Molecular Motions in a Fluxional (η^6-Indenyl)Tricarbonylchromium Hemichelate: a Density Functional Theory Molecular Dynamics Study

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--- Supporting Information ---

Full reference 55:

Gaussian 09, Revision D.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, 2013.

On the negligible influence of the damping function (PBE-D3 functional): First, the performance of the PBE-D3 functional (with zero damping, see method section for details) is evaluated, by performing TM optimizations on the six complexes shown in Figure 2, namely: $\boldsymbol{\eta^1}$**-3b$_1$**, $\boldsymbol{\eta^1}$**-3b$_2$**, *syn* $\boldsymbol{\eta^3}$**-3b$_1$**, *syn* $\boldsymbol{\eta^3}$**-3b$_2$**, *anti* $\boldsymbol{\eta^3}$**-3b** and **TS$_{rot}$**. As shown in Table S1, optimized distances at this level are within 0.036 Å (on the average) from the experimental structure in the case of $\boldsymbol{\eta^1}$**-3b$_1$**. Comparing PBE-D3 versus the previously employed PBE-D3(bj) functional in the cases of $\boldsymbol{\eta^1}$**-3b$_1$** and $\boldsymbol{\eta^3}$**-3b$_2$** reveals that the two levels provide very similar structures (see Table S1), with interatomic distances being within 0.025 Å of each other on the average for $\boldsymbol{\eta^1}$**-3b$_1$** and within 0.041 Å of each other on the average for $\boldsymbol{\eta^3}$**-3b$_2$**. The main deviations being found for weakly bonded atoms. Also, the relative energy of $\boldsymbol{\eta^3}$**-3b$_2$** *vs* $\boldsymbol{\eta^1}$**-3b$_1$** is 10.1 kcal/mol with PBE-D3(bj)[1] and 9.1 kcal/mol with PBE-D3, *i.e.* within 1.0 kcal/mol only. All these results indicate that PBE-D3 with zero damping provides a good agreement with both the experiment and calculations at the (previously employed)[2] PBE-D3(bj) level.

Details on the sampling procedure in metadynamics simulations: To ensure convergence, the DFT-MTD simulations **MTD1** and **MTD3** were performed in two stages: in a first stage, "traditional" metadynamics was performed using fixed hill height of 0.5 kcal/mol. Once all relevant free energy domains were "filled", well-tempered metadynamics[3] was employed in a second stage. In the latter, the initial hill height was still 0.5 kcal/mol throughout and ΔT was 2277 K (corresponding to a bias factor $\gamma = (T+\Delta T)/T = 8.05$). The time-evolution of Gaussian heights is given in Figure S1. This approach was inspired by the recent "Transition-Tempered metadynamics" method, described in Ref [4], and allows one to benefit from both the "fast" filling of the free energy wells by traditional metadynamics and the smooth convergence of well-tempered metadynamics. For the **MTD2** simulations, only the first stage of "standard" (fixed height) metadynamics was performed. The simulations were stopped once all relevant wells were filled. The convergence was checked by visual inspection of the free energy surfaces to ensure that symmetrical domains are found for equivalent conformers.

Computational level		**Cr-C10** Å	**Cr-C1** Å	**Cr-Pd (CV3)** Å	**Pd-C11** Å	**Pd-C13** Å	**Pd-C14** Å	**Pd-C21** Å	**Pd-C22** Å	**Pd-C23** Å	**Pd-C26** Å	**Pd-C27** Å	**CV1** Å	**CV2**	**CV4** °	**CV5** Å	**CV6** °
Complex η^1-3b$_1$																	
expt[a]		2.275	2.344	2.747	2.184	2.868	3.419	2.762	2.443	2.152	2.146	2.160	-1.234	4.415	-64.9	-0.319	75.7
ADF(bj) [a,b]	PBE-D3(BJ)	2.275	2.378	2.738	2.212	2.935	3.476	2.771	2.445	2.179	2.155	2.201	-1.264	4.341	-65.2	-0.326	74.4
TM [c]	PBE-D3	2.266	2.359	2.730	2.204	2.941	3.503	2.834	2.370	2.183	2.142	2.159	-1.300	4.540	-61.3	-0.464	77.1
CP2K-opt [c]	PBE-D3	2.267	2.365	2.731	2.211	2.939	3.501	2.770	2.396	2.172	2.154	2.195	-1.290	4.473	-63.3	-0.374	76.0
DFT-MD [c,d,e]	PBE-D3	2.284	2.382	2.757	2.230	2.960	3.520	2.815	2.452	2.188	2.174	2.209	-1.289	4.301	-63.8	-0.363	76.2
		(0.060)	(0.072)	(0.081)	(0.069)	(0.106)	(0.113)	(0.194)	(0.179)	(0.064)	(0.055)	(0.068)	(0.117)	(0.289)	(8.0)	(0.306)	(11.7)
Complex η^1-3b$_2$																	
TM [c]	PBE-D3	2.262	2.361	2.721	2.221	2.977	3.532	2.641	2.483	2.158	2.137	2.186	-1.311	4.350	-66.3	-0.158	-68.7
CP2K-opt [c]	PBE-D3	2.261	2.359	2.722	2.221	2.970	3.540	2.738	2.392	2.178	2.155	2.199	-1.309	4.480	-63.0	-0.345	-65.1
DFT-MD [c,d,f]	PBE-D3	2.281	2.384	2.747	2.246	2.988	3.544	2.663	2.542	2.195	2.176	2.214	-1.298	4.271	-67.9	-0.121	-69.7
		(0.064)	(0.081)	(0.080)	(0.076)	(0.109)	(0.121)	(0.225)	(0.205)	(0.084)	(0.058)	(0.074)	(0.128)	(0.300)	(9.6)	(0.374)	(12.0)
Complex *syn* η^3-3b$_1$																	
TM [c]	PBE-D3	2.385	2.385	3.276	2.293	2.196	2.294	3.222	3.222	2.145	2.154	2.145	-0.001	5.511	-96.5	0.000	0.1
CP2K-opt [c]	PBE-D3	2.382	2.382	3.262	2.310	2.208	2.304	3.161	3.176	2.159	2.166	2.156	0.006	5.446	-94.5	0.015	-0.4
DFT-MD [c,d,g]	PBE-D3	2.404	2.403	3.332	2.334	2.228	2.337	3.287	3.280	2.169	2.174	2.172	-0.002	5.201	-94.4	-0.007	-0.8
		(0.080)	(0.077)	(0.200)	(0.101)	(0.069)	(0.097)	(0.256)	(0.236)	(0.060)	(0.051)	(0.065)	(0.160)	(0.270)	(7.5)	(0.277)	(11.2)
Complex *syn* η^3-3b$_2$																	
ADF(bj) [b,c]	PBE-D3(BJ)	2.422	2.423	3.166	2.323	2.254	2.324	3.160	3.160	2.176	2.147	2.176	-0.001	5.340	-95.2	0.000	179.9
TM [c]	PBE-D3	2.396	2.396	3.236	2.289	2.205	2.289	3.232	3.232	2.157	2.124	2.157	0.000	5.520	-95.1	0.000	180.0
CP2K-opt [c]	PBE-D3	2.386	2.386	3.227	2.301	2.213	2.301	3.181	3.176	2.167	2.138	2.167	0.000	5.464	-94.2	-0.005	180.0
Complex *anti* η^3-3b																	
TM [c]	PBE-D3	2.285	2.285	*h*	2.268	2.200	2.268	*h*	*h*	2.156	2.119	2.156	0.000	5.578	-89.7	*h*	*h*
CP2K-opt [c]	PBE-D3	2.294	2.294	*h*	2.283	2.213	2.283	*h*	*h*	2.168	2.135	2.168	0.000	5.514	-89.6	*h*	*h*
Complex TS$_{rot}$																	
TM [c]	PBE-D3	2.323	2.343	2.850	2.213	3.117	3.698	4.188	2.310	2.136	2.146	2.225	-1.485	4.594	-97.6	-1.878	56.3

Table S1: Selected geometrical parameters in six stereoisomers of **3b**, computed at different DFT levels (interatomic distances are in Å and dihedral angles are in °). *a* from reference [2]. *b.* Geometry optimization at the ZORA/all-electron TZP level computed with the ADF software (see reference [2]). *c*. This work. *d.* Average distances from (unbiased) DFT-MD simulations (standard deviations are given in parenthesis). *e.* Averages over 100 ps of DFT-MD (simulation **MD2**). *f.* Averages over the last 60 ps of DFT-MD (simulation **MD3**). *g.* Averages over the first 30 ps of DFT-MD (simulation **MD3**). *h.* not reported.

ρ(Pd,X)			Indenyl			Carbonyl			2-methylallyl		
		Pd-Cr	**Pd-C11**	**Pd-C13**	**Pd-C14**	**Pd-C20**	**Pd-C21**	**Pd-C22**	**Pd-C23**	**Pd-C26**	**Pd-C27**
TM	**η^1-3b$_1$**	*a*	0.0820	*a*	*a*	*a*	*a*	0.0586	0.0899	0.0913	0.0936
	η^1-3b$_2$	*a*	0.0790	*a*	*a*	*a*	*a*	0.0488	0.0940	0.0921	0.0895
	***syn* η^3-3b$_1$**	*a*	*a*	0.0800	*a*	*a*	*a*	*a*	0.0963	0.0906	0.0964
	***syn* η^3-3b$_2$**	*a*	*a*	0.0797	*a*	*a*	*a*	*a*	0.0955	0.9469	0.0955
	***anti* η^3-3b**	*a*	*a*	0.0809	*a*	*a*	*a*	*a*	0.0950	0.0961	0.0950
	2 [b]	*a*	0.0887 [c]	0.0886 [c]	0.0887 [c]	*a*	*a*	*a*	0.0904	0.0892	0.0904
CP2K-opt	**η^1-3b$_1$**	*a*	0.0808	*a*	*a*	*a*	*a*	0.0559	0.0879	0.0890	0.0912
	η^1-3b$_2$	*a*	0.0790	*a*	*a*	*a*	*a*	0.0570	0.0903	0.0888	0.0872
	***syn* η^3-3b$_1$**	0.0178	*a*	0.0780	*a*	*a*	*a*	*a*	0.0938	0.0885	0.0943
	***syn* η^3-3b$_2$**	0.0183	*a*	0.0783	*a*	*a*	*a*	*a*	0.0934	0.0920	0.0934
	***anti* η^3-3b**	*a*	*a*	0.0788	*a*	*a*	*a*	*a*	0.0928	0.0931	0.0927
	2 [b]	*a*	0.0872 [c]	0.0865 [c]	0.0862 [c]	*a*	*a*	*a*	0.0889	0.0869	0.0885

Table S2: Density (a.u.) at bond critical points, as obtained from QTAIM analysis on TM-optimized and CP2K-optimized structures.

a. No bond critical point is obtained between this pair of atoms.

b. Complex **2** consists on the "[(benzene)Cr(CO)$_3$]…[Pd(2-methylallyl)$_2$]" contact pair (see structure in Figure S4).

c. These values correspond to the second 2-methylallyl ligand, in place of the indenyl ligand.

δ(Pd,X)			Indenyl			Carbonyl			2-methylallyl		
		Pd-Cr	**Pd-C11**	**Pd-C13**	**Pd-C14**	**Pd-C20**	**Pd-C21**	**Pd-C22**	**Pd-C23**	**Pd-C26**	**Pd-C27**
TM	**η^1-3b$_1$**	0.302	0.559	0.076	0.040	0.015	0.144	0.359	0.610	0.426	0.653
	η^1-3b$_2$	0.300	0.548	0.071	0.037	0.014	0.216	0.279	0.658	0.432	0.609
	***syn* η^3-3b$_1$**	0.103	0.421	0.386	0.421	0.008	0.063	0.063	0.691	0.431	0.691
	***syn* η^3-3b$_2$**	0.115	0.430	0.376	0.430	0.008	0.064	0.064	0.676	0.467	0.676
	***anti* η^3-3b**	0.033	0.460	0.374	0.460	0.003	0.005	0.005	0.673	0.451	0.673
	2 [a]	0.001	0.611 [b]	0.406 [b]	0.611 [b]	0.000	0.003	0.003	0.628	0.409	0.629
CP2K-opt	**η^1-3b$_1$**	0.299	0.557	0.078	0.040	0.015	0.164	0.341	0.605	0.419	0.648
	η^1-3b$_2$	0.303	0.554	0.072	0.037	0.015	0.177	0.343	0.643	0.418	0.602
	***syn* η^3-3b$_1$**	0.105	0.414	0.380	0.417	0.008	0.070	0.067	0.683	0.424	0.686
	***syn* η^3-3b$_2$**	0.116	0.426	0.372	0.425	0.008	0.069	0.070	0.671	0.458	0.671
	***anti* η^3-3b**	0.033	0.455	0.368	0.455	0.003	0.005	0.005	0.668	0.442	0.667
	2 [a]	0.001	0.607 [b]	0.399 [b]	0.604 [b]	0.000	0.003	0.004	0.625	0.401	0.625

Table S3: Delocalization indices, as obtained from QTAIM analysis on TM-optimized and CP2K-optimized structures.
a. Complex **2** consists on the "[(benzene)Cr(CO)$_3$]…[Pd(2-methylallyl)$_2$]" contact pair (see structure in Figure S1).
b. These values correspond to the second 2-methylallyl ligand, in place of the indenyl ligand.

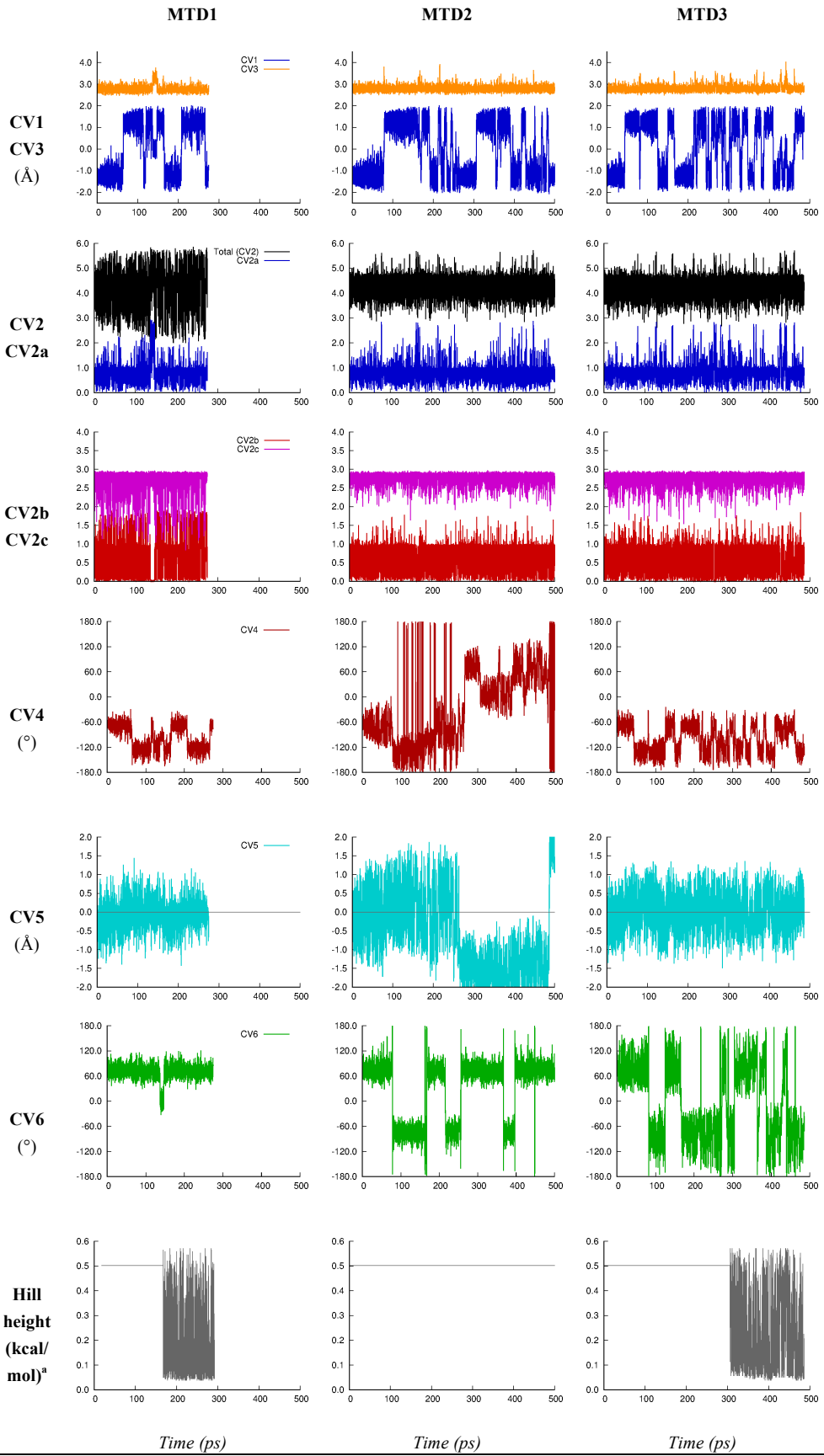


Figure S1: Time evolution (ps) of **CV1- CV6** in the course of metadynamics simulations (**MTD1-MTD3**) on complex **3b**. a. In well-tempered metadynamics runs (**MTD1** and **MTD3**), the hill height is multiplied by the bias factor (defined as $\gamma = (T + \Delta T)/T$, see Methods section for details).

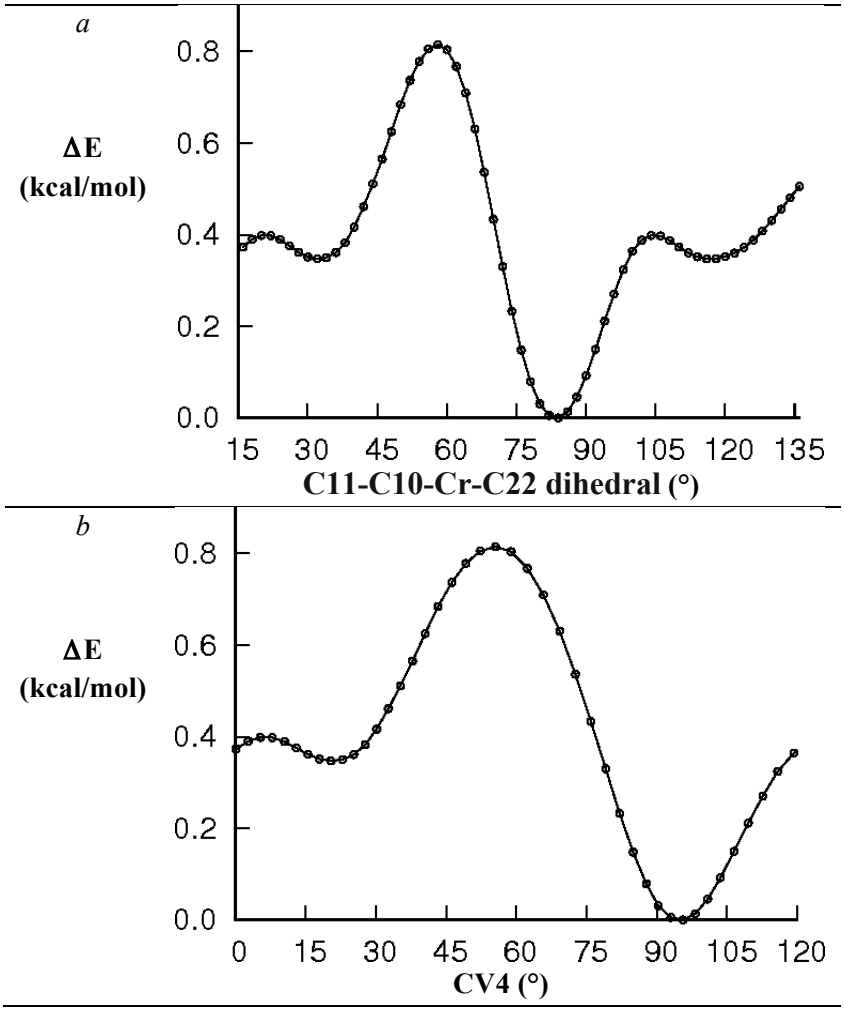
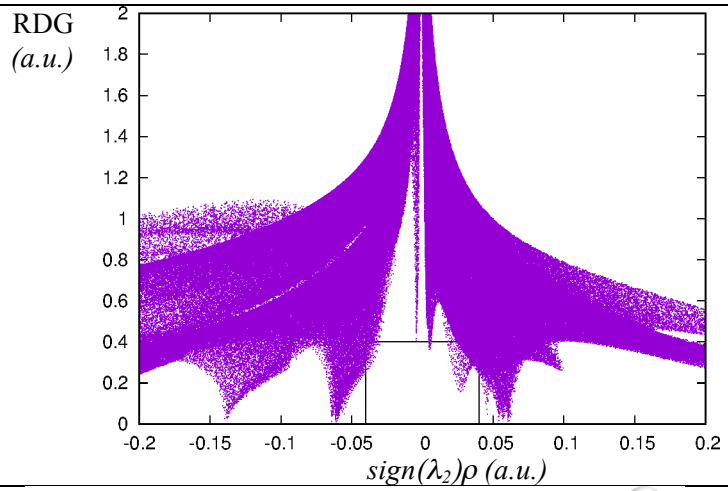


Figure S2: Energy profile for "$Cr(CO)_3$" rotation in complex **1**, obtained at the TM level. (a). Profile computed using the C11-C10-Cr-C22 dihedral as coordinate. (b) Same profile expressed in function of **CV4** (see Figure 1 for definition) instead of the C11-C10-Cr-C22 dihedral.

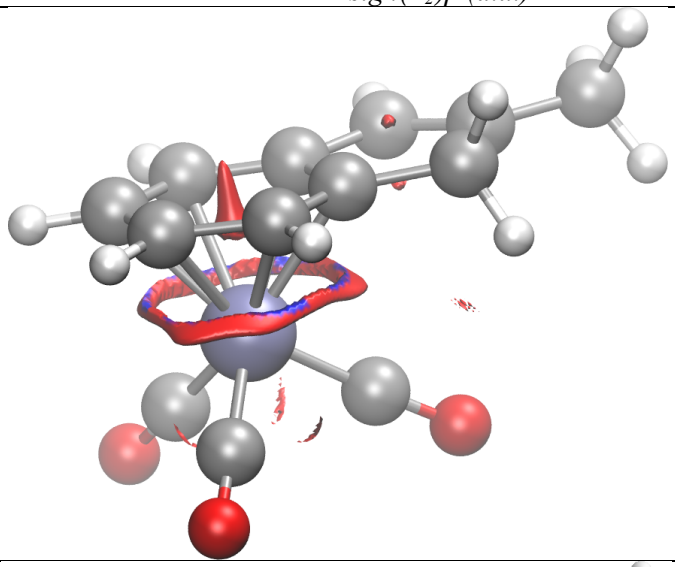
(a)

NCIplot



(b)

NCIs with NCIplot



(c)

NCIs with AIMAll

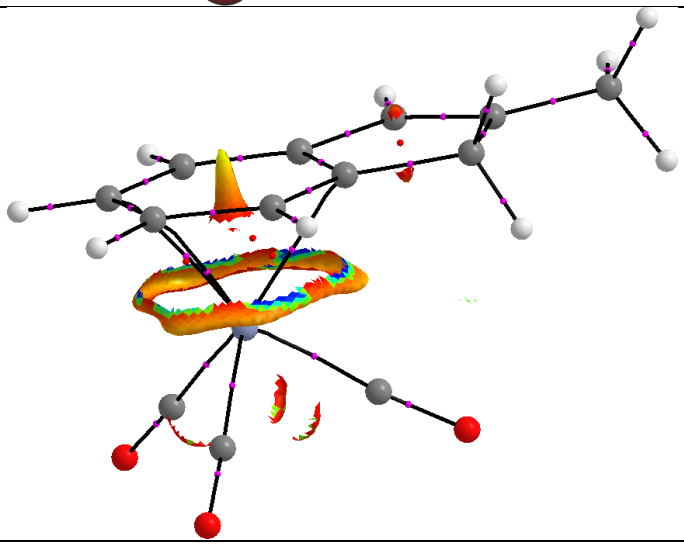


Figure S3: Non-covalent interactions (NCIs) in complex **1**. *(a)* Plot of the reduced density gradient (RDG, in a.u., see Ref [5] for definition) versus the electron density multiplied by the sign of the second Hessian eigenvalue (in a.u.). The black rectangle corresponds to the cutoffs that have been selected for plotting the NCIs (RDG < 0.4 a.u. and -0.04 < ρ < 0.04 a.u.). *(b)* NCIs plotted using NCIplot[5-6] and VMD.[7] *(c)* NCIs plotted using AIMAll.[8] The color code (according to the value of sign(λ_2)ρ) is: red +0.04, yellow +0.02, green 0.00, cyan -0.02 and blue -0.04 a.u..

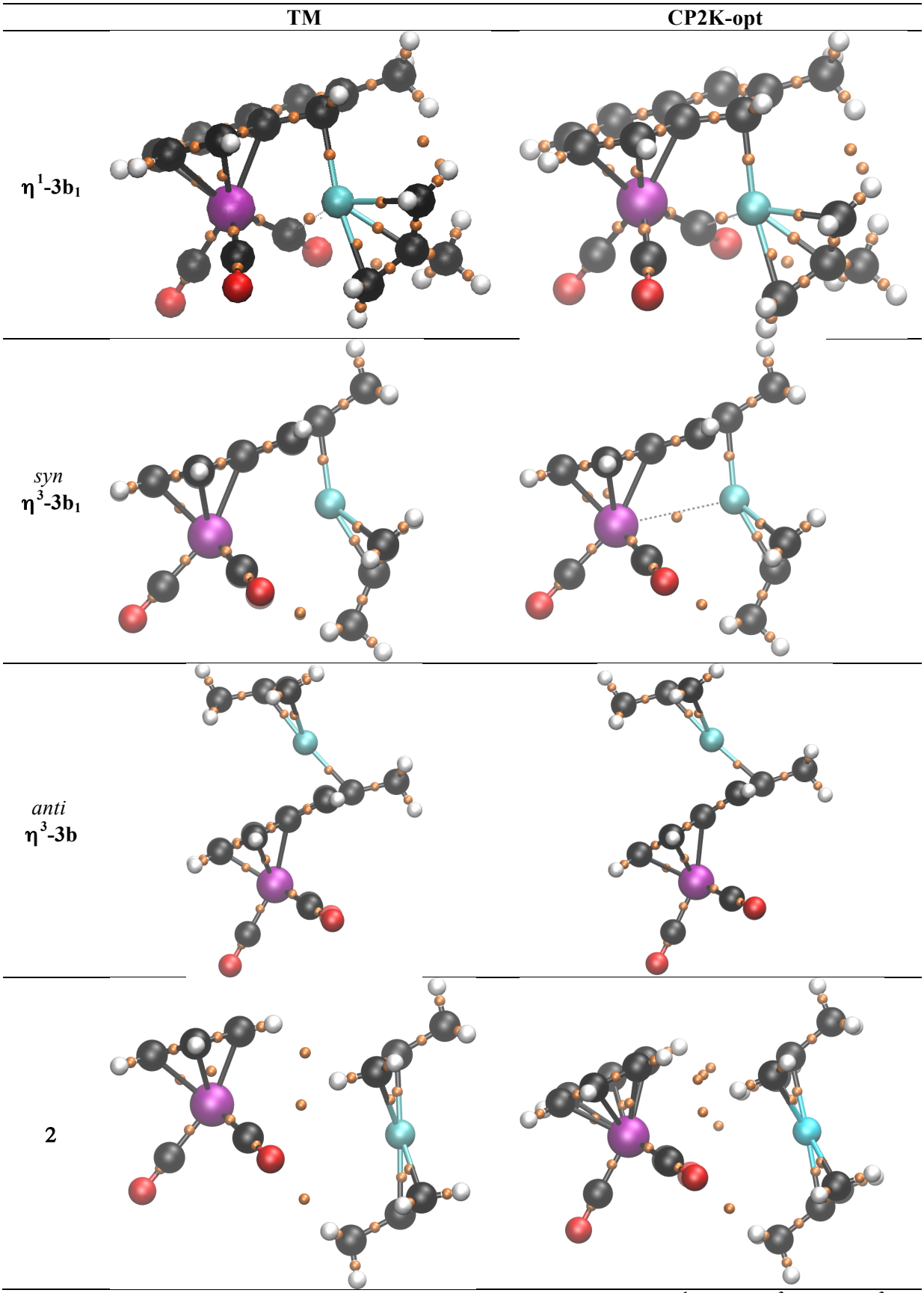


Figure S4: Location of bond critical points as obtained from QTAIM analysis on **η¹-3b₁**, *syn* **η³-3b₁**, *anti* **η³-3b** and **2**, on TM-optimized (*left column*) and CP2K-optimized structures (*right column*). Colors: H (white), C (black), O (red), Cr (purple) and Pd (cyan). Bond critical points are shown as orange spheres. Other types of critical points are omitted for clarity.

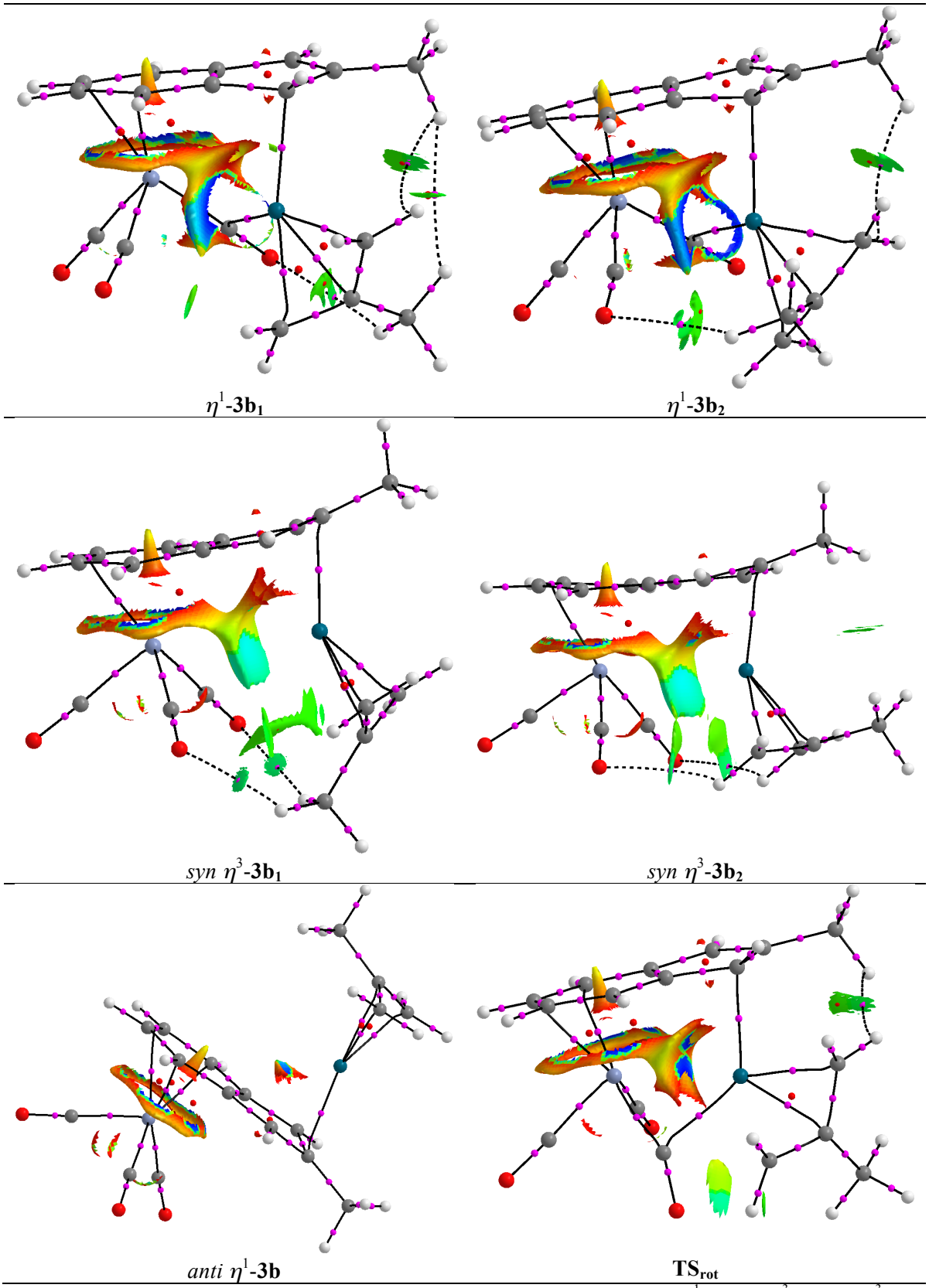


Figure S5: Results of QTAIM and NCI analyses on TM-optimized structures of η^1-**3b**, *syn* η^3-**3b**, *anti* η^3-**3b** and **TSrot**. Bond critical points are shown as purple spheres and bond paths are shown as black lines. NCI isosurfaces (s = 0.4 a.u.) are superimposed on the QTAIM structures, in the range of -0.04 < sign(λ_2)ρ < +0.04 a.u.. The color code (according to the value of sign(λ_2)ρ) is: red +0.04, yellow +0.02, green 0.00, cyan -0.02 and blue -0.04 a.u.. The labeling of selected atoms is shown in black.

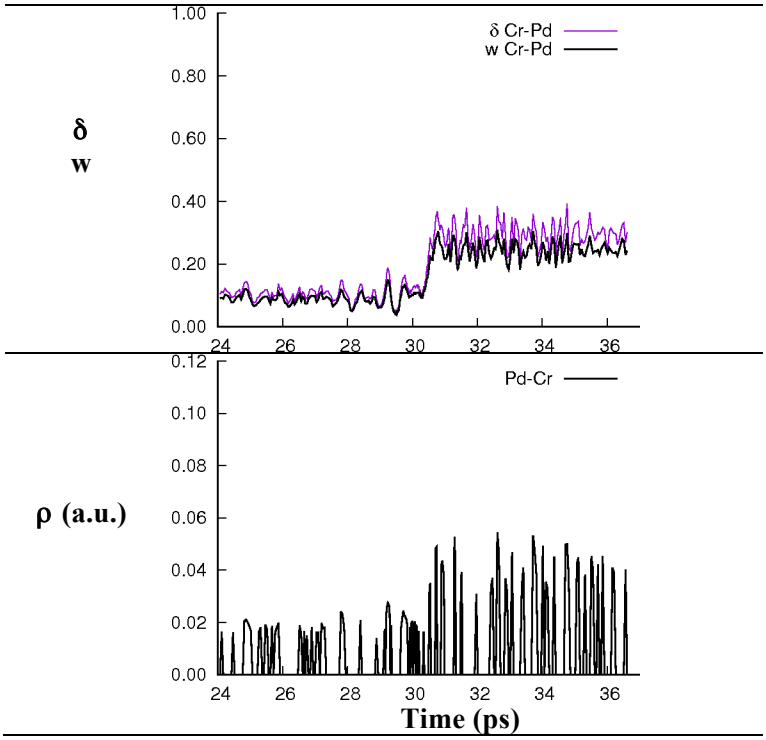


Figure S6: Time evolution (in ps) of the delocalization index (δ), the Wiberg bond index (w) and the density (ρ) (in a.u.) at the bond critical point between Pd and Cr atoms, as obtained from QTAIM and NBO analyses during the spontaneous $\eta^3 \rightarrow \eta^1$ process occurring in simulation **MD3.**

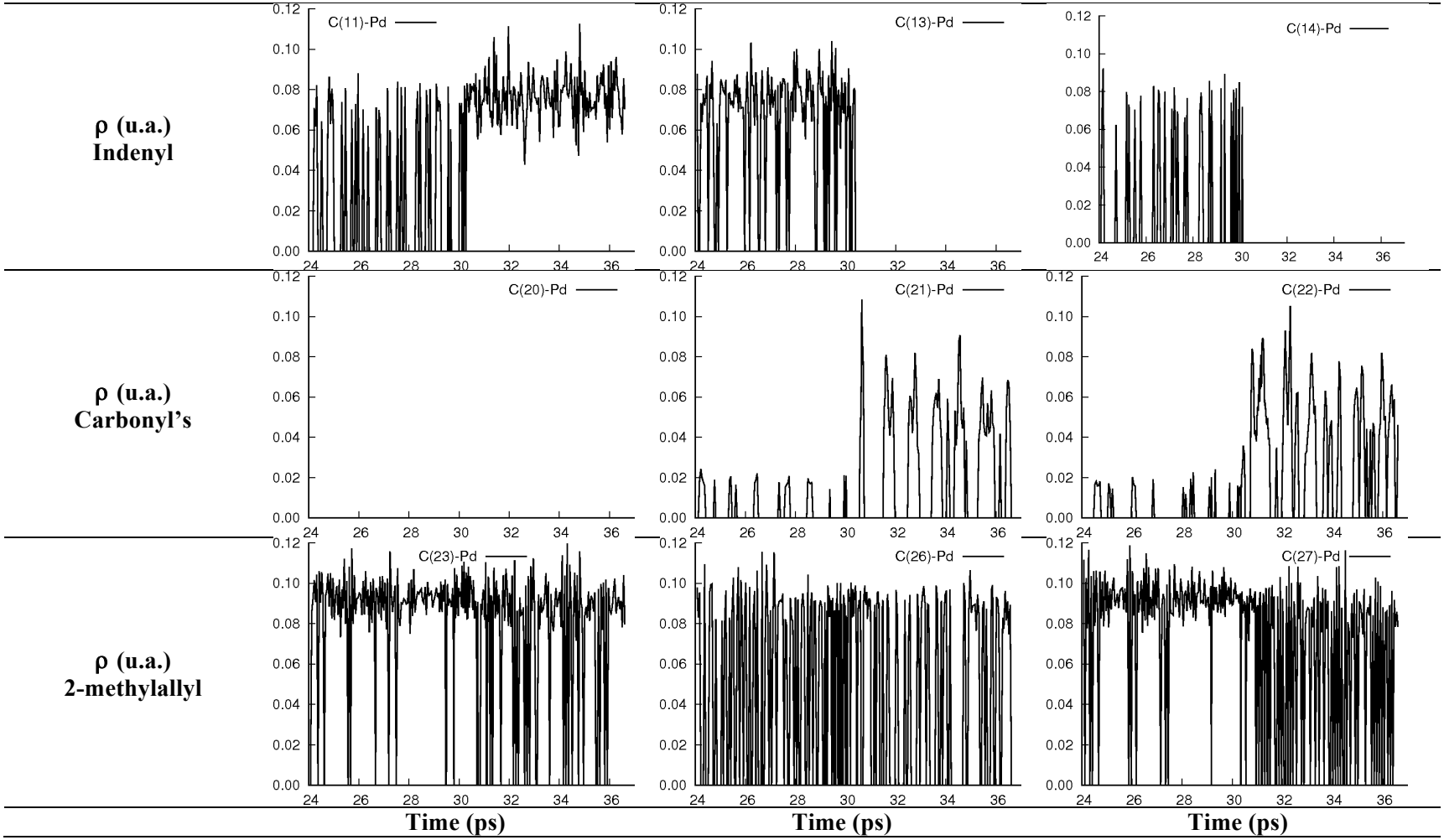


Figure S7: Time evolution (in ps) of the density (ρ in a.u.) at the bond critical point between Pd and: C atoms from the indenyl (*top*), carbonyl's (*middle*) and 2-methylallyl (*bottom*) ligands, as obtained from QTAIM analysis during the spontaneous $\eta^3 \rightarrow \eta^1$ process occurring in simulation **MD3.** ρ is set to zero when no bond critical point is found between the two atoms.

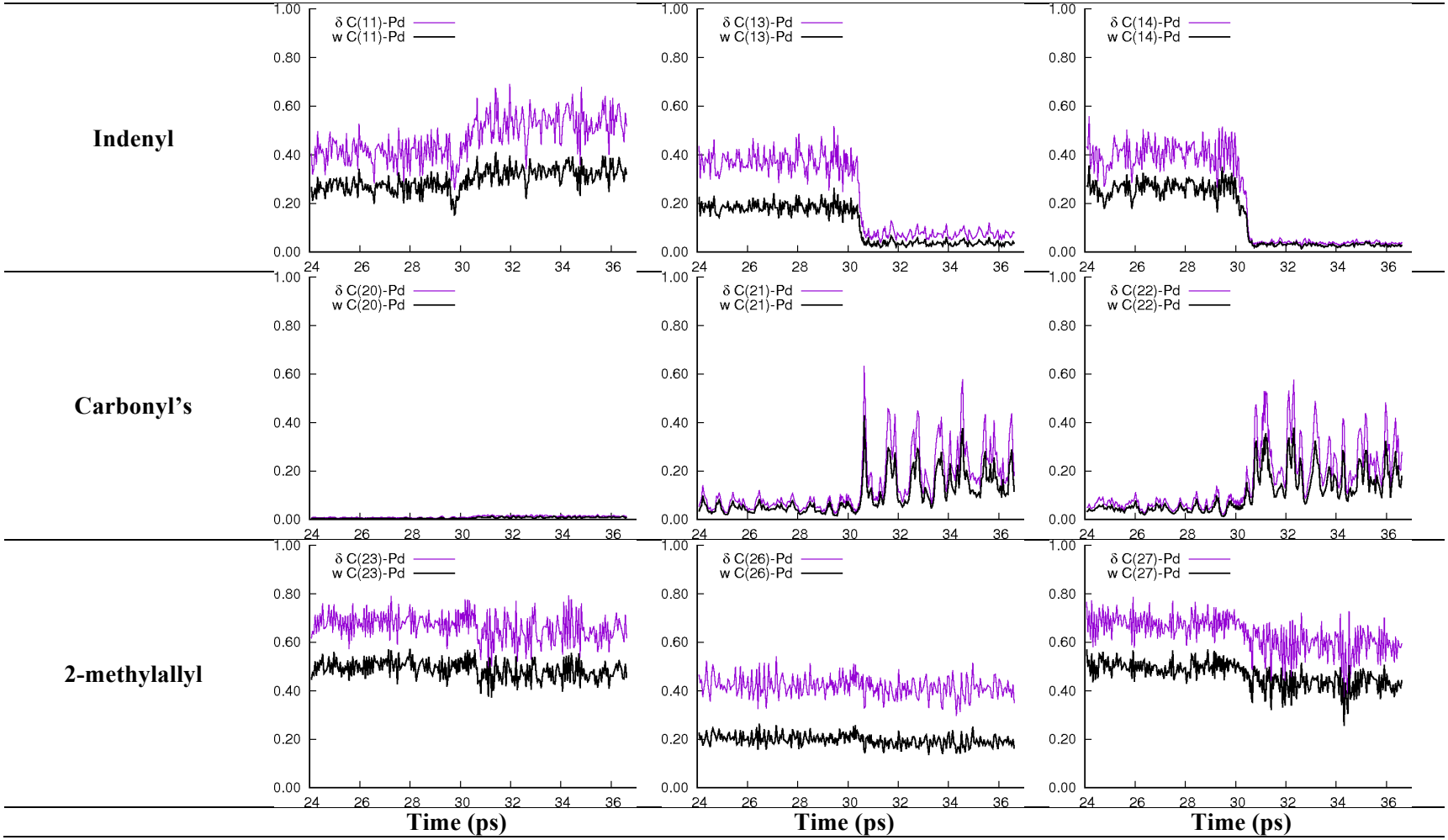


Figure S8: Time evolution (in ps) of the delocalization index (δ), the Wiberg bond index (w) between Pd and: C atoms from the indenyl (*top*), carbonyl's (*middle*) and 2-methylallyl (*bottom*) ligands, as obtained from QTAIM and NBO analyses during the spontaneous $\eta^3 \rightarrow \eta^1$ process occurring in simulation **MD3.**

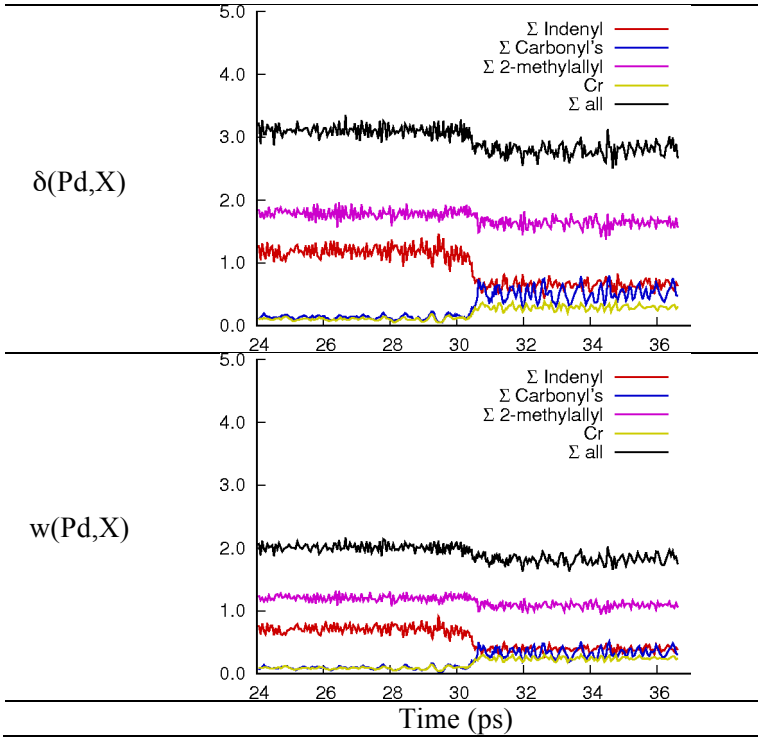


Figure S9: Summation of delocalisation indexes (*top*) and Wiberg bond indexes (*bottom*) during the spontaneous $\eta^3 \rightarrow \eta^1$ process occurring in simulation **MD3**.
In the case of delocalisation indices, "Σ indenyl" denotes δ(Pd,C11) + δ(Pd,C13) + δ(Pd,C14).
"Σ carbonyl's" is δ(Pd,C20) + δ(Pd,C21) + δ(Pd,C22). "Σ 2-methylallyl" is δ(Pd,C23) + δ(Pd,C26) + δ(Pd,C27). "Cr" is δ(Pd,Cr). "Σ all" is the sum of all the contributions. The same definition is adopted for Wiberg bond indexes. See Figures S6 and S8 for the detailed contributions.

XYZ coordinates (in Å).
Geometry optimizations at the "TM" level (PBE-D3/def2-TZVPP).

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η^1-3b$_1$ (energy = -2054.753267879 h)

C	6.1768311	5.3896379	8.3747860
C	5.4118061	6.4260489	8.9528689
H	4.9517405	6.2974523	9.9316562
C	5.2529549	7.6472436	8.2506782
H	4.6747790	8.4526199	8.7004212
C	5.8545851	7.8515447	6.9829439
H	5.7263067	8.8026123	6.4705860
C	6.7114172	6.8660132	6.4366897
H	7.2433950	7.0592153	5.5058289
C	6.9038717	5.6407337	7.1296515
C	7.7745721	4.5061109	6.8981425
H	8.1013495	4.2049839	5.9020838
C	7.4362996	3.5324098	7.9303359
C	6.5159500	4.0692896	8.8111427
H	6.1570735	3.6006018	9.7244771
C	8.0455202	2.1714837	8.0147542
H	9.1309851	2.2391602	8.1829065
H	7.9050003	1.6147782	7.0756232
H	7.6091120	1.5845430	8.8321361
C	7.4083189	8.7026807	9.7443551
C	8.7287688	8.4222664	7.6942482
C	8.4967926	6.5133039	9.7503624
C	11.3575916	6.6268574	8.1702567
H	11.4945712	7.2127363	7.2596702
H	11.4948502	7.1654933	9.1083159
C	11.4888134	5.2131891	8.1515173
C	11.1001813	4.5489732	6.9516999
H	11.0596242	3.4591328	6.9325983
H	11.2533985	5.0333581	5.9840918
C	11.8138457	4.4420069	9.4035852
H	11.3651676	3.4403077	9.3878467
H	11.4672176	4.9690560	10.3006043
H	12.9054714	4.3199728	9.4806905
O	7.4107863	9.5456803	10.5489037
O	9.4788566	9.1592565	7.1848861
O	8.9752609	6.0688583	10.7264979
Cr	7.4361898	7.3817762	8.4795387
Pd	9.4386535	5.6785507	7.7425315

38
η^1-3b$_2$ (Energy = -2054.752461131)

C	10.8195098	9.6017096	7.8344462
C	11.9616752	9.0085541	8.4213124
H	12.8158756	9.6181842	8.7127787
C	11.9848870	7.6100933	8.6369604
H	12.8578498	7.1539904	9.1007482
C	10.8792090	6.7912676	8.2862136
H	10.9181238	5.7201693	8.4726046
C	9.6883113	7.3807353	7.8012082
H	8.8089924	6.7641915	7.6180593
C	9.6311580	8.7856017	7.5949959
C	8.5539013	9.6828110	7.2290004
H	7.7079475	9.3701107	6.6155970
C	9.1669551	10.9987793	7.0913462

C	10.4925563	10.9494653	7.4825974
H	11.1636283	11.8005528	7.5709801
C	8.4340662	12.2115801	6.6205496
H	7.5937110	12.4485039	7.2893933
H	8.0052801	12.0487371	5.6197371
H	9.0930863	13.0871981	6.5729882
C	11.0569451	7.9169226	11.3011989
C	8.8096902	7.4028540	10.4701326
C	9.9229672	9.9844566	10.5596683
C	5.9434447	10.6102043	9.0758428
H	6.2260313	11.6381602	9.3152448
H	5.3668286	10.4780777	8.1592589
C	5.8326379	9.6430887	10.1167945
C	6.7318396	9.7731225	11.2074968
H	6.7883874	8.9774571	11.9504167
H	7.0805429	10.7574328	11.5254938
C	4.9621214	8.4228378	9.9680902
H	5.4096553	7.5511348	10.4614256
H	4.7819748	8.1832305	8.9120423
H	3.9854947	8.6136357	10.4396205
O	11.5761735	7.6436749	12.3082938
O	8.0215448	6.6804730	10.9500221
O	9.9397457	11.0188118	11.1073001
Cr	10.2099504	8.3422505	9.7367107
Pd	7.8133718	9.5615595	9.3194154

38

syn η^3**-3b$_1$** (energy = -2054.740204687 h)

C	7.8444135	11.0330292	8.4240338
C	8.1551443	11.1247029	7.0395322
H	8.6810627	11.9935210	6.6475596
C	7.7055743	10.1100657	6.1624357
H	7.8930758	10.1986503	5.0943982
C	7.0862746	8.9340813	6.6735708
H	6.8052228	8.1341659	5.9917302
C	6.9110793	8.7617968	8.0666030
H	6.4913189	7.8354804	8.4551057
C	7.2162606	9.8393350	8.9427897
C	7.0236989	10.0392199	10.3661140
H	6.4852620	9.3567733	11.0187570
C	7.3431741	11.4015606	10.6782796
C	8.0252719	11.9423713	9.5390518
H	8.3838957	12.9647301	9.4509033
C	6.9699152	12.1398606	11.9263926
H	6.9182456	11.4641745	12.7897926
H	5.9807475	12.6118543	11.8129176
H	7.6929731	12.9341157	12.1519737
C	9.8274854	8.1800625	6.2699940
C	9.5184069	7.7829157	8.7227982
C	10.6834780	9.9994584	7.7596345
C	10.0967821	9.1523236	12.2048681
H	9.7079059	9.6544982	13.0935953
H	9.9509114	8.0715391	12.1638409
C	11.1648854	9.7269262	11.4559080
C	11.1461260	11.1475458	11.3407555
H	11.8189517	11.6235138	10.6253753
H	10.8200215	11.7688768	12.1779016
C	12.1670260	8.8819289	10.7219493
H	11.7594804	7.8997169	10.4585231

H	13.0268912	8.7185643	11.3909840
H	12.5378171	9.3785846	9.8186829
O	10.3151197	7.5530204	5.4124054
O	9.7665510	6.8663582	9.4065379
O	11.7089203	10.5615898	7.8008869
Cr	9.0628245	9.1571428	7.5971138
Pd	9.2779389	10.3641414	10.6355660

38

syn **η^3-3b$_2$** (Energy = -2054.738751826)

C	0.4033640	1.7804277	0.7233460
C	1.6349858	1.7339762	1.4309516
H	1.6463900	1.6749427	2.5178818
C	2.8487756	1.8454233	0.7119839
H	3.7939725	1.8682049	1.2503768
C	2.8487548	1.8453836	-0.7121038
H	3.7939385	1.8681359	-1.2505318
C	1.6349411	1.7338749	-1.4310194
H	1.6463064	1.6747818	-2.5179419
C	0.4033395	1.7803893	-0.7233766
C	-0.9815613	1.8439523	-1.1537855
H	-1.3033488	1.9612098	-2.1854878
C	-1.8013248	2.0685478	0.0000151
C	-0.9815181	1.8439921	1.1537914
H	-1.3032749	1.9612907	2.1855038
C	-3.2292573	2.5203928	0.0000654
H	-3.7621161	2.1606003	-0.8896592
H	-3.2859079	3.6205816	0.0000011
H	-3.7620069	2.1607020	0.8899001
C	3.4582094	-0.8444451	0.0004478
C	1.3819318	-1.1607150	-1.3160782
C	1.3816220	-1.1606425	1.3160773
C	-2.0213540	-1.7649363	1.1985358
H	-1.1403141	-2.4057485	1.2500430
H	-2.4980684	-1.5419582	2.1543097
C	-2.7862257	-1.6773211	-0.0000428
C	-2.0212354	-1.7649141	-1.1985382
H	-2.4978642	-1.5419213	-2.1543583
H	-1.1401886	-2.4057230	-1.2499811
C	-4.2522300	-1.3403035	-0.0001309
H	-4.5339480	-0.7680907	0.8934661
H	-4.8416082	-2.2708657	-0.0003270
H	-4.5337708	-0.7678415	-0.8936251
O	4.4863486	-1.3999240	0.0008832
O	1.1362926	-1.9233356	-2.1677230
O	1.1359160	-1.9232562	2.1677081
Cr	1.8628658	0.0230265	0.0000264
Pd	-1.3709279	-0.0938803	0.0000380

38

anti **η^3-3b** (-2054.737433788)

C	0.4690693	1.9239765	0.7167341
C	1.6915216	1.7636901	1.4272098
H	1.6935658	1.6948176	2.5138298
C	2.9041223	1.6889584	0.7062552
H	3.8416536	1.5493098	1.2405732
C	2.9045422	1.7068718	-0.7208230

```
H     3.8424387    1.5807393   -1.2578670
C     1.6926212    1.8004916   -1.4407427
H     1.6955481    1.7594247   -2.5287305
C     0.4696442    1.9423314   -0.7271632
C    -0.9098371    2.1383973   -1.1554465
H    -1.2529156    2.0835071   -2.1854662
C    -1.7544298    2.0568429   -0.0044787
C    -0.9106787    2.1092579    1.1487274
H    -1.2545457    2.0287553    2.1768139
C    -3.2401858    1.8880520   -0.0070816
H    -3.4941503    0.8161665   -0.0208178
H    -3.6949159    2.3495844   -0.8928725
H    -3.6953747    2.3268646    0.8899649
C     2.9643530   -1.1300727   -0.0490874
C     0.7566857   -0.9230045   -1.3199947
C     0.7665931   -0.9589996    1.2409355
C    -0.9286815    5.8447533    1.2549450
H    -1.9956586    6.0669417    1.3205279
H    -0.3860736    5.8441345    2.2010961
C    -0.2148458    6.0876305    0.0463705
C    -0.9271054    5.8747570   -1.1687517
H    -0.3832512    5.8975395   -2.1139294
H    -1.9940121    6.0984760   -1.2302398
C     1.2734074    6.3212861    0.0501884
H     1.7475022    5.8811314    0.9370261
H     1.4739378    7.4037756    0.0640965
H     1.7484630    5.9038497   -0.8470726
O     3.8426037   -1.8994344   -0.0620568
O     0.2156898   -1.5453598   -2.1459034
O     0.2327806   -1.6055784    2.0528049
Cr    1.5918645    0.0789113   -0.0284437
Pd   -0.8834510    4.0769250    0.0209530
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38
TSrot (energy = -2054.730981493)
C     1.2229364    2.0302370    0.1309632
Cr    1.5654742   -0.2848123    0.0259988
C     0.3786043   -1.7159919    0.3706410
Pd   -1.2510838   -0.2743286   -0.4060793
C    -3.3470288    0.0146399   -0.6966524
C    -3.1274632   -1.2696531   -0.1021224
C    -3.5283415   -1.5694999    1.3168616
C     2.5927194    1.6832067    0.2718038
C     3.2307872    0.9220126   -0.7318033
C     2.4939048    0.4532594   -1.8649566
C     1.1201349    0.7189684   -1.9891525
C     0.4647807    1.4942945   -0.9848377
C    -0.9182596    1.8787102   -0.7949054
C    -0.9443430    2.7227420    0.3942944
C     0.3191801    2.7885002    0.9455001
C    -2.1791389    3.3774901    0.9210788
O     0.0583715   -2.7634618    0.8158229
C     1.6592778   -0.3071116    1.8498230
O     1.7290987   -0.3011331    3.0141575
C     2.6578875   -1.7401507   -0.0759520
O     3.3634270   -2.6654500   -0.1486722
C    -2.3392688   -2.1622089   -0.8553330
H     3.1583470    2.0126385    1.1423921
H     4.2825149    0.6635136   -0.6316109
H     2.9958319   -0.1634130   -2.6081197
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H     0.5585660    0.3148536   -2.8307583
H    -1.6010038    2.0486963   -1.6281904
H     0.5880957    3.2971382    1.8687842
H    -2.8911118    2.6305009    1.3061434
H    -2.7043203    3.9384299    0.1327458
H    -1.9470905    4.0712836    1.7386830
H    -2.3267857   -2.1031032   -1.9456317
H    -1.9889739   -3.0916869   -0.4104399
H    -3.8302062    0.7988374   -0.1123409
H    -3.4712074    0.0936945   -1.7792541
H    -3.5549995   -0.6573377    1.9268883
H    -2.8413217   -2.2881593    1.7806139
H    -4.5383074   -2.0079450    1.3269856
```

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