

Supporting Information

Insertion, Rearrangement and Coupling Processes in the Reactions of the Unsaturated Hydride Complex $[\text{W}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{H})(\mu\text{-PCy}_2)(\text{CO})_2]$ with Isocyanides.

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Table SX. Crystal Data for New Compounds.

compound	2a	5·CH₂Cl₂	6
mol formula	C ₂₉ H ₄₂ NO ₂ PW ₂	C ₃₃ H ₄₄ Cl ₂ NOPW ₂	C ₄₀ H ₄₇ N ₂ O ₄ PW ₂
mol wt	835.29	940.26	1018.47
cryst syst	triclinic	monoclinic	monoclinic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
radiation (λ , Å)	0.71073	0.71073	1.54184
<i>a</i> , Å	9.9462(4)	12.073(2)	10.9476(3)
<i>b</i> , Å	11.5852(4)	13.746(3)	12.7269(3)
<i>c</i> , Å	13.6719(5)	20.141(4)	27.6319(6)
α , deg	105.834(2)	90	90
β , deg	98.692(2)	107.077(3)	90.457(2)
γ , deg	107.361(2)	90	90
<i>V</i> , Å ³	1399.42(10)	3195.1(11)	3849.80(16)
<i>Z</i>	2	4	4
calcd density, gcm ⁻³	1.982	1.955	1.757
absorpt. coeff., mm ⁻¹	8.297	7.439	11.603
temperature, K	100(1)	100(2)	123(1)
θ range (deg)	1.6 to 25.68	1.76 to 26.43	3.2 to 71.86
index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	-12, 11; -14, 13; 0, 16	-15, 14; 0, 17; 0, 25	-13, 12; -15, 15; -33, 30
no. of reflns collected	36110	36841	26206
no. of indep reflns (<i>R</i> _{int})	5307 (0.0989)	6575 (0.0454)	7431 (0.0319)
reflns with <i>I</i> > 2 σ (<i>I</i>)	4137	5682	6702
<i>R</i> indexes [data with <i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> ₁ = 0.0421 w <i>R</i> ₂ = 0.082 ^b	<i>R</i> ₁ = 0.0215 w <i>R</i> ₂ = 0.0435 ^c	<i>R</i> ₁ = 0.0254 w <i>R</i> ₂ = 0.0597 ^d
<i>R</i> indexes (all data) ^a	<i>R</i> ₁ = 0.0613 w <i>R</i> ₂ = 0.0893 ^b	<i>R</i> ₁ = 0.0296 w <i>R</i> ₂ = 0.0461 ^c	<i>R</i> ₁ = 0.0308 w <i>R</i> ₂ = 0.0624 ^d
GOF	1.01	1.047	1.092
no. of restraints/params	0/ 310	0 / 367	0 / 448
$\Delta\rho$ (max, min), e Å ⁻³	1.647, - 1.358	1.144, - 0.92	0.901, - 0.829

^a $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. ^b $a = 0.0382$, $b = 0.0000$. ^c $a = 0.0134$, $b = 5.6119$. ^d $a = 0.0331$, $b = 1.4043$.

Computational Details

All the DFT computations were carried out using the GAUSSIAN09 package,¹ in which the hybrid method B3LYP was used with the Becke three-parameter exchange functional² and the Lee–Yang–Parr correlation functional.³ A accurate numerical integration grid (99,590) was used for all the calculations via the keyword Int=Ultrafine. Effective core potentials and their associated double- ζ LANL2DZ basis set were used for the metal atoms.⁴ The light elements (P, O, C, N and H) were described with the 6-31G* basis.⁵ Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from the X-ray data of compounds **2a** and **7**. Frequency analyses were performed for all the stationary points to ensure that a minimum structure with no imaginary frequencies was achieved. For the unstable intermediate **G** (**IntG**) a persistent low-magnitude imaginary vibrational frequency (*ca.* 4 cm⁻¹) was found; although, this should imply the existence of a minimum of identical or close energy, we did not follow the eigenvector of this imaginary frequency in search of another minimum.

(1) Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(2) Becke, A. D. J. Chem. Phys. 1993, 98, 5648.

(3) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785.

(4) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299.

(5) (a) Hariharan, P. C.; Pople, J. A. Theor. Chim. Acta 1973, 28, 213. (b) Petersson, G. A.; Al-Laham, M. A. J. Chem. Phys. 1991, 94, 6081. (c) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. J. Chem. Phys. 1988, 89, 2193.

Table S1. Cartesian Coordinates for the Optimized Structure of A1.

W	0.94453	-1.10409	-0.09622	H	-3.93462	1.22547	-1.07683
W	0.39693	1.57666	0.00865	H	-2.50126	1.80647	-1.92344
P	-1.32031	-0.17400	0.01606	C	-2.32959	-0.37018	1.61092
N	2.94054	0.03073	0.05602	H	-1.62422	0.02619	2.35467
O	0.86819	-0.98027	3.02022	C	-3.60798	0.49053	1.69141
O	0.86021	1.02758	-3.03079	H	-3.38131	1.53365	1.44251
C	0.90372	-0.94076	1.84538	H	-4.34085	0.14412	0.95069
C	0.69711	1.14059	-1.86803	C	-4.25001	0.41825	3.08902
C	2.46535	1.23292	0.16213	H	-3.56678	0.86998	3.82349
C	1.40236	-2.58092	-1.95526	H	-5.16971	1.01778	3.10706
H	1.67789	-2.19318	-2.92726	C	-4.54624	-1.03087	3.49987
C	2.29468	-3.01629	-0.93978	H	-5.31534	-1.44628	2.83124
H	3.37087	-3.00124	-1.00595	H	-4.96501	-1.06110	4.51396
C	1.54925	-3.44998	0.18181	C	-3.28057	-1.89560	3.41792
H	1.95592	-3.83055	1.10932	H	-3.51371	-2.93885	3.66842
C	0.16116	-3.29381	-0.12657	H	-2.55441	-1.54903	4.16741
H	-0.66606	-3.61272	0.48956	C	-2.62900	-1.82764	2.02480
C	0.07349	-2.75708	-1.45909	H	-3.29630	-2.29856	1.29035
H	-0.83156	-2.60476	-2.02681	H	-1.69795	-2.40290	2.03007
C	-0.38448	3.74692	-0.67486	H	3.17570	2.05199	0.34310
H	-0.68097	3.94036	-1.69709				
C	-1.24401	3.35622	0.38400				
H	-2.30707	3.18135	0.30025				
C	-0.46299	3.21061	1.56667				
H	-0.83271	2.91920	2.54140				
C	0.89010	3.52263	1.24189				
H	1.72050	3.53996	1.93482				
C	0.94275	3.85751	-0.15176				
H	1.81697	4.17655	-0.70246				
C	4.40084	-0.26693	0.19993				
C	4.96844	-0.62344	-1.18974				
H	4.90876	0.24525	-1.85479				
H	4.41417	-1.43442	-1.66583				
H	6.01998	-0.92530	-1.11300				
C	5.20930	0.93087	0.74209				
H	5.21535	1.78185	0.05324				
H	6.24996	0.61772	0.87833				
H	4.83163	1.26989	1.71303				
C	4.57757	-1.42345	1.20238				
H	4.18794	-1.13614	2.18495				
H	5.63999	-1.67052	1.31212				
H	4.05082	-2.32607	0.89113				
C	-2.45648	-0.32043	-1.49372				
H	-1.72486	-0.49411	-2.29593				
C	-3.43091	-1.51855	-1.47370				
H	-4.17480	-1.37478	-0.67917				
H	-2.90270	-2.44895	-1.23283				
C	-4.16862	-1.66648	-2.81722				
H	-3.44070	-1.91268	-3.60472				
H	-4.87004	-2.50948	-2.76577				
C	-4.90892	-0.37641	-3.19810				
H	-5.38929	-0.48852	-4.17850				
H	-5.71662	-0.19660	-2.47268				
C	-3.95577	0.82737	-3.20416				
H	-4.50801	1.74987	-3.42671				
H	-3.21872	0.70235	-4.01091				
C	-3.21144	0.97493	-1.86470				

G (a.u.): -1812.066734

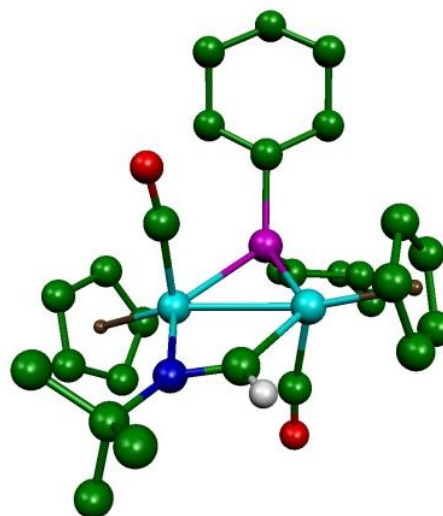


Table S2. Cartesian Coordinates for the Optimized Structure of B1

W	0.83603	-1.41974	-0.00828	H	-2.30592	1.85408	-2.00151
W	0.67133	1.47690	-0.19731	C	-2.15073	0.02925	1.71656
P	-1.23751	-0.04899	0.05987	H	-1.32633	0.32773	2.38086
N	2.33391	0.13283	0.33163	C	-3.24723	1.11050	1.82353
O	0.74751	-2.65331	2.84634	H	-2.86979	2.08008	1.47860
O	0.87567	0.89466	-3.27163	H	-4.08894	0.85068	1.16692
C	0.77204	-2.15579	1.77902	C	-3.76928	1.23904	3.26681
C	0.80015	1.00701	-2.10275	H	-2.95636	1.60553	3.91166
C	1.34376	0.15746	1.29889	H	-4.56569	1.99376	3.30929
C	0.81363	-2.18235	-2.35441	C	-4.27549	-0.10569	3.80798
H	0.69852	-1.50292	-3.18560	H	-5.16618	-0.41089	3.23821
C	2.04282	-2.55130	-1.73900	H	-4.59526	0.00134	4.85253
H	3.02239	-2.21493	-2.04795	C	-3.19885	-1.19362	3.68505
C	1.77179	-3.46652	-0.67785	H	-3.59240	-2.15981	4.02642
H	2.49958	-3.98175	-0.06702	H	-2.35602	-0.94974	4.34821
C	0.34415	-3.63982	-0.62197	C	-2.67996	-1.32421	2.24167
H	-0.19138	-4.29370	0.05236	H	-3.49667	-1.68226	1.60201
C	-0.23255	-2.84220	-1.65193	H	-1.88594	-2.07508	2.19959
H	-1.28595	-2.77974	-1.87956	H	1.50114	0.27551	2.36557
C	0.25856	3.72994	-0.98262				
H	0.06924	3.92716	-2.02980				
C	-0.72405	3.45718	-0.00024				
H	-1.79003	3.41871	-0.17238				
C	-0.06309	3.22217	1.24301				
H	-0.54162	3.02039	2.19106				
C	1.34284	3.36114	1.01995				
H	2.10958	3.29311	1.77747				
C	1.54441	3.67305	-0.36402				
H	2.48978	3.87161	-0.85024				
C	3.80545	0.16393	0.55383				
C	4.19783	1.38685	1.40410				
H	3.68123	1.38716	2.37030				
H	3.96652	2.31910	0.88109				
H	5.27540	1.37264	1.60229				
C	4.25133	-1.11734	1.28105				
H	3.74888	-1.21962	2.24879				
H	5.33289	-1.09200	1.45815				
H	4.02019	-2.00691	0.68848				
C	4.49104	0.27119	-0.81553				
H	4.28013	-0.60467	-1.43516				
H	5.57774	0.34652	-0.69461				
H	4.13806	1.15722	-1.35368				
C	-2.47963	-0.21269	-1.35800				
H	-1.83300	-0.54945	-2.18017				
C	-3.58635	-1.26972	-1.15800				
H	-4.25714	-0.94762	-0.35093				
H	-3.15929	-2.22748	-0.83694				
C	-4.41836	-1.46099	-2.43917				
H	-3.77552	-1.87109	-3.23259				
H	-5.20815	-2.20276	-2.26284				
C	-5.02695	-0.13414	-2.91529				
H	-5.57636	-0.28161	-3.85382				
H	-5.76242	0.21119	-2.17324				
C	-3.94414	0.93989	-3.09330				
H	-4.39987	1.89686	-3.37942				
H	-3.27966	0.65122	-3.92095				
C	-3.10181	1.12477	-1.81790				
H	-3.73847	1.53505	-1.02195				

G (a.u.): -1812.073734

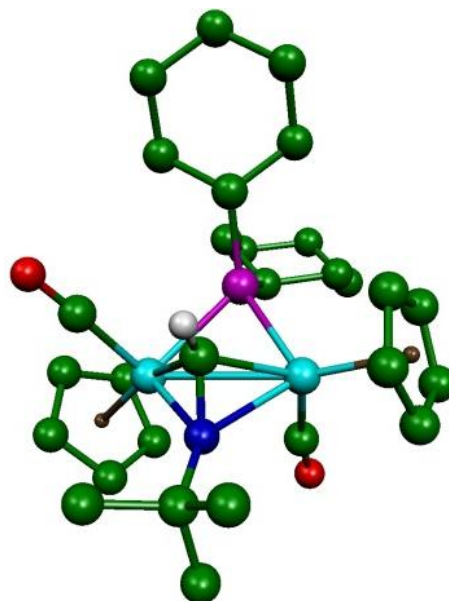


Table S3. Cartesian Coordinates for the Optimized Structure of C1

W	0.73732	-1.20948	-0.08870	H	-2.51673	2.06361	-1.78965
W	0.50167	1.46268	-0.01750	C	-2.42189	-0.20567	1.61829
P	-1.40829	-0.04748	0.02675	H	-1.67765	0.09593	2.36964
N	3.46537	0.60921	-0.02964	C	-3.61896	0.75862	1.74753
O	0.86444	-1.17315	3.04365	H	-3.30654	1.78614	1.52447
O	0.46593	1.32453	-3.14789	H	-4.38801	0.49832	1.00769
C	0.80152	-1.14359	1.87284	C	-4.24509	0.69284	3.15269
C	0.46119	1.33302	-1.97422	H	-3.51405	1.05667	3.89004
C	2.17662	0.27098	-0.06256	H	-5.10901	1.36833	3.20918
C	0.20483	-2.72654	-1.82174	C	-4.66152	-0.73929	3.51843
H	-0.39013	-2.40646	-2.66667	H	-5.47712	-1.05882	2.85220
C	1.63214	-2.64256	-1.71578	H	-5.06291	-0.77003	4.53965
H	2.29797	-2.26090	-2.47736	C	-3.48208	-1.71272	3.37759
C	2.01083	-3.21662	-0.46186	H	-3.80769	-2.73916	3.59264
H	3.01653	-3.34771	-0.09077	H	-2.71503	-1.46488	4.12580
C	0.81998	-3.65030	0.19295	C	-2.85167	-1.64576	1.97500
H	0.77104	-4.11094	1.17151	H	-3.57775	-2.01284	1.23708
C	-0.28662	-3.36277	-0.64223	H	-1.98308	-2.31168	1.92497
H	-1.32281	-3.56573	-0.41230	H	3.66471	1.60505	-0.05791
C	0.09671	3.83798	-0.31102				
H	-0.30296	4.23898	-1.23320				
C	-0.65901	3.46349	0.82689				
H	-1.73571	3.50751	0.91398				
C	0.23990	2.97734	1.81758				
H	-0.03232	2.61572	2.80084				
C	1.57084	3.07028	1.29425				
H	2.47797	2.81989	1.82883				
C	1.48561	3.60684	-0.02939				
H	2.31203	3.85807	-0.68078				
C	4.70944	-0.20743	0.09416				
C	5.86144	0.79850	0.26162				
H	5.71821	1.41752	1.15577				
H	5.94047	1.45983	-0.61065				
H	6.81492	0.27168	0.36812				
C	4.63010	-1.10472	1.33951				
H	4.55519	-0.49627	2.24756				
H	5.52665	-1.73107	1.41779				
H	3.75048	-1.75033	1.30166				
C	4.94312	-1.03156	-1.18266				
H	4.13102	-1.74049	-1.34539				
H	5.88118	-1.59476	-1.11062				
H	5.00172	-0.37607	-2.05880				
C	-2.55249	-0.08618	-1.48096				
H	-1.82721	-0.24988	-2.29091				
C	-3.56728	-1.24715	-1.52916				
H	-4.30786	-1.12705	-0.72682				
H	-3.06384	-2.20457	-1.34791				
C	-4.30669	-1.29244	-2.87928				
H	-3.58517	-1.52240	-3.67754				
H	-5.04030	-2.10950	-2.87645				
C	-4.99566	0.04389	-3.19171				
H	-5.47717	0.00234	-4.17729				
H	-5.79827	0.21583	-2.45861				
C	-3.99748	1.20943	-3.13198				
H	-4.51396	2.16251	-3.30735				
H	-3.26122	1.09915	-3.94160				
C	-3.25638	1.25532	-1.78383				
H	-3.97548	1.48841	-0.98722				

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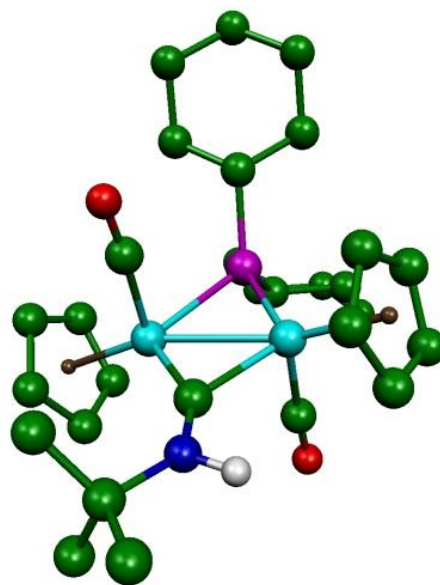


Table S4. Cartesian Coordinates for the Optimized Structure of IntG

W	-0.60422	1.27329	-0.08806	H	2.33661	-2.23018	-1.82416
W	-0.60166	-1.28059	0.03816	C	2.51396	0.09609	1.54727
P	1.46401	-0.00309	-0.02056	H	1.76291	-0.13454	2.31587
N	-3.36877	0.01900	0.27038	C	3.63665	-0.95560	1.66427
O	-0.93183	0.82403	2.97936	H	3.24206	-1.96006	1.46788
O	-0.35023	-1.51564	-3.07278	H	4.40502	-0.76637	0.90272
C	-0.81229	0.91117	1.81139	C	4.29782	-0.91274	3.05406
C	-0.43177	-1.38448	-1.91029	H	3.55940	-1.20879	3.81375
C	-2.42397	0.00010	-0.61753	H	5.10963	-1.65021	3.10285
C	-0.31417	3.02360	-1.73313	C	4.82878	0.49007	3.38339
H	0.02663	2.80288	-2.73676	H	5.64971	0.73657	2.69322
C	-1.66790	3.00461	-1.28237	H	5.25551	0.50723	4.39435
H	-2.53448	2.79183	-1.89404	C	3.72245	1.54718	3.25280
C	-1.68147	3.35437	0.10471	H	4.12871	2.54949	3.44162
H	-2.55639	3.47060	0.72868	H	2.95747	1.36947	4.02264
C	-0.32038	3.58959	0.50246	C	3.05616	1.50727	1.86584
H	0.00925	3.88807	1.48848	H	3.78986	1.80756	1.10603
C	0.51012	3.38854	-0.62969	H	2.23699	2.23369	1.82322
H	1.58702	3.48169	-0.64799	H	-2.69004	0.00289	-1.68447
C	-0.55265	-3.73704	-0.03179				
H	-0.29401	-4.27610	-0.93422				
C	0.35150	-3.34380	0.98461				
H	1.41599	-3.53344	0.99210				
C	-0.38274	-2.62915	1.97880				
H	0.01959	-2.20737	2.89044				
C	-1.75608	-2.59579	1.57676				
H	-2.56797	-2.13944	2.12499				
C	-1.85970	-3.27476	0.32006				
H	-2.76716	-3.44942	-0.24104				
C	-4.80283	0.05032	-0.10573				
C	-5.37183	1.33042	0.54149				
H	-4.94441	2.22519	0.07414				
H	-5.13299	1.35563	1.60911				
H	-6.46109	1.37100	0.42241				
C	-5.11992	0.04089	-1.61123				
H	-4.70289	0.91562	-2.12376				
H	-6.20549	0.05975	-1.75959				
H	-4.73254	-0.85779	-2.10483				
C	-5.44151	-1.18252	0.56649				
H	-5.05725	-2.10993	0.12602				
H	-6.53024	-1.17094	0.43745				
H	-5.21762	-1.19224	1.63793				
C	2.56793	-0.08469	-1.55139				
H	1.84298	0.13613	-2.34762				
C	3.67816	0.98306	-1.63351				
H	4.42437	0.80733	-0.84713				
H	3.26255	1.98223	-1.45463				
C	4.38314	0.94749	-3.00202				
H	3.66415	1.23302	-3.78409				
H	5.18584	1.69608	-3.02661				
C	4.94296	-0.44804	-3.31407				
H	5.39904	-0.45938	-4.31226				
H	5.74722	-0.68202	-2.60031				
C	3.84910	-1.52143	-3.21397				
H	4.27608	-2.51775	-3.38796				
H	3.10325	-1.35822	-4.00529				
C	3.14221	-1.48844	-1.84748				
H	3.85849	-1.77119	-1.06481				

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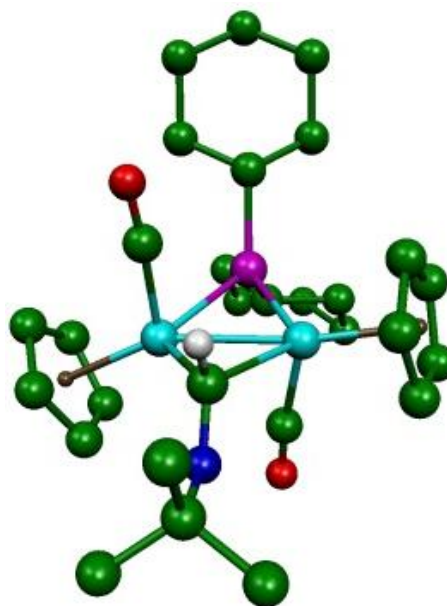


Table S5. Cartesian Coordinates for the Optimized Structure of A2

W	-0.68750	-0.95420	0.26334	H	3.68522	-3.67675	-2.99604
W	0.07334	1.64943	-0.16393	H	2.85320	-2.30973	-3.73125
P	1.64820	-0.23123	0.11326	C	2.86501	-2.25805	-1.56966
N	-2.51987	0.27483	-0.02342	H	3.48091	-2.65580	-0.75210
O	-0.53840	-1.22909	-2.83938	H	1.89132	-2.75477	-1.50821
O	-0.42483	1.54794	2.91890	H	-2.73718	2.25299	-0.50885
C	-0.59174	-1.04077	-1.67966	C	-3.91877	0.02879	-0.06471
C	-0.25451	1.49343	1.75363	C	-4.80031	0.78412	0.71587
C	-2.01589	1.45489	-0.26011	C	-6.18055	0.56200	0.66803
C	-1.21776	-2.12846	2.32322	H	-6.83352	1.16329	1.29053
H	-1.29817	-1.59534	3.26197	C	-6.69549	-0.43560	-0.16645
C	-2.27842	-2.39531	1.42279	O	-8.02132	-0.74420	-0.28919
H	-3.30569	-2.08339	1.55168	C	-5.81603	-1.20148	-0.94855
C	-1.75983	-3.07594	0.28628	H	-6.23284	-1.96530	-1.59788
H	-2.33428	-3.43944	-0.55420	C	-4.44763	-0.97353	-0.89653
C	-0.34447	-3.23348	0.47763	H	-4.40044	1.54451	1.38081
H	0.32880	-3.78367	-0.16348	H	-3.77316	-1.55367	-1.51851
C	-0.01584	-2.63590	1.74226	C	-8.95442	0.00347	0.47111
H	0.95534	-2.63686	2.21337	H	-9.93806	-0.39717	0.21853
C	1.04320	3.81183	0.21460	H	-8.92205	1.07135	0.21557
H	1.37313	4.11591	1.19890	H	-8.78330	-0.11191	1.55011
C	1.84844	3.21004	-0.78754				
H	2.89450	2.95809	-0.68764				
C	1.03803	2.97812	-1.93625				
H	1.36428	2.52674	-2.86452				
C	-0.27774	3.44623	-1.64899				
H	-1.11585	3.44125	-2.33266				
C	-0.27861	3.96585	-0.31203				
H	-1.11362	4.43037	0.19419				
C	2.72488	-0.25527	1.67349				
H	1.95908	-0.27957	2.46250				
C	3.61825	-1.50250	1.84788				
H	4.39633	-1.51035	1.07348				
H	3.03880	-2.42273	1.70709				
C	4.29913	-1.51673	3.22893				
H	3.53011	-1.60916	4.01029				
H	4.94278	-2.40173	3.31743				
C	5.11310	-0.23701	3.46820				
H	5.55163	-0.24733	4.47424				
H	5.95509	-0.20770	2.76029				
C	4.24534	1.01509	3.27603				
H	4.85264	1.92189	3.39618				
H	3.47646	1.04781	4.06179				
C	3.55457	1.02744	1.90042				
H	4.31683	1.12175	1.11465				
H	2.90205	1.90325	1.81942				
C	2.67664	-0.73476	-1.39700				
H	2.02266	-0.40500	-2.21635				
C	4.02283	0.00090	-1.56309				
H	3.87765	1.08471	-1.48561				
H	4.70787	-0.28150	-0.75261				
C	4.68634	-0.33842	-2.91072				
H	4.05932	0.04794	-3.72793				
H	5.65358	0.17535	-2.98882				
C	4.86810	-1.85272	-3.08685				
H	5.58672	-2.22001	-2.33861				
H	5.30282	-2.07150	-4.07062				
C	3.53370	-2.59233	-2.91502				

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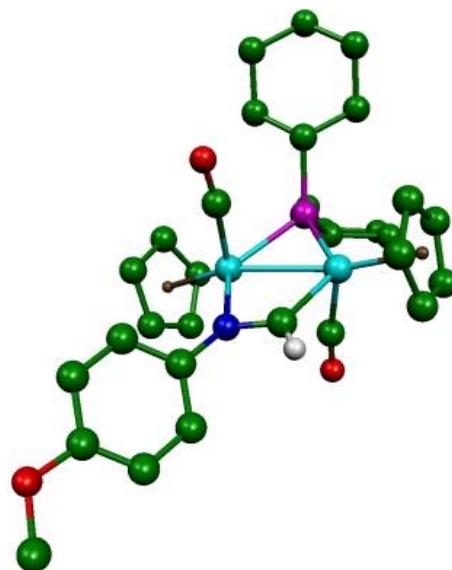


Table S6. Cartesian Coordinates for the Optimized Structure of B2

W	0.52272	-1.20087	-0.54484	H	-3.68732	-3.70398	2.94818
W	0.31049	1.52372	0.41830	H	-2.51180	-2.64616	3.71978
P	-1.58305	-0.04440	0.14015	C	-2.87894	-2.16879	1.64186
N	1.98643	0.15306	0.30911	H	-3.69270	-2.29123	0.91503
O	0.59967	-3.49345	1.56265	H	-2.04659	-2.78854	1.29779
O	0.11821	2.24407	-2.62571	H	1.29874	-0.56467	2.27102
C	0.55325	-2.60897	0.78881	C	3.39941	0.11748	0.37475
C	0.20035	1.87336	-1.51147	C	4.14619	0.99841	-0.41341
C	1.05787	-0.26424	1.25779	C	5.54390	0.98357	-0.38402
C	0.53335	-0.92274	-2.97957	H	6.09173	1.68310	-1.00532
H	0.37628	0.03245	-3.45726	C	6.21340	0.07907	0.44799
C	1.78390	-1.44387	-2.53587	O	7.57257	-0.01954	0.56269
H	2.74033	-0.94249	-2.61451	C	5.46779	-0.80739	1.24110
C	1.56847	-2.73380	-1.96560	H	6.00141	-1.50471	1.87964
H	2.32783	-3.41043	-1.59981	C	4.07986	-0.79212	1.20400
C	0.15212	-2.99303	-2.02585	H	3.62114	1.70683	-1.04831
H	-0.34296	-3.89719	-1.69916	H	3.51424	-1.49659	1.80672
C	-0.47270	-1.87199	-2.64709	C	8.37292	0.84579	-0.22294
H	-1.52845	-1.77536	-2.85438	H	8.20314	0.69134	-1.29732
C	-0.48853	3.68516	0.82755	H	9.40888	0.59798	0.01644
H	-1.20462	4.17177	0.18030	H	8.18854	1.90127	0.02015
C	-0.79103	2.93302	2.00410				
H	-1.78050	2.72324	2.38307				
C	0.43193	2.54176	2.61566				
H	0.53292	1.96242	3.52320				
C	1.49979	3.03161	1.81034				
H	2.55491	2.87239	1.99315				
C	0.94476	3.74905	0.70694				
H	1.49924	4.29061	-0.04674				
C	-2.86150	0.33426	-1.19696				
H	-2.22643	0.41974	-2.08978				
C	-3.90483	-0.77136	-1.46281				
H	-4.56617	-0.86965	-0.59191				
H	-3.41702	-1.74560	-1.58926				
C	-4.76406	-0.44174	-2.69723				
H	-4.12483	-0.43532	-3.59295				
H	-5.51137	-1.23078	-2.85272				
C	-5.45066	0.92470	-2.55584				
H	-6.01820	1.16125	-3.46495				
H	-6.18152	0.87657	-1.73462				
C	-4.42924	2.03286	-2.25987				
H	-4.94185	2.99150	-2.10609				
H	-3.77365	2.16585	-3.13289				
C	-3.56419	1.70043	-1.03090				
H	-4.19978	1.68872	-0.13558				
H	-2.81229	2.48197	-0.87875				
C	-2.44449	-0.68704	1.69885				
H	-1.62195	-0.61990	2.42674				
C	-3.60616	0.18170	2.22621				
H	-3.31139	1.23584	2.28099				
H	-4.45070	0.13202	1.52554				
C	-4.08404	-0.30232	3.60758				
H	-3.27246	-0.16453	4.33760				
H	-4.92226	0.31837	3.95085				
C	-4.49189	-1.78232	3.57551				
H	-5.38341	-1.89586	2.94042				
H	-4.77971	-2.11929	4.57971				
C	-3.36000	-2.65866	3.01968				

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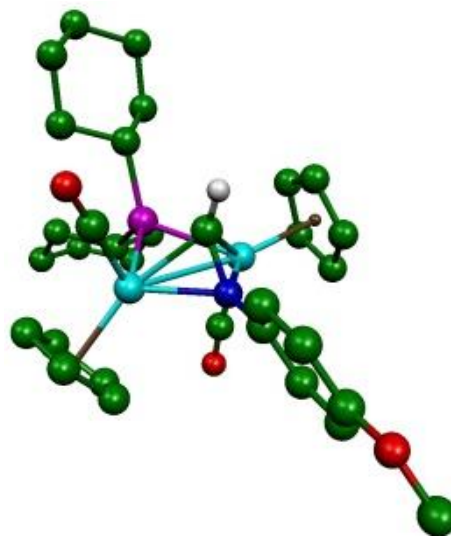


Table S7. Cartesian Coordinates for the Optimized Structure of C2

W	-0.58521	-0.96762	0.35298	H	3.72133	-3.81221	-2.80241
W	0.09025	1.58998	-0.16352	H	2.84228	-2.50609	-3.59195
P	1.72737	-0.19869	0.13864	C	2.93039	-2.31478	-1.43914
N	-2.99703	1.12851	-0.03025	H	3.58553	-2.64595	-0.62255
O	-0.65562	-1.54760	-2.72517	H	1.96957	-2.82271	-1.30038
O	0.08506	2.02417	2.94170	H	-3.14182	2.13384	-0.06766
C	-0.59196	-1.29906	-1.58036	C	-4.20683	0.37019	-0.02089
C	0.09884	1.81555	1.78745	C	-5.27201	0.77557	0.78490
C	-1.72993	0.69102	0.02269	C	-6.48715	0.08311	0.77563
C	-2.18259	-1.94046	1.80091	H	-7.29396	0.42233	1.41509
H	-3.07131	-1.39377	2.08303	C	-6.63861	-1.03891	-0.04681
C	-2.04644	-2.79183	0.66389	O	-7.77232	-1.79500	-0.13336
H	-2.82382	-3.02805	-0.04782	C	-5.57156	-1.44312	-0.86548
C	-0.71515	-3.33791	0.68400	H	-5.71505	-2.30118	-1.51506
H	-0.30410	-4.03874	-0.03008	C	-4.37349	-0.74097	-0.86127
C	-0.04915	-2.82931	1.83119	H	-5.15324	1.63836	1.43624
H	0.96626	-3.05012	2.12766	H	-3.55902	-1.03734	-1.51318
C	-0.94653	-1.96364	2.51688	C	-8.88361	-1.43037	0.66747
H	-0.72527	-1.40622	3.41869	H	-9.66641	-2.15757	0.44394
C	0.88392	3.87825	-0.28256	H	-9.24546	-0.42248	0.42287
H	1.34670	4.36760	0.56441	H	-8.64290	-1.47549	1.73823
C	1.56460	3.18783	-1.31551				
H	2.63337	3.03910	-1.38028				
C	0.59464	2.68765	-2.22920				
H	0.80082	2.11581	-3.12490				
C	-0.70149	3.09101	-1.76841				
H	-1.63893	2.90460	-2.27588				
C	-0.52489	3.83270	-0.55832				
H	-1.29708	4.32946	0.01351				
C	2.83784	-0.14297	1.67187				
H	2.08855	-0.08724	2.47506				
C	3.69643	-1.39858	1.92907				
H	4.46006	-1.49282	1.14532				
H	3.08147	-2.30491	1.87157				
C	4.40169	-1.32648	3.29592				
H	3.64393	-1.33565	4.09358				
H	5.02263	-2.21998	3.44396				
C	5.25481	-0.05595	3.42323				
H	5.71093	-0.00192	4.42023				
H	6.08466	-0.10570	2.70212				
C	4.41975	1.20316	3.14764				
H	5.05510	2.09787	3.18924				
H	3.66491	1.31892	3.93921				
C	3.70733	1.12876	1.78531				
H	4.45905	1.13802	0.98441				
H	3.08055	2.01568	1.64153				
C	2.72312	-0.78619	-1.36014				
H	2.04175	-0.51738	-2.18043				
C	4.05451	-0.04918	-1.61277				
H	3.89978	1.03647	-1.58914				
H	4.76739	-0.28030	-0.80969				
C	4.67745	-0.46145	-2.95930				
H	4.01870	-0.13138	-3.77639				
H	5.63577	0.05542	-3.10207				
C	4.87158	-1.98214	-3.05047				
H	5.62158	-2.29486	-2.30826				
H	5.27373	-2.25586	-4.03452				
C	3.55507	-2.72693	-2.78398				

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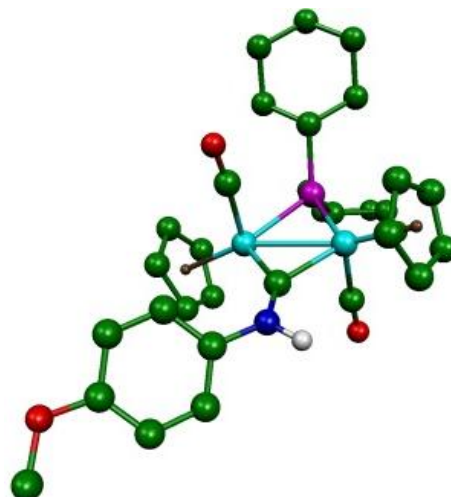


Table S8. Cartesian Coordinates for the Optimized Structure of A3

W	-0.68417	-1.01071	0.09102	H	3.95568	-3.76290	-2.73865
W	0.03843	1.60590	-0.33187	H	3.13797	-2.45467	-3.58878
P	1.64554	-0.23824	0.07502	C	3.01471	-2.30216	-1.43425
N	-2.53775	0.22413	-0.05316	H	3.59338	-2.63923	-0.56401
O	-0.46166	-0.87077	-3.00620	H	2.05582	-2.82878	-1.40259
O	-0.33387	1.69773	2.76847	H	-2.79528	2.21891	-0.44625
C	-0.53846	-0.81641	-1.82879	C	-3.94115	-0.03030	0.07759
C	-0.21166	1.57936	1.60313	C	-4.55392	0.13168	1.33886
C	-2.05828	1.40814	-0.30897	C	-5.91847	-0.15830	1.46214
C	-0.94601	-2.58535	1.94642	H	-6.39678	-0.03864	2.43149
H	-0.80860	-2.28325	2.97704	C	-6.66413	-0.58806	0.36635
C	-2.15782	-2.53058	1.21353	H	-7.72185	-0.81080	0.47885
H	-3.11260	-2.19054	1.58942	C	-6.04869	-0.72198	-0.87654
C	-1.90757	-2.98721	-0.12015	H	-6.63063	-1.04174	-1.73783
H	-2.64692	-3.11683	-0.89746	C	-4.68597	-0.44625	-1.04549
C	-0.51338	-3.32166	-0.20502	C	-3.76973	0.62828	2.53111
H	-0.01413	-3.75182	-1.06158	H	-3.44410	1.66665	2.39971
C	0.07208	-3.06187	1.07090	H	-2.85655	0.04660	2.69664
H	1.10453	-3.23031	1.33746	H	-4.37731	0.58104	3.44034
C	1.01834	3.78724	-0.14119	C	-4.05165	-0.56224	-2.41142
H	1.39747	4.15490	0.80283	H	-3.67030	0.40424	-2.76173
C	1.77298	3.12255	-1.14298	H	-4.78009	-0.92093	-3.14541
H	2.82374	2.87875	-1.08085	H	-3.19595	-1.24380	-2.41336
C	0.90737	2.81887	-2.23336				
H	1.18575	2.30659	-3.14536				
C	-0.39351	3.30394	-1.90999				
H	-1.26406	3.25708	-2.54993				
C	-0.32935	3.90529	-0.60861				
H	-1.13958	4.40140	-0.09201				
C	2.62157	-0.18694	1.70036				
H	1.80599	-0.18881	2.43781				
C	3.51830	-1.40668	2.00024				
H	4.34769	-1.44544	1.28162				
H	2.95886	-2.34147	1.87832				
C	4.10262	-1.33607	3.42343				
H	3.28200	-1.40226	4.15305				
H	4.75136	-2.20361	3.60232				
C	4.87888	-0.03126	3.65129				
H	5.24609	0.01729	4.68443				
H	5.76783	-0.02229	3.00266				
C	4.00774	1.19280	3.33464				
H	4.59146	2.11577	3.44843				
H	3.18467	1.25174	4.06155				
C	3.41588	1.12078	1.91579				
H	4.23045	1.18540	1.18126				
H	2.76085	1.98082	1.74117				
C	2.77296	-0.77878	-1.34860				
H	2.16313	-0.50425	-2.22050				
C	4.11198	-0.01982	-1.46148				
H	3.94241	1.06230	-1.43760				
H	4.74844	-0.25507	-0.59803				
C	4.86684	-0.39827	-2.74913				
H	4.28332	-0.06415	-3.61972				
H	5.82436	0.13744	-2.78975				
C	5.09641	-1.91314	-2.84563				
H	5.77702	-2.22776	-2.04016				
H	5.59482	-2.16327	-3.79090				
C	3.77268	-2.68046	-2.71953				

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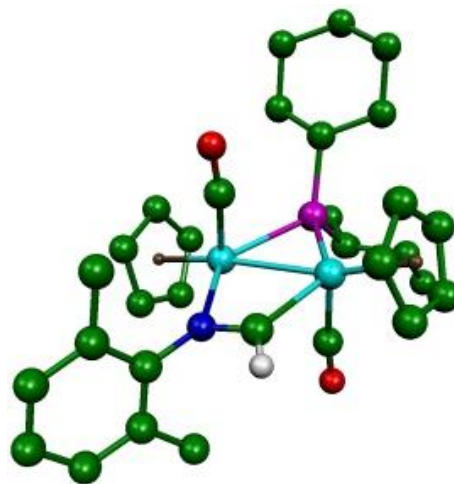


Table S9. Cartesian Coordinates for the Optimized Structure of B3

W	0.47293	-1.26760	-0.63665	H	-3.81648	-3.68764	2.81966
W	0.38051	1.44250	0.38374	H	-2.56655	-2.72199	3.59487
P	-1.57779	-0.03704	0.09773	C	-2.96254	-2.14940	1.54669
N	2.03619	-0.01991	0.26473	H	-3.80242	-2.19738	0.84162
O	0.36083	-3.59270	1.42916	H	-2.17872	-2.80284	1.15570
O	0.09092	2.17288	-2.64745	H	1.19475	-0.71006	2.19461
C	0.39336	-2.69107	0.67319	C	3.45847	-0.09802	0.33156
C	0.20922	1.80571	-1.53495	C	4.20104	0.64394	-0.62697
C	1.04522	-0.37866	1.17914	C	5.59872	0.60638	-0.59192
C	0.62410	-0.97802	-3.06635	H	6.15160	1.18328	-1.32949
H	0.65140	-0.00505	-3.53401	C	6.28353	-0.14756	0.35489
C	1.74683	-1.72671	-2.60758	H	7.36967	-0.16776	0.36819
H	2.78227	-1.41614	-2.66011	C	5.55115	-0.88462	1.27842
C	1.28671	-2.95518	-2.05699	H	6.07190	-1.48988	2.01667
H	1.90345	-3.75754	-1.67725	C	4.14972	-0.88448	1.29362
C	-0.15160	-2.95246	-2.14245	C	3.53934	1.48694	-1.68929
H	-0.80816	-3.75874	-1.84637	H	2.95632	2.30629	-1.25659
C	-0.54709	-1.72690	-2.76276	H	2.83779	0.91395	-2.30169
H	-1.56031	-1.44120	-3.00286	H	4.29506	1.91682	-2.35457
C	-0.36702	3.60576	0.86475	C	3.48077	-1.74952	2.34210
H	-1.10474	4.11299	0.25905	H	3.01972	-1.15636	3.14200
C	-0.62623	2.83146	2.03842	H	4.22930	-2.39068	2.81798
H	-1.59950	2.62511	2.45853	H	2.70837	-2.40142	1.92659
C	0.61945	2.42151	2.59045				
H	0.75479	1.82449	3.48198				
C	1.65500	2.92051	1.75093				
H	2.71567	2.74796	1.88441				
C	1.05978	3.66097	0.68554				
H	1.58657	4.21283	-0.08063				
C	-2.86045	0.43203	-1.20714				
H	-2.23327	0.54422	-2.10197				
C	-3.93115	-0.63741	-1.50843				
H	-4.58534	-0.75761	-0.63504				
H	-3.46667	-1.61589	-1.68201				
C	-4.79594	-0.23615	-2.71749				
H	-4.16702	-0.20559	-3.62000				
H	-5.56268	-1.00095	-2.89724				
C	-5.44920	1.13800	-2.50937				
H	-6.02143	1.42623	-3.40040				
H	-6.17153	1.07118	-1.68193				
C	-4.39899	2.20894	-2.17949				
H	-4.88718	3.17180	-1.97969				
H	-3.74985	2.36322	-3.05374				
C	-3.52871	1.80593	-0.97531				
H	-4.15433	1.77324	-0.07376				
H	-2.75688	2.56317	-0.80206				
C	-2.44465	-0.69665	1.64682				
H	-1.60702	-0.70120	2.36050				
C	-3.54898	0.21042	2.23041				
H	-3.20221	1.24672	2.31190				
H	-4.41050	0.22437	1.54910				
C	-4.01816	-0.29596	3.60681				
H	-3.18351	-0.22389	4.32008				
H	-4.81515	0.35410	3.99131				
C	-4.50206	-1.75152	3.53662				
H	-5.41483	-1.79748	2.92366				
H	-4.78002	-2.10847	4.53665				
C	-3.43250	-2.66417	2.91930				

G (a.u.): -1964.474314



Table S10. Cartesian Coordinates for the Optimized Structure of C3

W	-0.58196	-1.01437	0.10008	H	4.02102	-3.72942	-2.72541
W	0.06553	1.56244	-0.33685	H	3.20574	-2.41856	-3.57348
P	1.72125	-0.18827	0.07847	C	3.08708	-2.26382	-1.41905
N	-3.02069	1.05534	-0.26912	H	3.66599	-2.60267	-0.54931
O	-0.39132	-1.34394	-3.00778	H	2.12371	-2.78444	-1.38100
O	-0.17527	2.02531	2.75358	H	-3.17693	2.05966	-0.31803
C	-0.43339	-1.17840	-1.84556	C	-4.20798	0.27302	-0.03622
C	-0.06332	1.81032	1.60529	C	-4.83680	0.36625	1.22022
C	-1.74880	0.63563	-0.20863	C	-5.99536	-0.38835	1.44304
C	-2.08775	-2.08436	1.54555	H	-6.48717	-0.33210	2.41116
H	-2.89842	-1.53858	2.00577	C	-6.51781	-1.20526	0.44174
C	-2.14915	-2.77533	0.29602	H	-7.41571	-1.78829	0.62872
H	-3.01095	-2.84044	-0.35224	C	-5.89575	-1.26304	-0.80457
C	-0.88394	-3.42064	0.09740	H	-6.31813	-1.88182	-1.59265
H	-0.60846	-4.02470	-0.75735	C	-4.73871	-0.51883	-1.07102
C	-0.05713	-3.13883	1.21300	C	-4.28165	1.26543	2.30132
H	0.96182	-3.47377	1.34673	H	-4.40663	2.32728	2.04788
C	-0.78750	-2.30350	2.10556	H	-3.20922	1.10724	2.45693
H	-0.42781	-1.91882	3.05144	H	-4.79829	1.09604	3.25103
C	0.87045	3.83778	-0.44552	C	-4.10504	-0.55007	-2.44113
H	1.32262	4.32690	0.40710	H	-3.99259	0.46158	-2.84884
C	1.56365	3.14614	-1.47085	H	-4.71916	-1.12942	-3.13766
H	2.63240	2.99175	-1.52057	H	-3.10316	-0.98937	-2.41893
C	0.60646	2.65673	-2.40253				
H	0.82260	2.07992	-3.29288				
C	-0.69422	3.06476	-1.96199				
H	-1.62365	2.88265	-2.48511				
C	-0.53516	3.80181	-0.74692				
H	-1.31451	4.30389	-0.18979				
C	2.69086	-0.12754	1.70369				
H	1.87145	-0.06599	2.43458				
C	3.51474	-1.38650	2.04322				
H	4.34132	-1.49394	1.32796				
H	2.89628	-2.28661	1.94261				
C	4.09958	-1.30945	3.46559				
H	3.27522	-1.31362	4.19426				
H	4.70267	-2.20389	3.67076				
C	4.94135	-0.04031	3.66280				
H	5.30923	0.01553	4.69552				
H	5.83062	-0.09347	3.01662				
C	4.13586	1.21948	3.31238				
H	4.76607	2.11351	3.40921				
H	3.31341	1.33718	4.03312				
C	3.54933	1.14292	1.89149				
H	4.37125	1.14899	1.16328				
H	2.93975	2.03037	1.68823				
C	2.85551	-0.73892	-1.33409				
H	2.25113	-0.46177	-2.20989				
C	4.19756	0.01318	-1.44693				
H	4.03236	1.09707	-1.41527				
H	4.83383	-0.23020	-0.58533				
C	4.94857	-0.36723	-2.73619				
H	4.36574	-0.02893	-3.60588				
H	5.90995	0.16169	-2.77893				
C	5.16826	-1.88395	-2.83413				
H	5.84884	-2.20219	-2.02996				
H	5.66408	-2.13642	-3.78037				
C	3.84130	-2.64631	-2.70521				

G (a.u.): -1964.501748

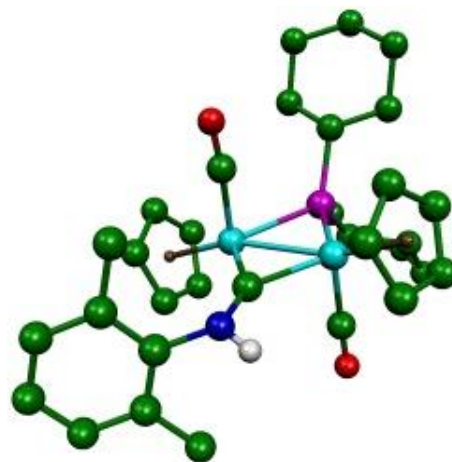


Table S11. Gibbs free energies (kcal/mol) of the different isomers, relative to the aminocarbyne isomers **C** in each case.

	1 (tBu)	2 (4-C₆H₄OMe)	3 (Xyl)
A	14.5	10.0	10.8
B	10.1	9.3	17.2
C	0	0	0
IntG	19.6		