Electronic Supplementary Material (ESI) for Dalton Transactions

SUPPORTING INFORMATION

On the isomerization of cyclooctyne into cycloocta-1,3-diene: Synthesis, characterization and structure of a dinuclear platinum(II) complex with a μ-η^2:η^2-1,3-COD ligand

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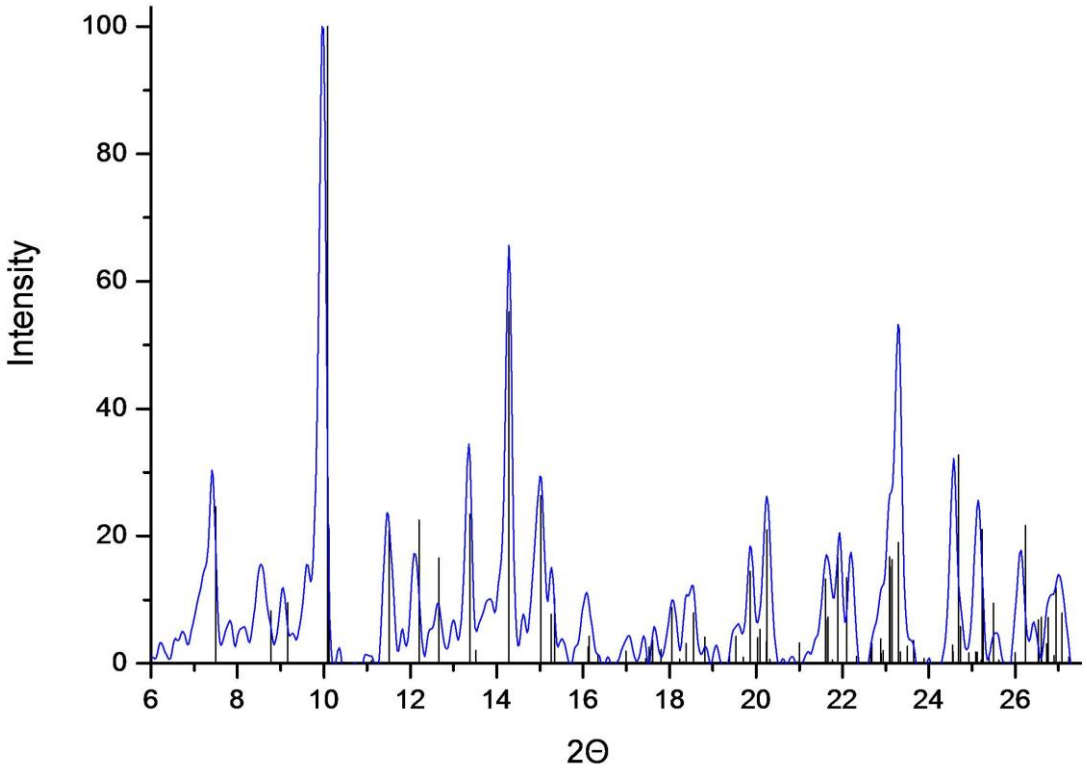
S1. Crystallographic and structure refinement data of $[K(18C6)]_2[(PtCl_3)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}1,3\text{-COD})]\cdot Me_2CO$ (**2**·Me_2CO).

Empirical formula	$C_{35}H_{66}Cl_6K_2O_{13}Pt_2$
M_r	1375.96
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.553(1)
b/Å	20.363(2)
c/Å	18.689(2)
β	98.39(1)
V/Å^3	5102.7(8)
Z	4
D_{calc}/g·cm^{-1}	1.791
M(Mo Kα)/mm^{-1}	0.71073
T/K	220(2)
μ (mm^{-1})	6.007
F(000)	2704
Θ range/°	1.95–25.9
Refln. Collected	34509
Refln. Obs. [$I > 2\sigma(I)$]	6642
Refln. Independent (R_{int})	9756
Data/restraints/parameters	9756/59/564
Goodness-of-fit on F^2	0.887
R_1 [$I > 2\sigma(I)$]	0.0349
wR_2 (all data)	0.0690
Largest difference peak and hole /e · Å^{-3}	1.293/–0.916
T_{min}/T_{max}	0.2488/0.5409

S2. Comparison of calculated XRD pattern obtained from single X-ray data (black vertical lines) and an experimentally measured XRD pattern of $[K(18C6)]_2[(PtCl_3)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}1,3\text{-}COD)]\cdot Me_2CO$ (**2**·Me_2CO).



S3. DFT calculations

The following section contains potential energies, sum of electronic and zero-point energies, Gibbs free energies (298.15 K), solvation energies (in $CHCl_3$, 298.15 K), calculated BSSE for the platinum–alkyne bonds and Cartesian coordinates of all structures calculated within this work.

cylooctyne (L1')

(file: COC.out / COC_PCM.out)

E(RB+HF–LYP)	–312.079357 a.u.
Sum of electronic and zero-point energies	–311.899786 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–311.931275 a.u.
ΔG_{solv}(PCM, 298.15 K)	1.3 kcal/mol

	x	*y*	*z*
C	0.77737	–1.47347	–0.07843
C	–0.41808	–1.54756	–0.21171
C	0.54934	1.30582	–0.57654
C	–1.78471	–1.03016	–0.18820
C	–0.92025	1.47693	–0.09689
C	–1.72093	0.32758	0.56289
H	–2.17193	–0.89790	–1.20547
H	0.56008	0.70447	–1.48958
H	–1.48681	1.82884	–0.96821
H	0.86949	2.30756	–0.88334
H	–2.47847	–1.70311	0.32614
H	–0.94469	2.30848	0.61816
H	–2.74403	0.69410	0.71042
H	–1.32043	0.12492	1.56087
C	2.02563	–0.73101	0.08987
H	2.62421	–0.76218	–0.82773
H	2.65489	–1.13271	0.88993
C	1.60840	0.73747	0.40699
H	1.22951	0.77161	1.43337
H	2.50751	1.36238	0.38746

cycloocta-1,3-diene (L2')

(file: COD.out / COD_PCM.out)

E(RB+HF–LYP)	–312.122953 a.u.
Sum of electronic and zero-point energies	–311.943283 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–311.973799 a.u.
ΔG_{solv}(PCM, 298.15 K)	1.0 kcal/mol

	x	*y*	*z*
C	–1.34143	0.83189	–0.75658
H	–2.40840	1.00995	–0.87378
C	–0.71012	0.17933	–1.74247
C	–0.71012	1.41842	0.48104
H	–1.27923	–0.08401	–2.63259
C	0.71012	–0.17933	–1.74247
C	–0.60492	0.47043	1.70117
H	–1.30391	2.28903	0.77671
H	0.29289	1.78735	0.24093
H	1.27923	0.08401	–2.63259
C	1.34143	–0.83189	–0.75658
C	0.60492	–0.47043	1.70117
H	–0.55269	1.08351	2.60739
H	–1.52665	–0.11781	1.78235
H	2.40840	–1.00995	–0.87378
C	0.71012	–1.41842	0.48104
H	0.55269	–1.08351	2.60739
H	1.52665	0.11781	1.78235
H	1.30391	–2.28903	0.77671
H	–0.29289	–1.78735	0.24093

cis-but-2-ene (L4')

(file: butene.out / butene_PCM.out)

E(RB+HF–LYP)	–157.271117 a.u.
Sum of electronic and zero-point energies	–157.163588 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–157.191471 a.u.
ΔG_{solv}(PCM, 298.15 K)	3.4 kcal/mol

	x	*y*	*z*
C	0.66718	0.66372	–0.00001
H	1.16515	1.63144	0.00003
C	–0.66718	0.66372	–0.00001
H	–1.16515	1.63144	0.00003
C	1.58945	–0.52190	0.00000
H	2.24537	–0.50346	–0.87776
H	2.24455	–0.50408	0.87839
H	1.05869	–1.47485	–0.00058
C	–1.58945	–0.52190	0.00000
H	–2.24455	–0.50408	0.87839
H	–2.24538	–0.50345	–0.87776
H	–1.05869	–1.47485	–0.00058

cyclooctene (L5')

(file: COE.out / COE_PCM.out)

E(RB+HF–LYP)	–313.339279 a.u.
Sum of electronic and zero-point energies	–313.136222 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–313.168584 a.u.
ΔG_{solv}(PCM, 298.15 K)	1.7 kcal/mol

	x	*y*	*z*
C	–1.93703	–0.14017	–0.20148
C	–1.35749	–1.33062	–0.03537
C	1.20640	1.22640	0.40175
C	0.00903	–1.59985	0.54569
C	1.97192	–0.00257	–0.12197
C	1.15085	–1.26323	–0.45715
H	0.14854	–1.03149	1.47147
H	0.92844	1.06442	1.44925
H	2.72654	–0.25936	0.63137
H	1.92225	2.05516	0.42420
H	0.06957	–2.65357	0.82889
H	2.53391	0.28211	–1.01930
H	1.84482	–2.10697	–0.52632
H	0.71126	–1.15672	–1.45267
C	–1.41251	1.21747	0.21422
H	–1.34600	1.27026	1.30917
H	–2.16695	1.95789	–0.06626
C	–0.05119	1.68285	–0.37246
H	0.01491	1.39132	–1.42607
H	–0.06566	2.77741	–0.36551
H	–1.89214	–2.20144	–0.40878
H	–2.90934	–0.13075	–0.68891

buta-1,3-diene

(file: but-1,3-diene.out)

E(RB+HF–LYP)	–156.038506 a.u.
Sum of electronic and zero-point energies	–155.953728 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–155.980177 a.u.

	x	*y*	*z*
C	–1.84487	0.10956	0.00015
H	–2.01570	1.18160	0.00044
H	–2.72232	–0.52570	0.00059
C	–0.60866	–0.39940	–0.00031
H	–0.47637	–1.47961	–0.00009
C	0.60867	0.39941	–0.00031
H	0.47637	1.47966	–0.00008
C	1.84487	–0.10957	0.00015
H	2.01569	–1.18161	0.00044
H	2.72232	0.52569	0.00059

buta-1,2-diene

(file: but-1,2-diene.out)

E(RB+HF–LYP)	–156.021362 a.u.
Sum of electronic and zero-point energies	–155.937787 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–155.964724 a.u.

	x	*y*	*z*
C	1.93686	–0.21452	0.00054
C	0.69249	0.17499	–0.00195
C	–0.55355	0.56008	0.00046
H	2.48117	–0.38211	–0.92442
H	2.47629	–0.38343	0.92813
H	–0.75973	1.62953	0.00231
C	–1.74557	–0.36550	–0.00002
H	–1.43479	–1.41104	–0.00188
H	–2.37133	–0.19293	0.88185
H	–2.37303	–0.19032	–0.88015

but-1-yne

(file: but-1-yne.out)

E(RB+HF–LYP)	–156.014867 a.u.
Sum of electronic and zero-point energies	–155.930458 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–155.957304 a.u.

	x	*y*	*z*
C	1.96012	–0.26253	0.00000
C	0.83379	0.15635	0.00000
C	–0.54226	0.64731	0.00000
H	–0.69120	1.28811	0.87614
H	–0.69120	1.28811	–0.87614
C	–1.58857	–0.48275	0.00000
H	–1.47666	–1.11458	0.88369
H	–2.59850	–0.06484	0.00000
H	–1.47666	–1.11458	–0.88369
H	2.95568	–0.63248	0.00000

but-2-yne

(file: but-2-yne.out)

E(RB+HF–LYP)	–156.024934 a.u.
Sum of electronic and zero-point energies	–155.941161 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–155.969948 a.u.

	x	*y*	*z*
C	0.60148	–0.00014	0.00003
C	–0.60148	–0.00014	0.00003
C	2.06017	0.00007	–0.00001
H	2.45633	–0.66522	–0.77311
H	2.45606	1.00233	–0.18969
H	2.45633	–0.33671	0.96273
C	–2.06017	0.00007	–0.00001
H	–2.45633	–0.66519	–0.77314
H	–2.45633	–0.33675	0.96272
H	–2.45606	1.00234	–0.18965

$[PtCl_3(COC)]^-$ (1a')

(file: PtCl3(COC).out / PtCl3(COC)_PCM.out)

E(RB+HF–LYP)	–1812.412183 a.u.
Sum of electronic and zero-point energies	–1812.227827 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–1812.272828 a.u.
ΔG_{solv}(PCM, 298.15 K)	–36.2 kcal/mol

	x	*y*	*z*
C	1.05024	0.07768	0.70837
C	1.07986	0.35242	–0.50906
C	3.76516	–0.89645	0.39552
C	1.83896	0.70331	–1.71773
C	4.20488	–0.02564	–0.80669
C	3.28143	1.09747	–1.32588
H	1.83594	–0.14084	–2.41877
H	2.97388	–1.57852	0.07454
H	4.41967	–0.70880	–1.63854
H	4.62378	–1.53055	0.64493
H	1.35641	1.54088	–2.23169
H	5.16433	0.44696	–0.55629
H	3.76976	1.53749	–2.20426
H	3.21479	1.89806	–0.58224
C	1.77508	–0.27559	1.93678
H	1.52153	–1.30564	2.21386
H	1.47270	0.36236	2.77374
C	3.29832	–0.15309	1.67474
H	3.55873	0.90895	1.61197
H	3.82705	–0.54665	2.54973
Pt	–0.93762	–0.01229	–0.00186
Cl	–1.19996	2.29940	0.41159
Cl	–3.27139	–0.28558	–0.12798
Cl	–0.60912	–2.32004	–0.41470

$[(PtCl_3)_2(COD)]^{2-}$ (2a')

(file: $(PtCl_3)_2$(COD).out / $(PtCl_3)_2$(COD)_PCM.out)

E(RB+HF–LYP)	–3312.686094 a.u.
Sum of electronic and zero-point energies	–3312.495855 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–3312.549985 a.u.
ΔG_{solv}(PCM, 298.15 K)	–106.5 kcal/mol

	x	*y*	*z*
C	–1.45480	1.42916	0.68017
H	–1.85073	1.57313	1.68227
C	–0.52759	0.37881	0.53405
C	–1.58274	2.64595	–0.21240
Pt	–2.56148	–0.32201	0.02660
H	–0.31344	–0.21028	1.41727
C	0.52760	0.37881	–0.53405
C	–0.72753	3.84809	0.24608
H	–2.63692	2.94210	–0.20478
H	–1.34823	2.39317	–1.24681
Cl	–4.42988	–1.67608	–0.51317
Cl	–2.31363	0.12889	–2.28579
Cl	–2.90201	–0.80998	2.31814
H	0.31344	–0.21028	–1.41727
C	1.45481	1.42916	–0.68017
Pt	2.56148	–0.32201	–0.02660
C	0.72754	3.84809	–0.24609
H	–1.20696	4.76741	–0.11559
H	–0.73694	3.91106	1.34226
H	1.85073	1.57314	–1.68227
C	1.58274	2.64595	0.21241
Cl	4.42988	–1.67608	0.51316
Cl	2.90201	–0.80998	–2.31814
Cl	2.31363	0.12889	2.28579
H	1.20696	4.76741	0.11558
H	0.73695	3.91105	–1.34226
H	2.63692	2.94210	0.20478
H	1.34823	2.39317	1.24681

$[PtCl_3(COD)]^-$ (3a')

(file: $PtCl_3$ (COD).out / $PtCl_3$(COD)_PCM.out)

E(RB+HF–LYP)	–1812.437260 a.u.
Sum of electronic and zero-point energies	–1812.252305 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–1812.295071 a.u.
ΔG_{solv}(PCM, 298.15 K)	–36.4 kcal/mol

	x	*y*	*z*
C	–3.108334	–0.495805	–1.586269
H	–3.591396	–1.278096	–2.169205
C	–1.774670	–0.430832	–1.616544
C	–4.035336	0.423010	–0.823773
H	–1.222228	–1.133566	–2.230621
C	–0.990973	0.588293	–0.874938
C	–4.339612	–0.007749	0.631863
H	–4.983366	0.474909	–1.371273
H	–3.632611	1.441763	–0.812027
H	–0.687660	1.452354	–1.462788
C	–1.058046	0.763315	0.521057
Pt	0.919227	0.012856	–0.016173
C	–3.308319	0.428346	1.684418
H	–5.311412	0.411415	0.922276
H	–4.452288	–1.097959	0.664938
H	–0.825376	1.757806	0.892387
C	–1.864436	–0.085845	1.478553
Cl	3.167134	–0.629754	0.216343
Cl	1.586589	2.279295	–0.185147
Cl	0.309520	–2.268847	0.106251
H	–3.660371	0.071876	2.659967
H	–3.301894	1.524702	1.749055
H	–1.348963	–0.070409	2.443875
H	–1.878949	–1.125752	1.152074

[$PtCl_3$(cis-but-2-ene)]$^-$ (4a')

(file: PtCl3(butene).out / PtCl3(butene)_PCM.out)

E(RB+HF–LYP)	–1657.588982 a.u.
Sum of electronic and zero-point energies	–1657.475276 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–1657.514871 a.u.
ΔG_{solv}(PCM, 298.15 K)	–35.3 kcal/mol

	x	*y*	*z*
C	–1.55199	–1.01459	0.70389
H	–1.12659	–1.89691	1.17347
C	–1.55201	–1.01469	–0.70370
H	–1.12666	–1.89709	–1.17316
C	–2.50372	–0.24755	1.58673
H	–3.37389	–0.88049	1.81203
H	–2.02649	0.00717	2.53624
H	–2.85002	0.67845	1.13256
C	–2.50377	–0.24776	–1.58660
H	–2.02659	0.00677	–2.53618
H	–3.37399	–0.88069	–1.81175
H	–2.84999	0.67833	–1.13257
Pt	0.23867	0.00558	–0.00002
Cl	1.31199	–2.10466	0.00013
Cl	–0.77927	2.14474	–0.00003
Cl	2.33828	1.07147	–0.00015

$[PtCl_3(COE)]^-$ (5a')

(file: PtCl3(COE).out / PtCl3(COE)_PCM.out)

E(RB+HF–LYP)	–1813.659112 a.u.
Sum of electronic and zero-point energies	–1813.450212 a.u.
Sum of electronic and thermal Gibbs free energies (298.15 K)	–1813.493844 a.u.
ΔG_{solv}(PCM, 298.15 K)	–36.0 kcal/mol

	x	*y*	*z*
C	0.91127	0.77996	0.80288
C	0.93545	0.84870	–0.60232
C	4.06401	–0.62995	0.57013
C	1.88017	0.08432	–1.50150
C	4.39963	0.06840	–0.76215
C	3.26326	0.79592	–1.51087
H	1.97028	–0.95499	–1.18835
H	3.51763	–1.55558	0.36390
H	4.82224	–0.69826	–1.42392
H	5.02122	–0.94855	1.00071
H	1.46151	0.06280	–2.51096
H	5.20799	0.79171	–0.59199
H	3.59368	0.95368	–2.54361
H	3.14229	1.79946	–1.08881
C	1.75198	–0.12895	1.67642
H	1.58887	–1.17482	1.41474
H	1.39290	–0.01145	2.70339
C	3.27845	0.16189	1.64349
H	3.46340	1.23871	1.54487
H	3.68023	–0.11895	2.62336
H	0.62304	1.80097	–1.02457
H	0.57622	1.68402	1.30338
Pt	0.96431	–0.00186	0.00015
Cl	1.80418	2.20472	0.14650
Cl	–3.16584	–0.82636	–0.12685
Cl	–0.19180	–2.23752	–0.16614