$	—	C^c–Ti14	2.60
$C^6 - Ti^5$	—	C^c–Ti11	2.59
$C^6 - Ti^3$	$C^c - Ti^i$	C^c–Ti1	2.10
$C^6 - Ti^3$	$C^c - Ti^i$	C^c–Ti3	2.43
$C^6 - Ti^3$	$C^c - Ti^i$	C^c–Ti5	3.81
$C^6 - Ti^3$	$C^c - Ti^i$	C^c–Ti7	3.54
$C^6 - Ti^3$	$C^c - Ti^o$	C^c–Ti4	2.37
$C^6 - Ti^3$	$C^c - Ti^o$	C^c–Ti2	3.71
$C^6 - Ti^3$	$C^c - Ti^o$	C^c–Ti6	3.70
$C^6 - Ti^3$	$C^c - Ti^o$	C^c–Ti8	3.64
$Ti^3 - C^4$	$Ti^i - C$	Ti1–C132	2.36
$Ti^3 - C^4$	$Ti^i - C$	Ti1–C134	2.34
$Ti^3 - C^4$	$Ti^i - C$	Ti3–C132	2.39
$Ti^3 - C^4$	$Ti^i - C$	Ti3–C134	2.20
$Ti^3 - C^4$	$Ti^o - C$	Ti2–C132	2.12
$Ti^3 - C^4$	$Ti^o - C$	Ti4–C134	2.17
$Ti^3 - C^4$	$Ti^i - C$	Ti1–C152	2.21
$Ti^3 - C^4$	$Ti^i - C$	Ti1–C156	2.24
$Ti^3 - C^4$	$Ti^i - C$	Ti5–C152	2.15
$Ti^3 - C^4$	$Ti^i - C$	Ti5–C156	2.36
$Ti^3 - C^4$	$Ti^o - C$	Ti2–C152	2.01
$Ti^3 - C^4$	$Ti^o - C$	Ti6–C156	2.02
$Ti^3 - C^4$		Ti1 – C16	2.09
$Ti^3 - C^4$		Ti6 – C16	1.93
$Ti^3 - C^4$		Ti3 – C34	1.95
$Ti^3 - C^4$		Ti4 – C34	1.93
$Ti^3 - C^4$		Ti2 – C25	2.00
$Ti^3 - C^4$		Ti5 – C25	1.95
$Ti^5 - C^4$		Ti7 – C47	2.00
$Ti^5 - C^4$		Ti7 – C67	2.10
$Ti^5 - C^4$		Ti7 – C78	2.03
$Ti^5 - C^4$		Ti8 – C38	1.99
$Ti^5 - C^4$		Ti8 – C58	2.15
$Ti^5 - C^4$		Ti8 – C78	2.01

$Ti^5 - C^4$		Ti11–C16	2.01
$Ti^5 - C^4$		Ti11–C47	2.06
$Ti^5 - C^4$		Ti11–C67	2.02
$Ti^5 - C^4$		Ti12–C67	2.07
$Ti^5 - C^4$		Ti12–C58	2.08
$Ti^5 - C^4$		Ti12–C78	2.17
$Ti^5 - C^4$		Ti13–C34 4	2.27
$Ti^5 - C^4$		Ti13–C47	2.23
$Ti^5 - C^4$		Ti13–C38	2.12
$Ti^5 - C^4$		Ti13–C37	2.16
$Ti^5 - C^4$		Ti14–C25	2.05
$Ti^5 - C^4$		Ti14–C38	2.03
$Ti^5 - C^4$		Ti14–C58	2.03
	$Ti^i - Ti^o$	Ti1–Ti2	2.88
	$Ti^i - Ti^o$	Ti3–Ti4	2.69
	$Ti^i - Ti^o$	Ti1–Ti4	3.22
	$Ti^i - Ti^o$	Ti2–Ti3	3.64
	$Ti^i - Ti^o$	Ti1–Ti6	2.87
	$Ti^i - Ti^o$	Ti2–Ti5	2.94
	$Ti^i - Ti^o$	Ti5–Ti6	4.09
	$Ti^i - Ti^i$	Ti1–Ti3	3.54
	$Ti^i - Ti^i$	Ti1–Ti5	3.66
	C – C	C132–C134	1.34
	C – C	C152–C156	1.38

Table Supp 6 Interatomic distances (Å) for the optimised structure, **11/13**, of $[Ti_{11}C_{13}]$ and $[Ti_{11}C_{13}]^+$: actual symmetry C_1, approximate symmetry C_{3v}.

Bond antecedent	Bond type in Ti_8C_{13}	Bond	$[Ti_{11}C_{13}]^0$ lyp/b88e	$[Ti_{11}C_{13}]^+$ vwn/b88e
C^c–Ti^5		C^c–Ti12	3.34	3.35
C^c–Ti^5		C^c–Ti13	3.34	3.35
C^c–Ti^5		C^c–Ti14	3.34	3.36
	C^c–Ti^i	C^c–Ti1	2.02	2.02
	C^c–Ti^i	C^c–Ti3	1.90	1.89
	C^c–Ti^i	C^c–Ti5	1.90	1.89
	C^c–Ti^i	C^c–Ti7	1.90	1.89
	C^c–Ti^o	C^c–Ti2	3.24	3.27
	C^c–Ti^o	C^c–Ti4	3.24	3.27
	C^c–Ti^o	C^c–Ti6	3.24	3.28
	C^c–Ti^o	C^c–Ti8	3.74	3.71
	Ti^i – Ti^o	Ti1–Ti2	2.95	3.00
	Ti^i – Ti^o	Ti1–Ti4	2.95	2.99
	Ti^i – Ti^o	Ti1–Ti6	2.95	2.99
	Ti^i – Ti^o	Ti3–Ti2	3.12	3.16
	Ti^i – Ti^o	Ti3–Ti4	3.07	3.12
	Ti^i – Ti^o	Ti5–Ti2	3.08	3.11
	Ti^i – Ti^o	Ti5–Ti6	3.15	3.19
	Ti^i – Ti^o	Ti7–Ti4	3.13	3.18
	Ti^i – Ti^o	Ti7–Ti6	3.08	3.11
	Ti^i – Ti^i	Ti1–Ti3	3.00	3.02
	Ti^i – Ti^i	Ti1–Ti5	3.01	3.03
	Ti^i – Ti^i	Ti1–Ti7	3.00	3.02
	Ti^i – Ti^i	Ti3–Ti5	3.23	3.21
	Ti^i – Ti^i	Ti3–Ti7	3.24	3.22
	Ti^i – Ti^i	Ti5–Ti7	3.24	3.21
	C – C	C132–C134	1.36	1.34
	C – C	C152–C156	1.37	1.34
	C – C	C174–C176	1.36	1.34
	Ti^i – C	Ti1–C132	2.26	2.26
	Ti^i – C	Ti1–C134	2.27	2.26
	Ti^i – C	Ti1–C152	2.26	2.26
	Ti^i – C	Ti1–C156	2.25	2.26
	Ti^i – C	Ti1–C174	2.27	2.27
	Ti^i – C	Ti1–C176	2.27	2.27
	Ti^i – C	Ti3–C132	2.35	2.38
	Ti^i – C	Ti3–C134	2.32	2.35
	Ti^i – C	Ti5–C152	2.33	2.35
	Ti^i – C	Ti5–C156	2.35	2.37

	Ti^{i} – C	Ti7–C174	2.34	2.38
	Ti^{i} – C	Ti7–C176	2.33	2.36
	Ti^{o} – C	Ti2–C132	2.00	2.04
	Ti^{o} – C	Ti2–C152	2.01	2.04
	Ti^{o} – C	Ti4–C134	2.00	2.04
	Ti^{o} – C	Ti4–C174	2.01	2.04
	Ti^{o} – C	Ti6–C156	2.01	2.05
	Ti^{o} – C	Ti6–C176	2.01	2.04
Ti^{3} – C^{4}		Ti2–C25	1.98	1.97
Ti^{5} – C^{4}		Ti14–C25	1.92	1.93
Ti^{3} – C^{4}		Ti4–C34	1.98	1.97
Ti^{5} – C^{4}		Ti13–C34	1.92	1.93
Ti^{3} – C^{4}		Ti6–C67	1.97	1.97
Ti^{5} – C^{4}		Ti12–C67	1.92	1.93
Ti^{3} – C^{4}		Ti5–C25	2.37	2.37
Ti^{3} – C^{4}		Ti3–C25	2.36	2.35
Ti^{3} – C^{4}		Ti3–C34	2.36	2.36
Ti^{3} – C^{4}		Ti7–C34	2.38	2.38
Ti^{3} – C^{4}		Ti7–C67	2.36	2.35
Ti^{3} – C^{4}		Ti5–C67	2.39	2.40
Ti^{3} – C^{4}		Ti3–C38	2.27	2.23
Ti^{3} – C^{4}		Ti5-C58	2.26	2.22
Ti^{3} – C^{4}		Ti7-C78	2.26	2.21
Ti^{3} – C^{4}		Ti8–C38	2.04	2.05
Ti^{3} – C^{4}		Ti8–C58	2.05	2.05
Ti^{3} – C^{4}		Ti8–C78	2.05	2.05
Ti^{5} – C^{4}		Ti12–C58	2.09	2.12
Ti^{5} – C^{4}		Ti12–C78	2.08	2.09
Ti^{5} – C^{4}		Ti13–C38	2.08	2.09
Ti^{5} – C^{4}		Ti13–C78	2.09	2.12
Ti^{5} – C^{4}		Ti14–C38	2.08	2.11
Ti^{5} – C^{4}		Ti14–C58	2.09	2.09
		Ti1–C^{c}–Ti3		101
		Ti1–C^{c}–Ti5		101
		Ti1–C^{c}–Ti7		101
		Ti3–C^{c}–Ti5		116
		Ti5–C^{c}–Ti7		117
		Ti3–C^{c}–Ti7		117