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Influence of Hydrogen Diffusion on Pt-Decorated Carbon Nanocones for Enhancing Hydrogen Storage Capacity: DFT Mechanistic Study

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Content

1. System validation

Table S1. H_2 adsorption energy from different calculation method

Method	Pt-4CNC				Pt-v4CNC			
	E_{Pt}	d(Pt-C)	E_{H2}	d(H-Pt)	E_{Pt}	d(Pt-C)	E_{H2}	d(H-Pt)
B3LYP/ 6-31G(d,p),LANL2DZ	-2.83	2.12, 2.12	-0.80	1.73	-6.42	1.98, 2.03, 2.00	-0.56	1.94
B3LYP-D3/ 6-311G(d,p),cc-pCTZ-PP	-3.15	2.10, 2.10	-1.03	1.71	-7.31	1.97, 2.02, 2.02	-0.48	1.84, 1.85
B3LYP-D3/6-311G(d,p),cc-pCTZ-PP //B3LYP/6-31G(d,p), LANL2DZ	-3.33	2.12, 2.12	-1.10	1.73	-7.35	1.98, 2.03, 2.00	-0.41	1.94

Table S2. The effect of H-termination toward the Pt binding and H_2 adsorption

Reaction	System	Pt-v4CNC (H-termination)	Pt-v4CNC (non H-termination)
Pt binding	E_{Pt}	-6.60 (-7.15)	-6.42 (-7.31)
	d(Pt-C)	1.97, 1.99, 1.99 (1.97, 1.99, 1.99)	1.98, 2.03, 2.00 (1.97, 2.02, 2.02)
H_2 adsorption	E_{H2}	-0.27(-0.55)	-0.56 (-0.48)
	d(H_2-Pt)	1.95, 1.97 (1.98, 1.99)	1.94, 1.94 (1.84, 1.85)
Spillover Reaction	Ea1	0.39 (0.37)	0.37 (0.46)
	Ea2	0.80 (0.78)	0.78 (0.85)

Note: the results were obtained from full geometry optimization at B3LYP/6-31G(d,p), LANL2DZ and B3LYP-D3/6-311G(d,p),cc-pCTZ-PP (in parentheses)

2. Pt binding on top of CNC

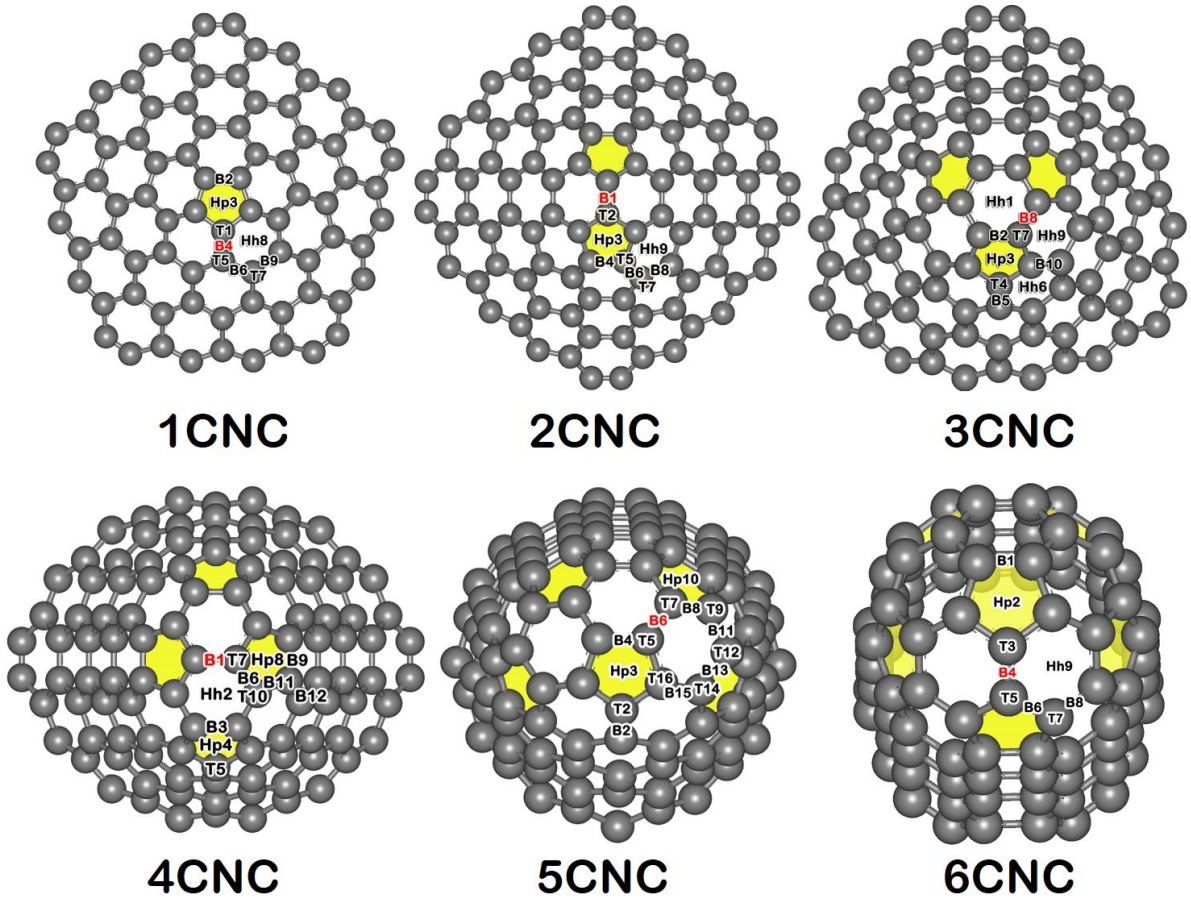

Figure S1. Possible adsorption sites for Pt binding on top of CNC with difference cone shape

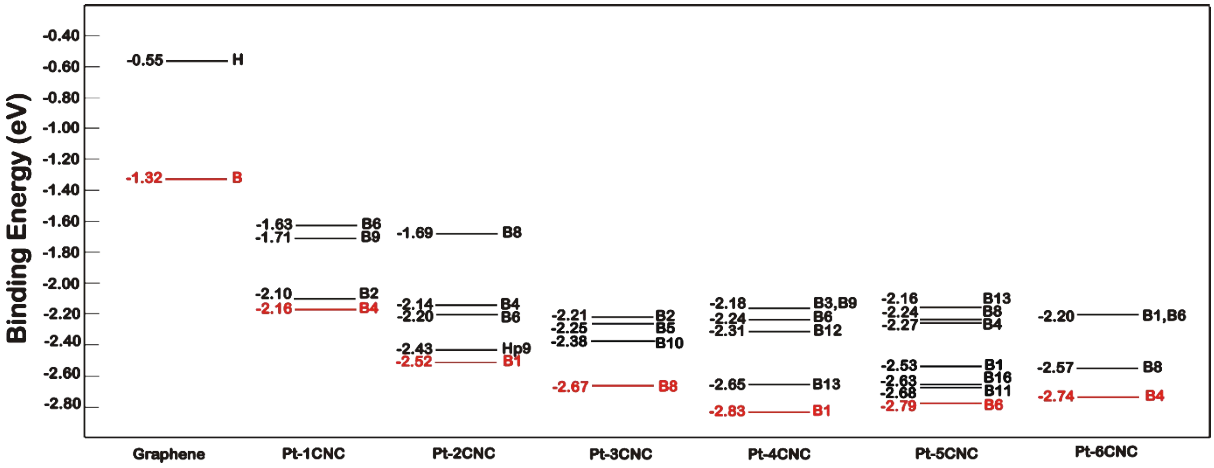

Figure S2. Pt binding energy diagram of Pt-*x*CNC structures (*x* = 1 to 6) from full geometry optimization at B3LYPD/6-31G(d,p)/LANL2DZ

1. Detail of π-orbital axis vector (POAV) analysis method

We describe CNC curvature of CNC using the π-orbital axis vector (POAV) analysis method. The POAV analysis provides a complete description of the electronic structure of non-planar conjugated organic molecules such as fullerenes, carbon nanotubes, and carbon nanoribbons. Current interest in these carbon nanomaterials has led to development of various POAV analytical methods. The method may be applied to the various metrics of interest, including pyramidalization angle, dihedral angle, hybridization, and resonance integrals. In this work, we calculate the pyramidalization angle and hybridization at a particular conjugated carbon atom follow the suggestion from R. C. Huddon [1]. The quantity of interest can be calculated via determination of the three angles made by the σ-bonds (θ_{12}, θ_{23}, θ_{31}) at the conjugated carbon atom in a complex. Six CNCs were fully optimized. **Table S1** lists bond lengths between pentagons and POAV analysis results for six CNC configurations. The POAV analysis provides an explanation for the electronic structure of non-planar conjugated organic molecules. In a theoretical POAV section, the π-orbital axis vector is the vector that delineates equal angles ($\theta_{\sigma\pi}$) for each of the three σ-bonds of a conjugated C-C atom. The pyramidalization angle is defined as $\theta_P = (90 - \theta_{\sigma\pi})^o$. The π-orbital of a sp^2 hybridized carbon atom coordinates with a Pt atom decorating the CNC. So, interactions with the coordinating carbon π-orbital accounts for our POAV results.

Table S3. Structural and electronic properties of Pt-decorated CNC complexes. $\mathbf{E_{bind}}$ = Pt binding energy, **dc-c** = bond distance between pentagons (Å), $\mathbf{d_{Pt-C}}$ = bond distance between Pt and C atoms at the tips (Å), $\mathbf{Q_{Pt}}$ and $\mathbf{Q_C}$ = electronic charge on Pt and C atoms. Note that Ci and Cj are the carbon atoms directly contacted with Pt at the B-site adsorption.

CNCs	$\mathbf{E_{bind}}$ /eV	$\mathbf{d_{Ci-Cj}}$ /Å	$\mathbf{d_{Pt-Ci,\ Cj}}$ /Å	**POAV of Ci**	$\mathbf{A_{Ci-Pt-Cj}}$	$\mathbf{Q_{Pt}}$	$\mathbf{Q_{Ci,\ Cj}}$
Pt-1CNC	-2.16	1.45	2.05 2.13	14.60°	39.91	0.10	-0.31 -0.31
Pt-2CNC	-2.52	1.44	2.07 2.07	14.77	40.64	0.14	-0.28 -0.28
Pt-3CNC	-2.67	1.48	2.06 2.06	15.11	40.95	0.18	-0.25 -0.25
Pt-4CNC	-2.83	1.51	2.05 2.05	15.60	42.10	0.20	-0.23 -0.23
Pt-5CNC	-2.79	1.51	2.05 2.05	15.33	43.43	0.22	-0.22 -0.22
Pt-6CNC	-2.74	1.50	2.06 2.05	14.91	43.09	0.21	-0.22 -0.21

3. H_2 adsorption and migration

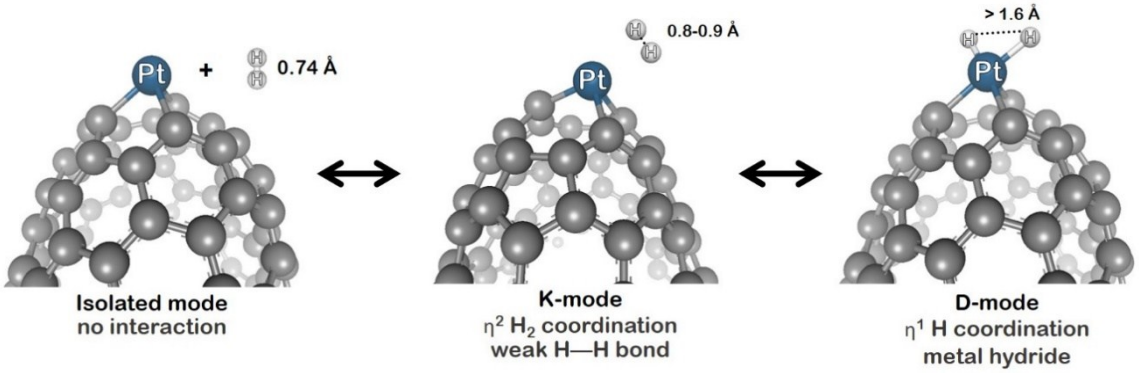

Figure S3. H_2 adsorption modes of Pt-*v*4CNC

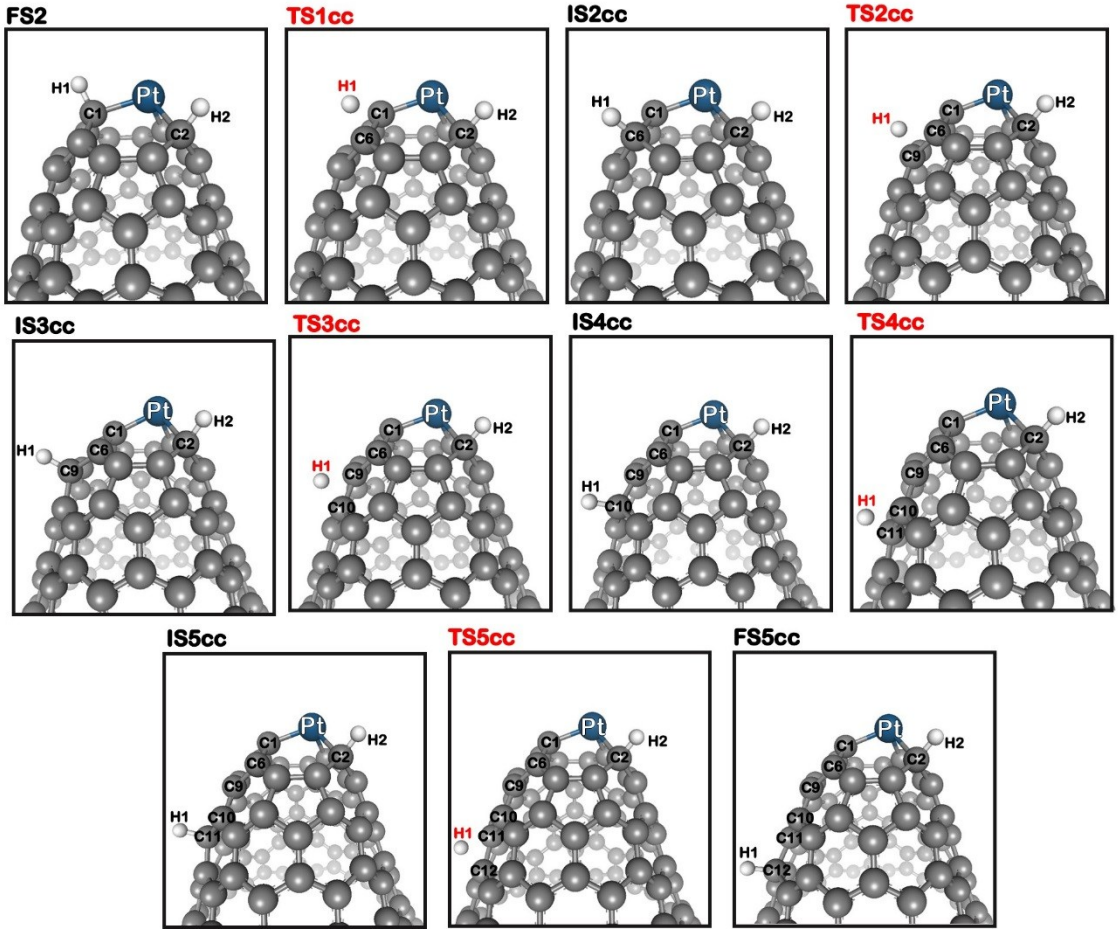

Figure S4. Optimized structures H-diffusion through C-C route for the first adsorbed H_2 molecule

Table S4. Structural and electronic properties of hydrogen spillover mechanism study. $\mathbf{d_i}$ = bond distance between H and initial atom (Å), $\mathbf{d_f}$ = bond distance between H and final atom (Å), $\mathbf{d_{i\text{-}f}}$= bond distance between initial atom and final atom (Å),$\mathbf{Q_{Pt}}$ and $\mathbf{Q_i}$, $\mathbf{Q_f}$, $\mathbf{Q_H}$ are electronic charge on initial atom, final atom and H atom, respectively.

Name	Distance			Charge		
	$\mathbf{d_i}$	$\mathbf{d_f}$	$\mathbf{d_{i\text{-}f}}$	$\mathbf{Q_i}$	$\mathbf{Q_f}$	$\mathbf{Q_H}$
1st H_2 migration						
H_2-diss	1.64(Pt)	2.59(C1)	1.92	0.31(Pt)	-0.19(C1)	0.06
TS1	1.81(Pt)	1.82(C1)	2.00	0.43(Pt)	-0.37(C1)	0.03
IS2	1.63(Pt)	2.58(C2)	1.97	0.42(C1)	-0.26(C1)	0.05
TS2	1.74(Pt)	1.53(C2)	1.99	0.48(Pt)	-0.44(C2)	0.13
FS2	2.36(Pt)	1.11(C2)	2.11	0.46(Pt)	-0.40(C2)	0.19
2nd H_2 migration						
IS3	1.59(Pt)	2.77(C3)	2.05	0.04(Pt)	-0.29(C3)	0.05
TS3	1.62(Pt)	1.61(C3)	2.09	0.05(Pt)	-0.44(C3)	0.15
IS4(A)	1.65(Pt)	3.24(C4)	3.29	0.21(Pt)	0.01(C4)	0.01
IS4(B)	1.10(C1)	2.19(C6)	1.50	-0.33(C1)	0.05(C6)	0.20
TS4A	1.66(Pt)	2.48(C4)	3.16	0.28(Pt)	-0.11(C4)	-0.02
IS5A	1.10(C4)	3.78(C5)	3.42	0.33(C4)	-0.22(C5)	0.15
TS5A	1.31(C4)	1.38(C5)	1.50	-0.16(C4)	-0.19(C5)	0.20
FS5A	2.17(C4)	1.10(C5)	1.53	0.00(C4)	-0.24(C5)	0.16
TS4B	1.31(C1)	1.35(C8)	1.50	-0.34(C1)	-0.15(C8)	0.24
IS5B	1.65(Pt)	2.48(C1)	1.95	0.33(Pt)	-0.23(C1)	0.02
TS5B	1.74(Pt)	1.74(C1)	1.96	0.41(Pt)	-0.34(C1)	0.04

FS5B	2.42(Pt)	1.11(C1)	2.13	0.35(Pt)	-0.36(C1)	0.35
3rd H_2 migration						
IS6	1.09(C1)	2.11(C7)	1.50	-0.25(C1)	0.11(C7)	0.20
TS6	1.41(C1)	1.29(C7)	1.43	-0.19(C1)	-0.11(C7)	0.22
IS7	1.64(Pt)	2.47(C1)	1.85	0.10(Pt)	-0.12(C1)	0.07
TS7	1.72(Pt)	1.76(C1)	1.87	0.21(Pt)	-0.24(C1)	0.07
IS8	1.11(C3)	2.20(C8)	1.53	-0.39(C3)	0.02(C8)	0.18
TS8	1.48(C3)	1.27(C8)	1.49	-0.35(C3)	-0.16(C8)	0.20
IS9	1.65(Pt)	2.90(C3)	1.96	0.28(Pt)	-0.19(C3)	0.02
TS9	1.68(Pt)	2.63(C3)	1.93	0.20(Pt)	-0.23(C3)	-0.02
FS9	2.36(Pt)	1.11(C3)	2.09	0.37(Pt)	-0.34(C3)	0.17

4. Examples of optimized structural

Cartesian Coordinates of Pt-v4CNC

	Coordinates (Angstroms)		
Atom type	X	Y	Z
C	5.30210700	-1.01877300	4.46176800
C	4.07498300	-0.38898500	4.71758900
C	3.84041700	0.84405500	5.27950800
C	2.72279100	1.65510700	5.17468000
C	2.45907600	3.01303000	5.26084800
C	1.42326700	3.72852200	4.70659300
C	1.34818200	5.10595800	4.45148900
C	0.70711800	5.73680800	3.42808600
C	0.82199900	6.96799000	2.76001400
C	0.46812100	7.28527800	1.50089700
C	2.90155700	-1.09573300	4.21621100
C	1.62943700	-0.51556900	4.42231800
C	1.50657800	0.86900900	4.77499200
C	0.29874500	1.55265300	4.41413600
C	0.29572900	2.95028100	4.20576200
C	-0.60156600	3.55466900	3.29308300
C	-0.30364800	4.84431200	2.74968500
C	-0.70760500	5.10462500	1.42001100
C	0.48184200	-1.25737500	4.00096400

C	-0.79311400	-0.61555800	4.01652400
C	-0.85169900	0.81213000	3.99319600
C	-1.87608300	1.44604000	3.22243800
C	-1.62359200	2.74945000	2.69699500
C	-2.14035400	3.09019500	1.41143300
C	-1.90787900	-1.33546800	3.59253900
C	-3.04619500	-0.68602600	3.03570000
C	-2.95368500	0.67133500	2.66425800
C	-3.57365500	1.07601100	1.43061300
C	0.71585200	8.38405000	0.61742100
C	-0.16504700	6.20422100	0.69660100
C	-1.52912600	4.16697800	0.71131000
C	-3.00585500	2.18664800	0.71321100
C	6.77679400	-2.25188800	2.75919600
C	5.60699600	-1.85779000	3.42973300
C	4.37861200	-2.41366200	2.75272700
C	3.08109300	-2.15945000	3.29951000
C	1.92575100	-2.75759500	2.70097800
C	0.63094500	-2.45321400	3.22979500
C	-0.51799500	-3.11191300	2.67364300
C	-1.80712800	-2.64271600	3.02796600
C	-2.98528000	-2.90510700	2.26209400
C	-3.77508600	-1.64837600	2.26906200
C	-4.57383500	-1.18622200	1.24630600
C	8.02465900	-2.93328900	0.61743400
C	6.92131000	-2.70521800	1.49997200
C	5.67487700	-2.83477500	0.69663300
C	4.44988800	-2.88283800	1.42072100
C	3.25821800	-3.24663900	0.71182100
C	2.02667100	-3.36469800	1.41368500
C	0.84662700	-3.78190100	0.71487100
C	-0.39746400	-3.83184600	1.43514100
C	-1.57450500	-4.12235800	0.71303900
C	-2.90017100	-3.73049500	1.14576000
C	-3.79765200	-3.76180800	0.00000000
C	-1.57450500	-4.12235800	-0.71303700
C	0.84662700	-3.78190200	-0.71487000
C	3.25821800	-3.24664000	-0.71182000
C	5.67487700	-2.83477500	-0.69663200
C	-4.36755100	0.13207200	0.72010500
C	-4.57383500	-1.18622200	-1.24630600
C	-4.36755100	0.13207100	-0.72010600
C	-3.57365500	1.07601100	-1.43061400
C	-3.00585500	2.18664800	-0.71321300
C	-2.14035400	3.09019400	-1.41143400
C	-1.52912500	4.16697800	-0.71131200
C	-0.70760400	5.10462400	-1.42001300
C	-0.16504600	6.20422100	-0.69660400
C	0.46812200	7.28527700	-1.50090000
C	0.71585300	8.38405000	-0.61742400

C	-2.90017100	-3.73049500	-1.14575900
C	-2.98527900	-2.90510800	-2.26209300
C	-3.77508600	-1.64837700	-2.26906200
C	-3.04619400	-0.68602700	-3.03570100
C	-2.95368400	0.67133400	-2.66425800
C	-1.87608300	1.44603900	-3.22243900
C	-1.62359200	2.74944900	-2.69699600
C	-0.60156500	3.55466700	-3.29308400
C	-0.30364700	4.84431000	-2.74968700
C	0.70712000	5.73680500	-3.42808800
C	0.82200100	6.96798700	-2.76001600
C	-0.39746400	-3.83184700	-1.43514000
C	-0.51799500	-3.11191400	-2.67364200
C	-1.80712800	-2.64271800	-3.02796600
C	-1.90787900	-1.33546900	-3.59253800
C	2.02667100	-3.36469900	-1.41368300
C	1.92575100	-2.75759600	-2.70097700
C	0.63094600	-2.45321600	-3.22979400
C	0.48184200	-1.25737600	-4.00096300
C	-0.79311300	-0.61556000	-4.01652400
C	-0.85169900	0.81212800	-3.99319600
C	4.44988800	-2.88283900	-1.42072000
C	4.37861200	-2.41366300	-2.75272600
C	3.08109300	-2.15945200	-3.29950900
C	2.90155700	-1.09573400	-4.21621000
C	1.62943700	-0.51557100	-4.42231800
C	1.50657800	0.86900700	-4.77499200
C	0.29874600	1.55265100	-4.41413600
C	0.29573000	2.95027900	-4.20576300
C	6.92131000	-2.70521800	-1.49997100
C	6.77679300	-2.25188700	-2.75919400
C	5.60699600	-1.85779000	-3.42973200
C	5.30210800	-1.01877400	-4.46176800
C	4.07498300	-0.38898800	-4.71758800
C	3.84041700	0.84405200	-5.27950800
C	2.72279200	1.65510500	-5.17467900
C	2.45907800	3.01302800	-5.26084700
C	1.42326800	3.72851900	-4.70659300
C	1.34818500	5.10595600	-4.45149100
C	8.02465900	-2.93328900	-0.61743200
Pt	-5.34204800	-2.54077100	0.00000000

Reference

[1] R.C. Haddon, Comment on the relationship of the pyramidalization angle at a conjugated carbon atom to the σ bond angles, J. Phys. Chem. A (2001) 105(16) 4164-4165.