Supplementary Information

Photoinduced formation of a platina-α-lactone – a carbon dioxide complex of platinum. Insights from femtosecond mid-infrared spectroscopy.

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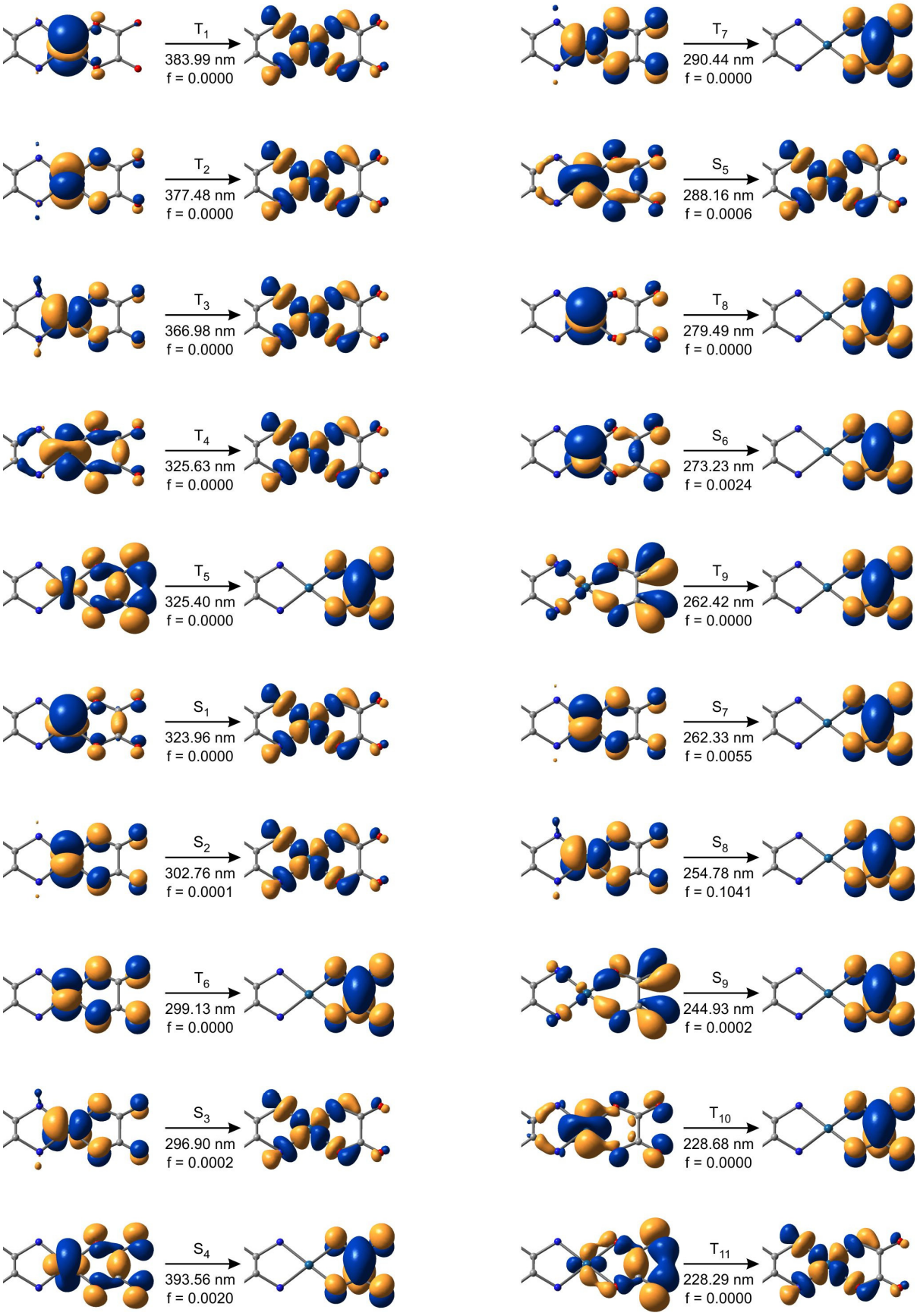
Content:

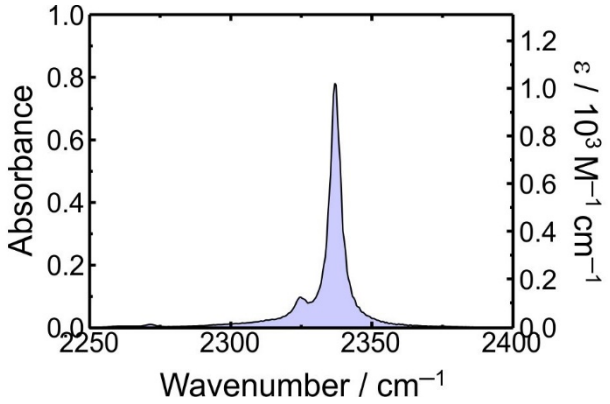
Figure S1. Natural transition orbitals, excitation wavelengths, and oscillator strengths of the twenty lowest singlet and triplet excitations at the relaxed geometry of the singlet ground state of oxaliplatin, [**1**]. Level of theory: B3LYP/GenECP



Infrared spectrum of carbon dioxide in DMSO

To estimate the extinction coefficient of CO_2 in liquid DMSO solution, a volume of 10 mL of the pure solvent was filled into a round-bottom flask, which was closed with a rubber septum. The septum itself was pierced with two capillaries serving as gas inlet and outlet. The inlet capillary was connected to a frit, which in turn was immersed in the liquid. Gaseous CO_2 (purity 99.998% Air Liquide) was allowed to bubble through the solvent for about 20 minutes at a flow rate of 1 L/min while maintaining the total gas pressure above the liquid at 1 atm. According to Yin et al.[1] the Henry constant of CO_2 in DMSO amounts to 652 Pa m^3 mol^{-1}. Accordingly, the saturation concentration of CO_2 in the solution was 0.153 mol L^{-1}. The solution was transferred into an IR-transmission cell with an optical thickness of 50 µm and its infrared spectrum was measure with an 5700 FT-IR spectrometer (Thermo Electron Corp.) at a wavenumber resolution of 0.5 cm^{-1}. As can be seen in Figure S3, a peak absorbance of this solution at 2337 cm^{-1} was 0.78. Given the above concentration, we can use Lambert-Beer's law to derive a peak molar decadic extinction coefficient of $\varepsilon(CO_2)$ = 1017 L mol^{-1} cm^{-1}.

Figure S2. FTIR-Spectrum of carbon dioxide dissolved in DMSO.



The peak extinction coefficient of oxaliplatin at 1702 cm^{-1} is equal to $\varepsilon([\mathbf{1}])$ = 2424 L mol^{-1} cm^{-1}. The 1702 cm^{-1}-bleaching amplitude after 200 ps, denoted here $\Delta OD_\infty([\mathbf{1}])$, corresponds to the absorption of all oxaliplatin complexes that have not returned to their ground state during this time window. If each of these molecules has been photochemically transformed into the product complex [**2**] by loosing a neutral CO_2-molecule, the ratio of the asymptotic CO_2-absorption at 2337 cm^{-1}, $\Delta OD_\infty(CO_2)$, to the parent bleaching magnitude at 1702 cm^{-1}, $|\Delta OD_\infty([\mathbf{1}])|$, is equal to the ratio of the peak extinction coefficients, i.e. $\varepsilon(CO_2)$ / $\varepsilon([\mathbf{1}])$ = 1017 / 2424 = 0.42. This value is in excellent agreement with the absorption-to-bleach ratio of 0.278 / 0.722 = 0.39 that can be derived directly from the pump-probe data. The primary quantum yield for CO_2-formation can be calculated from the 1702 cm^{-1}-bleaching amplitude, $\Delta OD_0([\mathbf{1}])$, at the earliest delays (i.e. at 500 fs, the signal amplitude is 3.764). We then have $\Phi(CO_2)$ = 0.278 · 2424 / (3.764 · 1017) = 18%, in excellent agreement with a primary quantum yield for photoconversion of 15 % derived from the ratio, $\Delta OD_0([\mathbf{1}])/\Delta OD_\infty([\mathbf{1}])$ (cf. main paper).

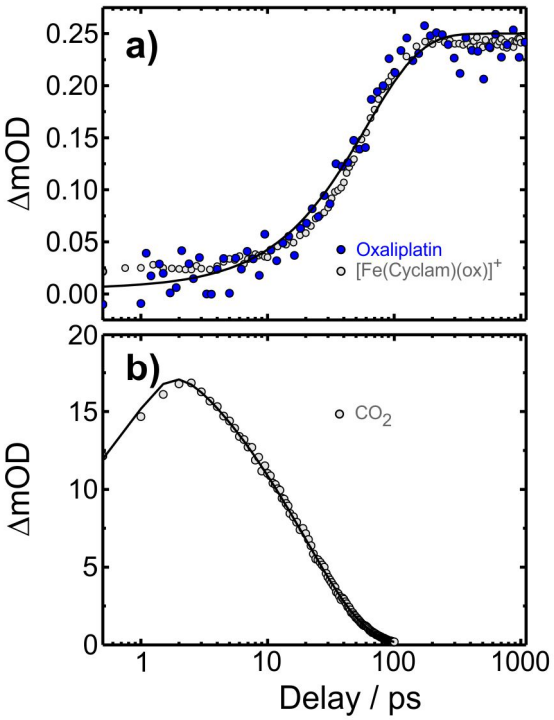
Fitting the pump-probe kinetics traces

Table S1. Optimized parameters of the nonlinear least-squares fits of the 266 nm-pump / IR-probe kinetic traces displayed in Figure 4 (main paper)

$\tilde{\nu}_{probe}/cm^{-1}$	A_0	A_1	τ_1/ps	A_2	τ_2/ps	A_3	τ_3/ps	A_4	τ_4/ps
2337	0.250	–0.250	60						
1717	0.105	0.040	100	–1.05	5.1			0.5	0.65
1702	–0.570	–0.400	50	–3.80	4.7	1.1	0.9		
1693	–0.045			1.48	5.6	–3.0	1.5	1.25	0.4
1678	–0.240	–0.180	50	–1.00	6.5	0.45	1.3		
1656	–0.045			1.15	5.0	–0.8	1.2		
1634	0.030					1.37	2.4	–0.6	0.6

Kinetic growth of the carbon dioxide absorption

Figure S3. a) Comparison of the kinetic build-up of the ν_3-absorption of carbon dioxide generated from oxaliplatin (blue circles, this work) and from $[Fe(cyclam)(ox)]^+$ (gray circles, from Ref. [2]) Both data sets were recorded in DMSO solution. Within the signal-to-noise ratio, both kinetics are identical. The solid curve is the monoexponential fit with a rise time of 60 ps. b) Decay of the n = 1 $\rightarrow$ 2 absorption of the anti-symmetric stretching vibration of CO_2 dissolved in DMSO obtained from a pure IR-pump/IR-probe experiment. The solid curve is a monoexponential fit (including convolution with the instrument response function) with a decay time of 22.5 ps.



DFT-energetics

Figure S4. Relative energies of the parent's excited states and the final product states. Singlet states are colored in blue, triplet states are colored in red. The gray dashed lines connect complementary singlet-triplet electronic configurations of the parent. Note, that the energy of the singlet metal-centered state with seesaw structure was obtained from a broken-symmetry calculation whereas those of the metal-centered singlet states with square-planar and T-shaped coordination were obtained from a TDDFT-calculation. The broken-symmetry solution is of course spin-contaminated with an $<S^2>$-value of 0.7983. We refrained here from carrying out the simple spin-projection correction according to Yamaguchi.[3]

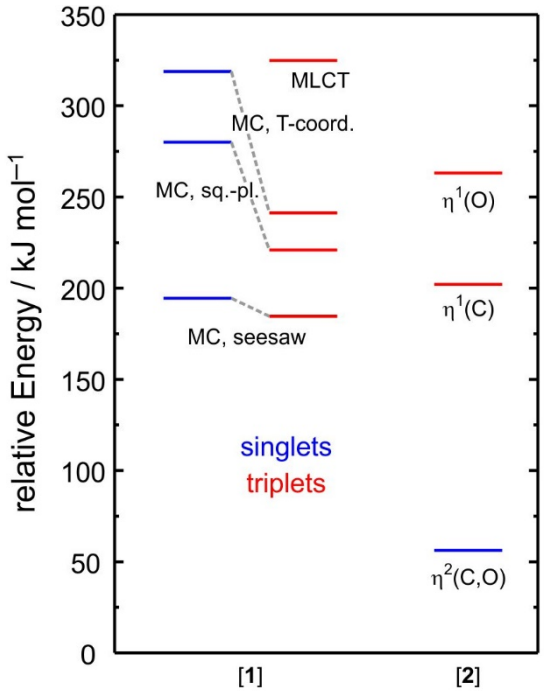
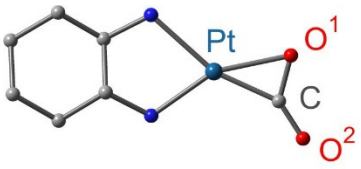
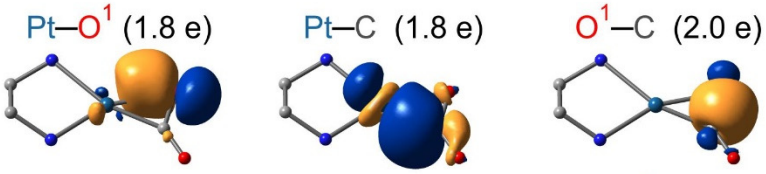


Figure S5. Natural bond orbitals, occupancies, and compositions for the product complex, (carbon dioxide)[(1R,2R)-cyclohexanediamine]platinum in its singlet ground state, $^{1}[\mathbf{2}]_{trig.}$ – η^2(C,O). Level of theory: B3LYP/GenECP



metallacyclic σ-bonds

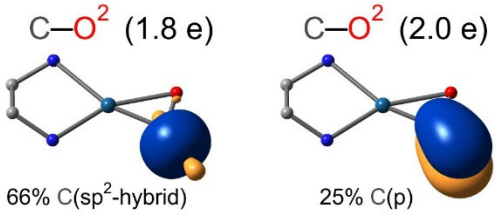


12% Pt (pd-hybrid)
88% O^1(p)

44% Pt (sd-hybrid)
56% C(sp^2-hybrid)

66% O^1(sp^2-hybrid)
34% C(sp^2-hybrid)

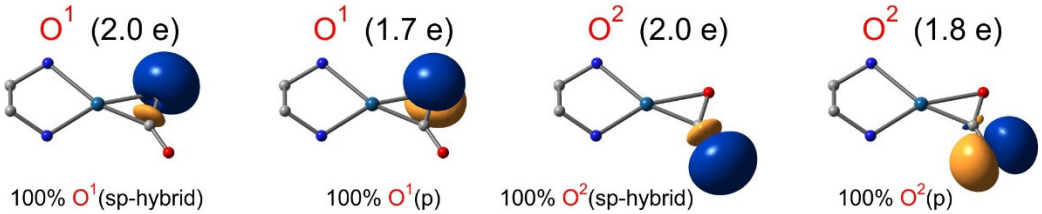
carbonyl σ and π-bond:



66% C(sp^2-hybrid)
34% O^2(sp^2-hybrid)

25% C(p)
75% O^1(p)

4 lone pairs:



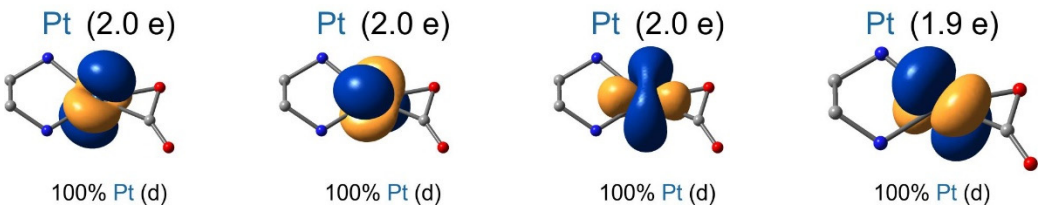
100% O^1(sp-hybrid)

100% O^1(p)

100% O^2(sp-hybrid)

100% O^2(p)

4 lone pairs:



100% Pt (d)

100% Pt (d)

100% Pt (d)

100% Pt (d)

NBO-analysis of [Pt(chda)(CO_2)] – singlet ground state from spin-restricted DFT

Natural atomic orbital occupancies at Pt

l_{ang}	AO-type	Occupancy	energy
s	Cor(5s)	1.99669	-3.84727
p_y	Cor(5p)	1.99833	-2.14044
p_x	Cor(5p)	1.99330	-2.13106
p_z	Cor(5p)	1.99862	-2.12371
d_{xy}	Val(5d)	1.85940	-0.26020
d_{yz}	Val(5d)	1.96098	-0.24363
d_{xz}	Val(5d)	1.91385	-0.24272
d_{z2}	Val(5d)	1.85519	-0.23021
d_{x2-y2}	Val(5d)	1.28249	-0.22390
s	Val(6s)	0.70086	0.07423
p_z	Val(6p)	0.01231	0.08174
p_y	Val(6p)	0.04631	0.31406
p_x	Val(6p)	0.09532	0.40774
accum.	Rydberg	0.01276	

Sum over NOA occupancies : 17.72641
Effective [core] electrons : 60
Total number of electrons : 77.72641
with [core] = [Kr] $4d^{10}$ $4f^{14}$

Natural electron configuration:
$Pt^{+0.27}$ $[core]^{60}$ $5s^{2.00}$ $5p^{5.99}$ $5d^{8.87}$ $6s^{0.70}$ $6p^{0.15}$

Idealized natural electron configuration:
Pt^0 $[core]^{60}$ $5s^2$ $5p^6$ $5d^9$ $6(sp)^1$

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  1. (1.79248) BD( 1) Pt( 1) - O( 2)
     ( 12.14%)   0.3484 * Pt( 1) s(  6.33%) p 8.43( 53.43%) d 6.12( 38.74%) f 0.23(  1.49%)
     ( 87.86%)   0.9373 * O( 2)  s(  5.27%) p17.95( 94.61%) d 0.02(  0.12%) f 0.00(  0.00%)

  2. (1.83010) BD( 1) Pt( 1) - C( 3)
     ( 44.06%)   0.6638 * Pt( 1) s( 44.53%) p 0.23( 10.12%) d 1.02( 45.25%) f 0.00(  0.09%)
     ( 55.94%)   0.7479 * C( 3)  s( 31.30%) p 2.19( 68.60%) d 0.00(  0.07%) f 0.00(  0.03%)

  4. (1.99273) BD( 1) O( 2)  - C( 3)
     ( 66.38%)   0.8148 * O( 2)  s( 29.91%) p 2.34( 69.92%) d 0.01(  0.16%) f 0.00(  0.00%)
     ( 33.62%)   0.5798 * C( 3)  s( 31.31%) p 2.19( 68.53%) d 0.01(  0.16%) f 0.00(  0.01%)

  5. (1.99859) BD( 1) C( 3)  - O( 4)
     ( 24.64%)   0.4964 * C( 3)  s(  0.00%) p 1.00( 99.84%) d 0.00(  0.15%) f 0.00(  0.00%)
     ( 75.36%)   0.8681 * O( 4)  s(  0.00%) p 1.00( 99.66%) d 0.00(  0.32%) f 0.00(  0.02%)

  6. (1.99521) BD( 2) C( 3)  - O( 4)
     ( 35.23%)   0.5936 * C( 3)  s( 37.97%) p 1.63( 61.95%) d 0.00(  0.06%) f 0.00(  0.02%)
     ( 64.77%)   0.8048 * O( 4)  s( 39.36%) p 1.53( 60.06%) d 0.01(  0.57%) f 0.00(  0.01%)

 29. (1.99008) LP ( 1) Pt( 1)    s(  2.46%) p 0.01(  0.03%) d39.59( 97.51%) f 0.00(  0.00%)
 30. (1.98567) LP ( 2) Pt( 1)    s(  4.27%) p 0.00(  0.02%) d22.40( 95.71%) f 0.00(  0.00%)
 31. (1.97599) LP ( 3) Pt( 1)    s(  6.55%) p 0.05(  0.31%) d14.23( 93.14%) f 0.00(  0.00%)
 32. (1.92327) LP ( 4) Pt( 1)    s(  0.00%) p 0.00(  0.01%) d 1.00( 99.99%) f 0.00(  0.00%)
 33. (0.07733) LP*( 5) Pt( 1)    s(  3.17%) p29.57( 93.74%) d 0.84(  2.67%) f 0.13(  0.42%)
 34. (0.01050) LP*( 6) Pt( 1)    s(  0.00%) p 1.00( 95.07%) d 0.01(  0.96%) f 0.04(  3.97%)
 33. (0.07733) LP*( 5) Pt( 1)    s(  3.17%) p29.57( 93.74%) d 0.84(  2.67%) f 0.13(  0.42%)
 34. (0.01050) LP*( 6) Pt( 1)    s(  0.00%) p 1.00( 95.07%) d 0.01(  0.96%) f 0.04(  3.97%)

 35. (1.96571) LP ( 1) O( 2)     s( 64.80%) p 0.54( 35.19%) d 0.00(  0.02%) f 0.00(  0.00%)
 36. (1.73737) LP ( 2) O( 2)     s(  0.00%) p 1.00( 99.84%) d 0.00(  0.15%) f 0.00(  0.01%)
 37. (1.97160) LP ( 1) O( 4)     s( 60.06%) p 0.66( 39.87%) d 0.00(  0.07%) f 0.00(  0.00%)
 38. (1.82162) LP ( 2) O( 4)     s(  0.46%) p99.99( 99.27%) d 0.56(  0.26%) f 0.04(  0.02%)

247. (0.24356) BD*( 1) Pt( 1) - O( 2)
     ( 87.86%)   0.9373 * Pt( 1) s(  6.33%) p 8.43( 53.43%) d 6.12( 38.74%) f 0.23(  1.49%)
     ( 12.14%)  -0.3484 * O( 2)  s(  5.27%) p17.95( 94.61%) d 0.02(  0.12%) f 0.00(  0.00%)
248. (0.26839) BD*( 1) Pt( 1) - C( 3)
     ( 55.94%)   0.7479 * Pt( 1) s( 44.53%) p 0.23( 10.12%) d 1.02( 45.25%) f 0.00(  0.09%)
     ( 44.06%)  -0.6638 * C( 3)  s( 31.30%) p 2.19( 68.60%) d 0.00(  0.07%) f 0.00(  0.03%)
250. (0.08519) BD*( 1) O( 2)  - C( 3)
     ( 33.62%)   0.5798 * O( 2)  s( 29.91%) p 2.34( 69.92%) d 0.01(  0.16%) f 0.00(  0.00%)
     ( 66.38%)  -0.8148 * C( 3)  s( 31.31%) p 2.19( 68.53%) d 0.01(  0.16%) f 0.00(  0.01%)
251. (0.31439) BD*( 1) C( 3)  - O( 4)
     ( 75.36%)   0.8681 * C( 3)  s(  0.00%) p 1.00( 99.84%) d 0.00(  0.15%) f 0.00(  0.00%)
     ( 24.64%)  -0.4964 * O( 4)  s(  0.00%) p 1.00( 99.66%) d 0.00(  0.32%) f 0.00(  0.02%)
252. (0.03723) BD*( 2) C( 3)  - O( 4)
     ( 64.77%)   0.8048 * C( 3)  s( 37.97%) p 1.63( 61.95%) d 0.00(  0.06%) f 0.00(  0.02%)
     ( 35.23%)  -0.5936 * O( 4)  s( 39.36%) p 1.53( 60.06%) d 0.01(  0.57%) f 0.00(  0.01%)
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Figure S6. CASSCF(18,12)-active space for the product complex mode, (carbon dioxide)(ethanediamine)platinum in its singlet ground state, $^{1}[\mathbf{2}]_{trig.}$ – η^{2}(C,O).

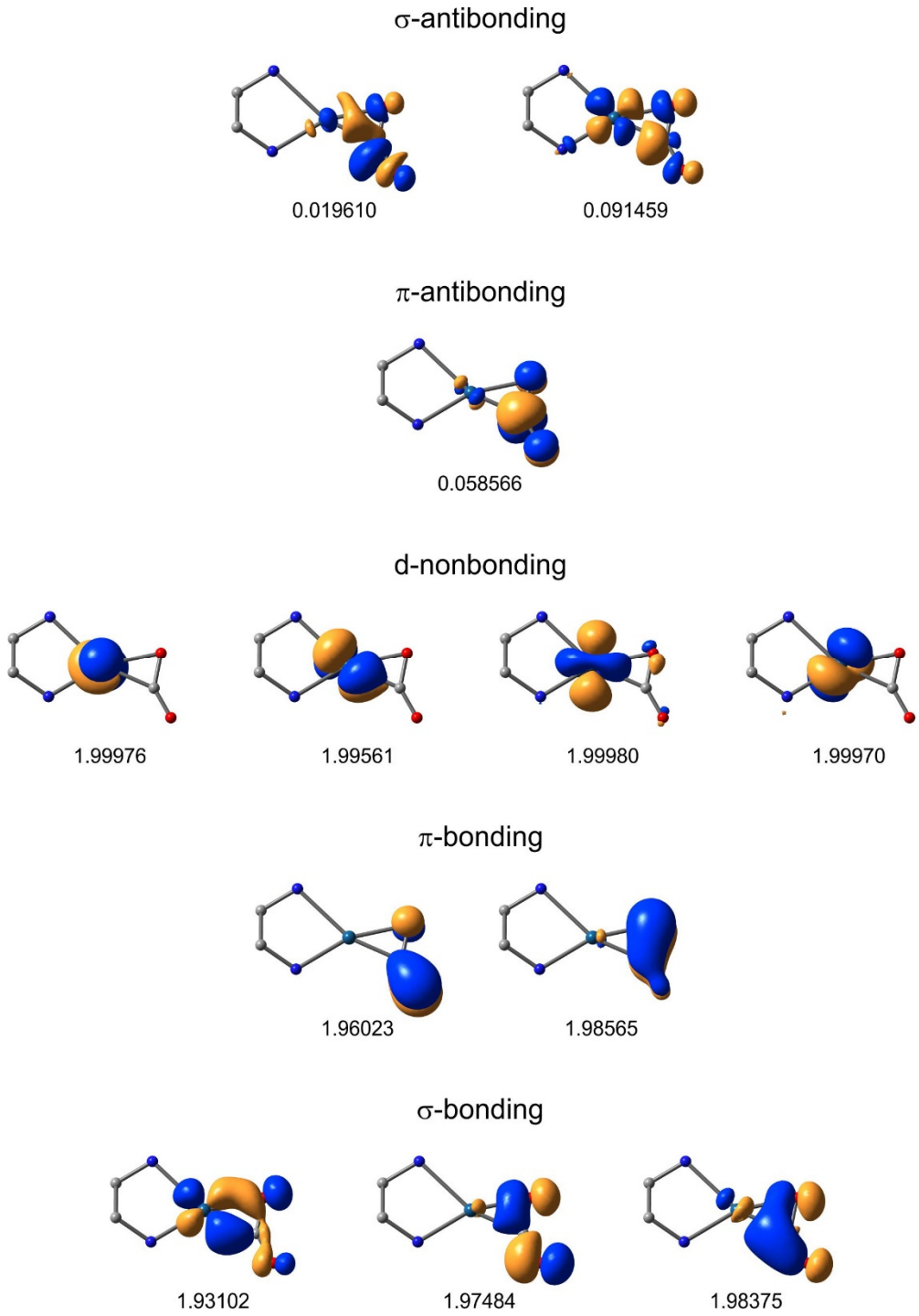
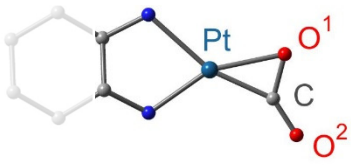
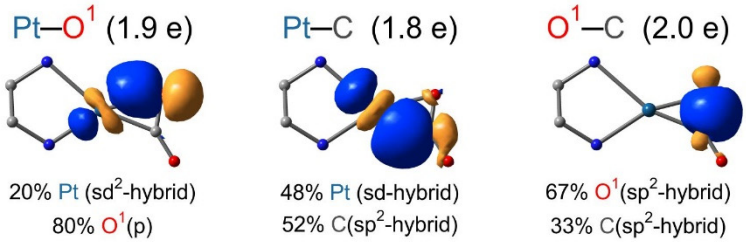


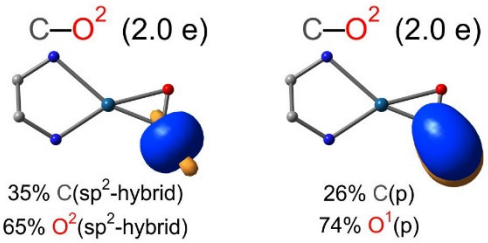
Figure S7. Natural bond orbitals, occupancies, and compositions for the product complex, (carbon dioxide)(ethylene diamine)platinum in its singlet ground state, $^{1}[\mathbf{2}]_{trig.}$ – η^2(C,O). Level of theory: CASSCF(18,12)/GenECP



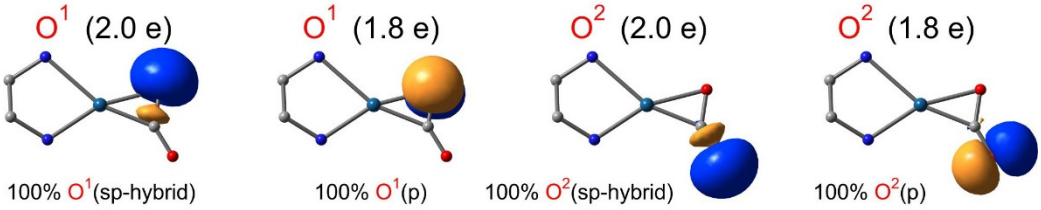
metallacyclic σ-bonds



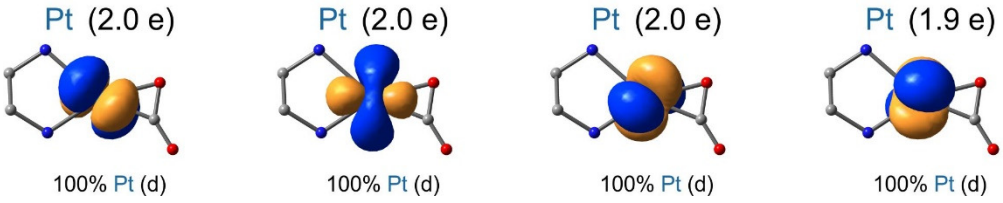
carbonyl σ and π-bond:



4 lone pairs:



4 lone pairs:



NBO-analysis of [Pt(en)(CO_2)] – singlet ground state from CAS(18,12)

Natural atomic orbital occupancies at Pt

l_{ang}	AO-type	Occupancy	energy
s	Cor(5s)	1.99996	
py	Cor(5p)	1.99986	
pz	Cor(5p)	1.99984	
px	Cor(5p)	1.99964	
dyz	Val(5d)	1.96162	
dxz	Val(5d)	1.95320	
dz2	Val(5d)	1.86990	
dxy	Val(5d)	1.84046	
dx2y2	Val(5d)	1.33534	
s	Val(6s)	0.63096	
px	Ryd(6p)	0.00590	
dxy	Ryd(6d)	0.00222	
pz	Ryd(6p)	0.00220	
py	Ryd(6p)	0.00190	
accum.	Rydberg	0.01276	

Sum over NOA occupancies : 17.603
Effective [core] electrons : 60
Total number of electrons : 77.603
with [core] = [Kr] $4d^{10}$ $4f^{14}$

Natural electron configuration:
$Pt^{+0.40}$ [core]^{60} $5s^{2.00}$ $5p^{6.00}$ $5d^{8.96}$ $6s^{0.63}$ $6p^{0.01}$

Idealized natural electron configuration:
Pt^{0} [core]^{60} $5s^{2}$ $5p^{6}$ $5d^{9}$ $6s^{1}$

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 22. (1.88206) BD( 1) Pt(1) - O(2)
     ( 19.57%)   0.4424 * Pt(1) s( 33.22%) p  0.01(  0.32%) d 2.00( 66.33%) f 0.00(  0.13%)
     ( 80.43%)   0.8968 * O(2)  s(  4.28%) p 22.28( 95.33%) d 0.09(  0.39%) f 0.00(  0.00%)

 23. (1.81348) BD( 1) Pt(1) - C(3)
     ( 48.01%)   0.6929 * Pt(1) s( 53.43%) p  0.01(  0.47%) d 0.86( 46.04%) f 0.00(  0.06%)
     ( 51.99%)   0.7210 * C(3)  s( 28.68%) p  2.48( 70.98%) d 0.01(  0.30%) f 0.00(  0.05%)

 24. (1.98890) BD( 1) O(2) - C(3)
     ( 67.26%)   0.8201 * O(2)  s( 31.77%) p 2.13( 67.56%) d 0.02(  0.66%) f 0.00(  0.01%)
     ( 32.74%)   0.5722 * C(3)  s( 33.76%) p 1.96( 66.03%) d 0.01(  0.17%) f 0.00(  0.04%)

 25. (1.99892) BD( 1) C(3) - O(4)
     ( 25.92%)   0.5091 * C(3)  s(  0.00%) p 1.00( 99.71%) d 0.00(  0.26%) f 0.00(  0.03%)
     ( 74.08%)   0.8607 * O(4)  s(  0.00%) p 1.00( 99.57%) d 0.00(  0.41%) f 0.00(  0.01%)

 26. (1.99444) BD( 2) C(3) - O(4)
     ( 35.25%)   0.5937 * C(3)  s( 39.15%) p 1.55( 60.69%) d 0.00(  0.11%) f 0.00(  0.05%)
     ( 64.75%)   0.8047 * O(4)  s( 40.21%) p 1.47( 59.03%) d 0.02(  0.74%) f 0.00(  0.02%)

 12. (1.99422) LP( 1) Pt(1)      s(  4.50%) p 0.00(  0.01%) d21.22( 95.49%) f 0.00(  0.00%)
 13. (1.99100) LP( 2) Pt(1)      s(  1.37%) p 0.03(  0.04%) d72.09( 98.59%) f 0.00(  0.00%)
 14. (1.98544) LP( 3) Pt(1)      s(  6.88%) p 0.00(  0.01%) d13.53( 93.11%) f 0.00(  0.00%)
 15. (1.96248) LP( 4) Pt(1)      s(  0.00%) p 1.00(  0.02%) d99.99( 99.98%) f 0.01(  0.00%)

 16. (0.98806) LP( 1) O(2)       s( 63.88%) p 0.56( 36.04%) d 0.00(  0.08%) f 0.00(  0.00%)
 17. (0.88278) LP( 2) O(2)       s(  0.00%) p 1.00( 99.66%) d 0.00(  0.33%) f 0.00(  0.01%)
 18. (0.98789) LP( 1) O(4)       s( 58.77%) p 0.70( 41.12%) d 0.00(  0.11%) f 0.00(  0.00%)
 19. (0.90504) LP( 2) O(4)       s(  0.91%) p99.99( 98.77%) d 0.34(  0.31%) f 0.02(  0.01%)

 38. (0.35966) BD*( 1) Pt(1) - O(2)
     ( 80.43%)   0.8968 * Pt(1) s( 33.22%) p 0.01(  0.32%) d 2.00( 66.33%) f 0.00(  0.13%)
     ( 19.57%)  -0.4424 * O(2)  s(  4.28%) p22.28( 95.33%) d 0.09(  0.39%) f 0.00(  0.00%)

 39. (0.26206) BD*( 1) Pt(1) - C(3)
     ( 51.99%)   0.7210 * Pt(1) s( 53.43%) p 0.01(  0.47%) d 0.86( 46.04%) f 0.00(  0.06%)
     ( 48.01%)  -0.6929 * C(3)  s( 28.68%) p 2.48( 70.98%) d 0.01(  0.30%) f 0.00(  0.05%)

 40. (0.07382) BD*( 1) O(2) - C(3)
     ( 32.74%)   0.5722 * O(2)  s( 31.77%) p 2.13( 67.56%) d 0.02(  0.66%) f 0.00(  0.01%)
     ( 67.26%)  -0.8201 * C(3)  s( 33.76%) p 1.96( 66.03%) d 0.01(  0.17%) f 0.00(  0.04%)

 41. (0.25764) BD*( 1) C(3) - O(4)
     ( 74.08%)   0.8607 * C(3)  s(  0.00%) p 1.00( 99.71%) d 0.00(  0.26%) f 0.00(  0.03%)
     ( 25.92%)  -0.5091 * O(4)  s(  0.00%) p 1.00( 99.57%) d 0.00(  0.41%) f 0.00(  0.01%)

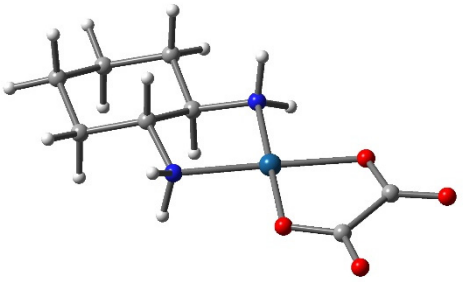
 42. (0.02992) BD*( 2) C(3) - O(4)
     ( 64.75%)   0.8047 * C(3)  s( 39.15%) p 1.55( 60.69%) d 0.00(  0.11%) f 0.00(  0.05%)
     ( 35.25%)  -0.5937 * O(4)  s( 40.21%) p 1.47( 59.03%) d 0.02(  0.74%) f 0.00(  0.02%)
```

Optimized geometry of [Pt(chda)(C_2O_4)] – singlet ground state from spin-restricted DFT

[**1**](S_0): E(RB3LYP) = -843.326113893 E_h

Pt	0.033685	1.449387	0.164037
O	0.388717	3.422508	-0.169734
C	1.646811	3.713917	-0.308871
O	2.069553	4.837457	-0.519692
O	2.058960	1.353827	0.027754
C	2.625908	2.502478	-0.188002
O	3.829466	2.662093	-0.293953
N	-2.020956	1.558772	0.328960
N	-0.313529	-0.560584	0.473418
H	-2.256013	1.954883	1.238775
H	-2.421823	2.185225	-0.365573
H	-0.174813	-1.055772	-0.407299
H	0.351953	-0.960260	1.131269
C	-2.612848	0.193530	0.197837
C	-1.709984	-0.771278	0.960629
C	-4.060273	0.096995	0.672615
H	-2.560890	-0.055843	-0.873624
C	-2.196315	-2.211695	0.828397
H	-1.707216	-0.479644	2.022812
C	-4.564473	-1.347500	0.552681
H	-4.116567	0.425463	1.725278
H	-4.691687	0.781405	0.084914
C	-3.652383	-2.328123	1.297813
H	-1.541968	-2.880440	1.408951
H	-2.120269	-2.519701	-0.229340
H	-5.593241	-1.412879	0.938879
H	-4.608930	-1.627355	-0.514255
H	-4.004716	-3.361349	1.155927
H	-3.700552	-2.123622	2.381528

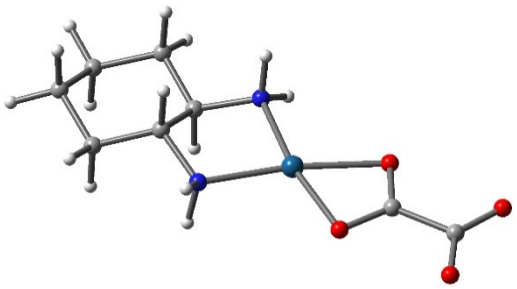
Square-planar coordination
$\kappa^2(O^1,O^2)$ planar oxalate



[**1**](S_0): E(RB3LYP) = -843.292815899 E_h

Pt	0.048884	1.455673	0.155330
O	2.107292	1.715359	-0.050166
C	1.953975	2.970396	-0.222132
O	0.747641	3.384786	-0.191705
O	4.273369	3.388218	-0.410734
C	3.155778	3.932808	-0.450183
O	2.841930	5.121218	-0.641340
N	-2.003295	1.547349	0.331984
N	-0.317486	-0.547577	0.474597
H	-2.223722	1.942135	1.246457
H	-2.397262	2.183638	-0.357758
H	-0.174044	-1.038905	-0.407990
H	0.354780	-0.937794	1.131447
C	-2.609517	0.189993	0.197547
C	-1.711001	-0.770754	0.963809
C	-4.057674	0.101717	0.669220
H	-2.556357	-0.059702	-0.873670
C	-2.191749	-2.212280	0.831273
H	-1.710009	-0.478038	2.025642
C	-4.560570	-1.343911	0.549638
H	-4.116386	0.432425	1.720859
H	-4.686632	0.784657	0.077394
C	-3.650193	-2.325218	1.296601
H	-1.540144	-2.879636	1.416195
H	-2.112085	-2.521845	-0.225569
H	-5.589686	-1.408879	0.934673
H	-4.603922	-1.623933	-0.517224
H	-4.003391	-3.357870	1.153551
H	-3.700614	-2.121014	2.380177

Square-planar coordination
$\kappa^2(O^1,O^{1'})$ planar oxalate

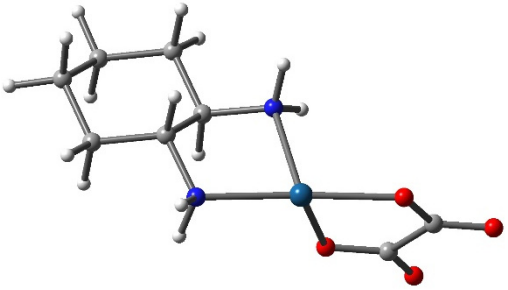


Optimized geometries of [Pt(chda)(C_2O_4)] – triplet states from spin-unrestricted DFT

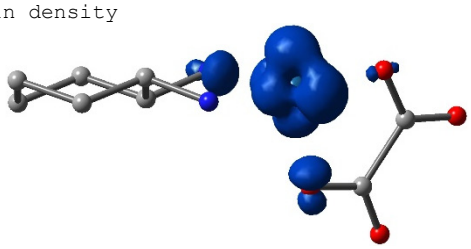
$^{3\text{-MC}}$[**1**]$_{\text{seesaw}}$: E(UB3LYP) = -843.252064947 E_h

Pt	0.602766	1.086005	0.838281
O	1.535381	2.951201	0.929348
C	1.666877	3.596444	-0.183565
O	2.184713	4.701273	-0.272448
O	0.625708	1.711953	-1.309073
C	1.123445	2.884730	-1.472741
O	1.199239	3.464304	-2.551895
N	-1.641416	1.506114	0.742754
N	-0.187762	-0.895200	0.846095
H	-1.968515	1.845562	1.643237
H	-1.807064	2.235242	0.056755
H	-0.009315	-1.317510	-0.062783
H	0.300617	-1.474704	1.523399
C	-2.308492	0.242573	0.363323
C	-1.649002	-0.908073	1.129177
C	-3.822100	0.263027	0.593094
H	-2.105669	0.097175	-0.710521
C	-2.289575	-2.255097	0.795292
H	-1.755623	-0.706959	2.207583
C	-4.459510	-1.087190	0.246881
H	-4.014002	0.500454	1.654783
H	-4.269977	1.073029	-0.003443
C	-3.802694	-2.226610	1.030807
H	-1.812419	-3.045202	1.396394
H	-2.084775	-2.489230	-0.264864
H	-5.540868	-1.051347	0.451571
H	-4.348344	-1.276141	-0.835308
H	-4.240857	-3.195756	0.745860
H	-4.001413	-2.093994	2.108787

Seesaw coordination
$\kappa^2(O^1,O^2)$ planar oxalate



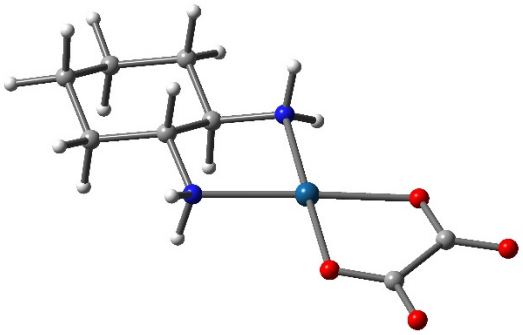
Spin density



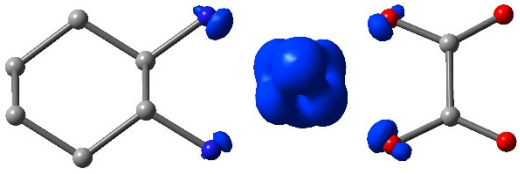
$^{3\text{-MC}}$[**1**]$_{\text{sq.-pl.}}$: E(UB3LYP) = -843.241935732 E_h

Pt	0.131338	1.518893	0.154324
O	0.652325	3.598197	-0.200199
C	1.902028	3.867472	-0.339934
O	2.344096	4.989257	-0.573746
O	2.378478	1.512971	0.028199
C	2.901564	2.660122	-0.194732
O	4.108573	2.875500	-0.299661
N	-2.181521	1.546464	0.333373
N	-0.382707	-0.629966	0.438207
H	-2.419843	1.933933	1.242794
H	-2.591927	2.158419	-0.363757
H	-0.281582	-1.098443	-0.459578
H	0.281742	-1.070782	1.066616
C	-2.696644	0.167806	0.199480
C	-1.764788	-0.793850	0.948260
C	-4.143626	0.020545	0.679754
H	-2.644481	-0.079580	-0.874126
C	-2.258039	-2.239535	0.850723
H	-1.739421	-0.487595	2.007302
C	-4.632430	-1.427389	0.576599
H	-4.198901	0.354670	1.731461
H	-4.789856	0.695176	0.096291
C	-3.703756	-2.377582	1.337149
H	-1.585660	-2.893663	1.428105
H	-2.191456	-2.562514	-0.203802
H	-5.661604	-1.502089	0.961507
H	-4.670020	-1.724508	-0.486269
H	-4.037656	-3.420614	1.221177
H	-3.748620	-2.149422	2.416616

Square-planar coordination
$\kappa^2(O^1,O^2)$ planar oxalate



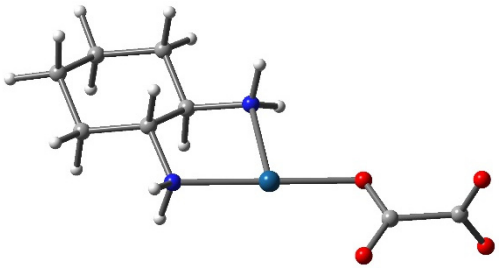
Spin density



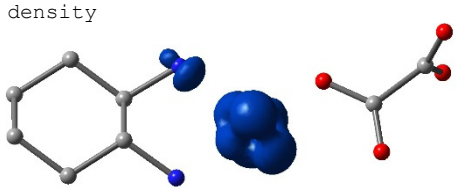
$^{3\text{-MC}}$[**1**]$_{\text{T-coord.}}$: E(UB3LYP) = -843.234200554 E_h

Pt	0.437691	0.977899	0.144957
O	3.237727	2.117387	-0.266293
C	2.427471	3.047366	-0.281965
O	1.142954	2.911457	-0.153328
O	3.179024	5.109670	0.599809
C	2.891857	4.505266	-0.457890
O	2.947609	4.919573	-1.637270
N	-1.824814	1.410956	0.342193
N	-0.352441	-1.001065	0.394896
H	-1.964542	1.825809	1.260185
H	-2.132194	2.086271	-0.349634
H	-0.339108	-1.463352	-0.513037
H	0.242354	-1.558163	1.002122
C	-2.540339	0.124671	0.213445
C	-1.742828	-0.972358	0.927727
C	-3.976059	0.185742	0.744240
H	-2.559051	-0.111857	-0.863153
C	-2.435230	-2.330633	0.807209
H	-1.654889	-0.697089	1.991290
C	-4.675773	-1.172804	0.632170
H	-3.944759	0.500455	1.802669
H	-4.533530	0.961009	0.195972
C	-3.872644	-2.271370	1.334147
H	-1.850021	-3.089751	1.349739
H	-2.441989	-2.629521	-0.256334
H	-5.688344	-1.104200	1.059420
H	-4.799301	-1.431673	-0.433928
H	-4.357469	-3.250510	1.197961
H	-3.853453	-2.076171	2.420605

T-coordination
$\kappa^1(O^1)$ D_{2d}-symmetrical (twisted) oxalate



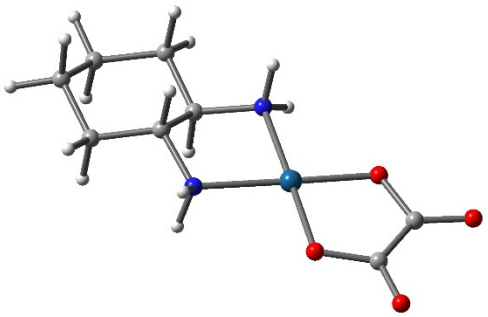
Spin density



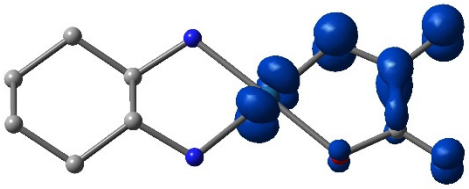
$^{3\text{-MLCT}}$[**1**]$_{\text{sq.-pl.}}$: E(UB3LYP) = -843.202410053 E_h

Pt	0.060799	1.472145	0.174248
O	0.336357	3.329079	-0.154686
C	1.719167	3.651461	-0.326865
O	1.964534	4.865814	-0.533570
O	2.044726	1.331124	0.012938
C	2.616031	2.545845	-0.230691
O	3.857363	2.620355	-0.352493
N	-2.029399	1.576154	0.364031
N	-0.305002	-0.561968	0.505740
H	-2.261155	1.958108	1.280254
H	-2.435489	2.209853	-0.320680
H	-0.153032	-1.052996	-0.376311
H	0.360222	-0.960166	1.165695
C	-2.605636	0.206820	0.213071
C	-1.709453	-0.764749	0.978453
C	-4.059734	0.099429	0.666410
H	-2.538904	-0.031304	-0.860195
C	-2.193924	-2.204780	0.832619
H	-1.713326	-0.480048	2.042357
C	-4.558179	-1.344855	0.526942
H	-4.132522	0.419376	1.720522
H	-4.683523	0.787056	0.074618
C	-3.655761	-2.326935	1.280866
H	-1.546153	-2.874998	1.418497
H	-2.102658	-2.506967	-0.225535
H	-5.592972	-1.414794	0.895550
H	-4.584136	-1.617254	-0.542468
H	-4.002192	-3.360490	1.128075
H	-3.720442	-2.128420	2.364740

square-planar coordination
$\kappa^2(O^1,O^2)$ planar oxalate



Spin density

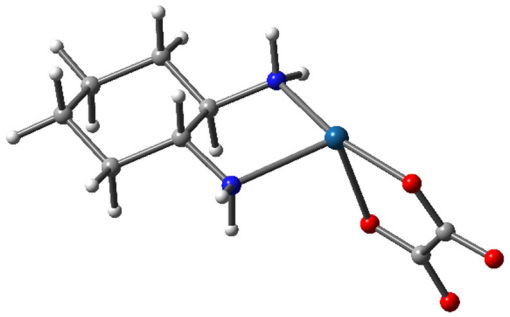


Optimized geometry of [Pt(chda)(C_2O_4)] – open-shell singlet state from spin-unrestricted DFT

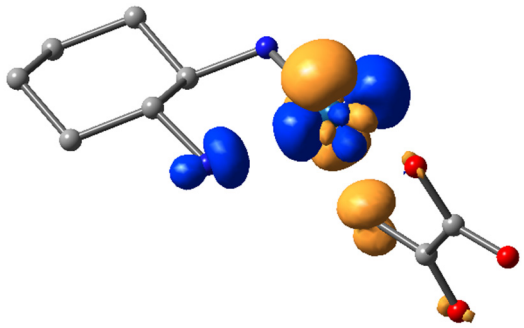
$^{1\text{-MC}}$[**1**]$_{\text{seesaw}}$: E(UB3LYP) = -843.255809591 E_h

Pt	-0.155887	1.993556	0.871827
O	1.803292	2.697709	0.942823
C	2.351168	3.040816	-0.183393
O	3.455317	3.560832	-0.261555
O	0.382663	2.207611	-1.312561
C	1.529649	2.749822	-1.482781
O	2.026956	3.014754	-2.574894
N	-2.230855	1.691634	0.814130
N	-0.325742	-0.304557	0.672625
H	-2.576557	1.882546	1.755510
H	-2.636123	2.397044	0.205832
H	-0.099234	-0.533834	-0.292714
H	0.352727	-0.783047	1.257803
C	-2.656560	0.331882	0.390639
C	-1.706178	-0.686209	1.028605
C	-4.116005	0.042724	0.737805
H	-2.517697	0.292391	-0.700693
C	-2.086134	-2.116177	0.637894
H	-1.776258	-0.579087	2.123179
C	-4.497435	-1.391114	0.358224
H	-4.254655	0.187327	1.824772
H	-4.768359	0.770661	0.230673
C	-3.549251	-2.411015	0.997772
H	-1.410264	-2.823265	1.143399
H	-1.934235	-2.240812	-0.446922
H	-5.536466	-1.591087	0.660031
H	-4.461247	-1.498810	-0.740560
H	-3.812678	-3.431447	0.682109
H	-3.664595	-2.378771	2.095204

Twisted seesaw coordination
$\kappa^2(O^1,O^2)$ planar oxalate



Spin density

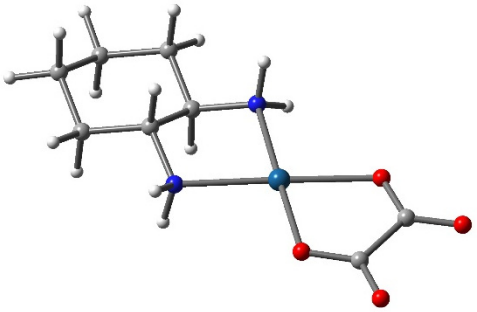


Optimized geometries of [Pt(chda)(C_2O_4)] – excited singlet state from TD-DFT

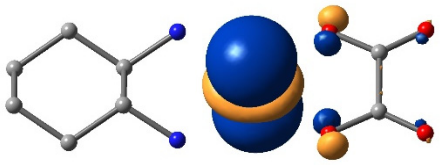
$^{1\text{-MC}}$[**1**]$_{\text{sq.-pl.}}$: E(TD-B3LYP) = -843.219459407 E_h

Pt	0.124144	1.515340	0.145528
O	0.630330	3.633956	-0.167837
C	1.877106	3.900126	-0.311630
O	2.332038	5.018582	-0.538157
O	2.329483	1.538150	0.036131
C	2.866760	2.682756	-0.177792
O	4.074991	2.881782	-0.279013
N	-2.138907	1.521740	0.309464
N	-0.380242	-0.667470	0.405638
H	-2.379333	1.920036	1.213911
H	-2.536793	2.134029	-0.395095
H	-0.291993	-1.125884	-0.498185
H	0.294165	-1.107475	1.023359
C	-2.678176	0.149575	0.184049
C	-1.754074	-0.817665	0.933527
C	-4.124555	0.031629	0.672019
H	-2.634512	-0.103318	-0.888453
C	-2.269146	-2.256896	0.857940
H	-1.714709	-0.501348	1.989255
C	-4.633035	-1.411107	0.590562
H	-4.170705	0.380360	1.719317
H	-4.764003	0.706782	0.081796
C	-3.713041	-2.364205	1.358173
H	-1.602388	-2.912690	1.439805
H	-2.215625	-2.595449	-0.192273
H	-5.660785	-1.466056	0.982375
H	-4.681130	-1.721645	-0.467992
H	-4.064852	-3.403245	1.261427
H	-3.745409	-2.118494	2.434281

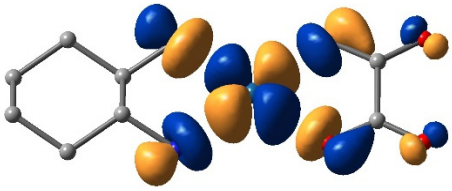
Square-planar coordination
$\kappa^2(O^1,O^2)$ planar oxalate



HOTO



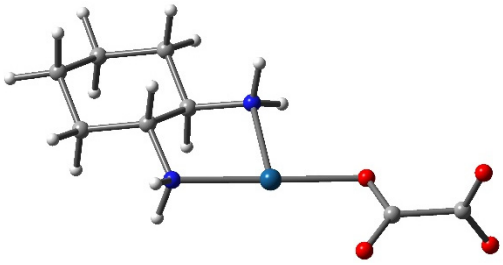
LUTO



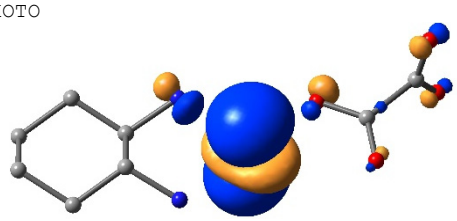
$^{1\text{-MC}}$[**1**]$_{\text{T-coord.}}$: E(TD-B3LYP) = -843.204697116 E_h

Pt	0.385266	0.977908	0.082958
O	3.142598	2.113422	-0.295360
C	2.346653	3.059001	-0.329348
O	1.062356	2.938087	-0.244647
O	3.106731	5.099794	0.594408
C	2.849169	4.508520	-0.477371
O	2.954063	4.926510	-1.651718
N	-1.758673	1.385391	0.404108
N	-0.338304	-1.028727	0.428940
H	-1.857731	1.758695	1.346522
H	-2.078318	2.099464	-0.244442
H	-0.302903	-1.539411	-0.451310
H	0.269611	-1.527889	1.071628
C	-2.503590	0.117574	0.238754
C	-1.732926	-0.998522	0.949649
C	-3.946567	0.206352	0.742455
H	-2.506903	-0.096624	-0.842329
C	-2.445913	-2.343300	0.807605
H	-1.654717	-0.735457	2.016914
C	-4.662102	-1.141285	0.595309
H	-3.931711	0.507134	1.804912
H	-4.478769	0.996188	0.190225
C	-3.893604	-2.259804	1.304480
H	-1.886020	-3.114087	1.359949
H	-2.435435	-2.638129	-0.256892
H	-5.684090	-1.061371	0.997054
H	-4.761706	-1.384776	-0.476852
H	-4.393689	-3.228348	1.149743
H	-3.894867	-2.073293	2.392580

T-coordination
$\kappa^1(O^1)$ D_{2d}-symmetrical (twisted) oxalate



HOTO



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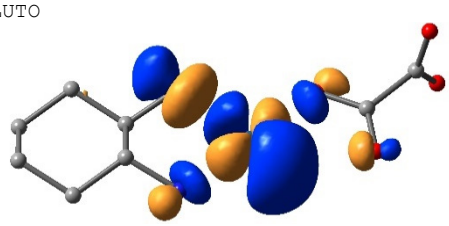
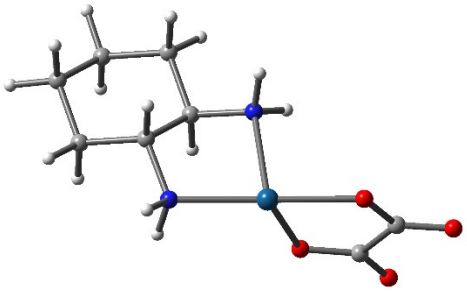


Optimized geometries of [Pt(chda)(C_2O_4)] – triplet states from TD-DFT with closed-shell reference

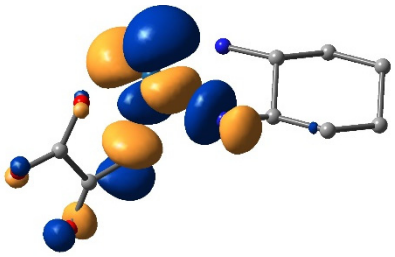
$^{3\text{-MC}}$[**1**]$_{\text{seesaw}}$: E(TD-B3LYP) = -843.256707740 E_h

Pt	0.604228	1.093952	0.874181
O	1.371973	3.042652	0.924058
C	1.566224	3.617546	-0.216881
O	2.018754	4.748239	-0.340117
O	0.735690	1.603519	-1.299487
C	1.186130	2.789367	-1.497559
O	1.333109	3.302568	-2.603149
N	-1.636999	1.515147	0.791172
N	-0.173871	-0.897531	0.861283
H	-1.955791	1.829908	1.703716
H	-1.820046	2.260716	0.127660
H	0.010681	-1.303201	-0.054005
H	0.303261	-1.494233	1.531380
C	-2.300453	0.258012	0.390381
C	-1.640061	-0.910525	1.130126
C	-3.812777	0.275989	0.629473
H	-2.103388	0.134919	-0.687280
C	-2.284469	-2.245768	0.755462
H	-1.754071	-0.737616	2.212670
C	-4.458035	-1.060275	0.249242
H	-3.996511	0.484245	1.698827
H	-4.260301	1.105421	0.059864
C	-3.797774	-2.223382	0.994548
H	-1.808650	-3.055964	1.330155
H	-2.081658	-2.446359	-0.312036
H	-5.537425	-1.026897	0.464866
H	-4.357358	-1.217032	-0.839046
H	-4.237312	-3.182911	0.680646
H	-3.993744	-2.124433	2.076634

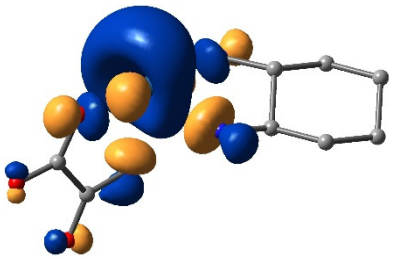
Twisted seesaw coordination
$\kappa^2(O^1,O^2)$ planar oxalate



HOTO



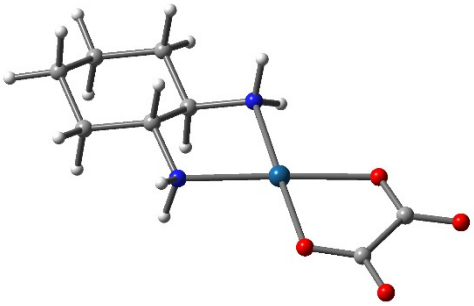
LUTO



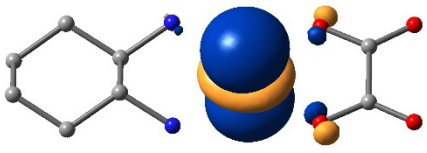
$^{3\text{-MC}}$[**1**]$_{\text{sq.-pl.}}$: E(TD-B3LYP) = -843.244370805 E_h

Pt	0.130845	1.517808	0.155717
O	0.651268	3.600412	-0.190342
C	1.900676	3.868838	-0.333165
O	2.343484	4.991353	-0.563485
O	2.377828	1.512075	0.024049
C	2.900224	2.659727	-0.196877
O	4.107029	2.875175	-0.306447
N	-2.180680	1.546781	0.334094
N	-0.382310	-0.632838	0.431873
H	-2.423338	1.932023	1.243078
H	-2.593162	2.158433	-0.361849
H	-0.286395	-1.101625	-0.466088
H	0.282110	-1.078127	1.056930
C	-2.695217	0.167734	0.197906
C	-1.763269	-0.793993	0.946411
C	-4.142751	0.020503	0.675893
H	-2.641595	-0.078911	-0.875848
C	-2.258037	-2.239350	0.854469
H	-1.734915	-0.484847	2.004595
C	-4.631459	-1.427496	0.575923
H	-4.199947	0.357225	1.726707
H	-4.788018	0.693852	0.089807
C	-3.703775	-2.375019	1.341080
H	-1.585889	-2.891552	1.434358
H	-2.191562	-2.566630	-0.198754
H	-5.661345	-1.501330	0.959014
H	-4.666865	-1.727997	-0.486093
H	-4.038171	-3.418362	1.229662
H	-3.749155	-2.141968	2.419513

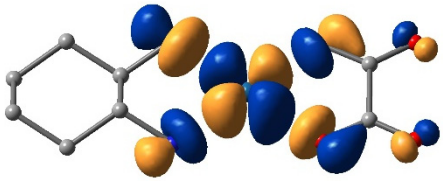
square-planar coordination
$\kappa^2(O^1,O^2)$ planar oxalate



HOTO



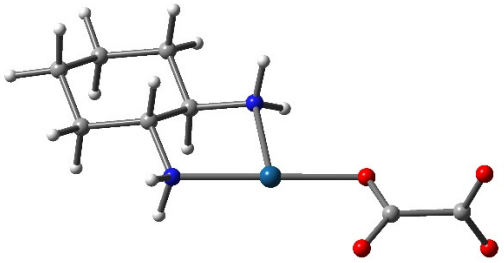
LUTO



$^{3\text{-MC}}$[**1**]$_{\text{T-coord.}}$: E(TD-B3LYP) = -843.235290898 E_h

Pt	0.435588	0.991148	0.149142
O	3.223616	2.108867	-0.254367
C	2.425971	3.050966	-0.277550
O	1.140724	2.931327	-0.150478
O	3.206303	5.107682	0.592596
C	2.912998	4.499764	-0.461629
O	2.977585	4.906141	-1.643552
N	-1.836948	1.415254	0.345624
N	-0.354553	-0.992288	0.390169
H	-1.981027	1.827150	1.263930
H	-2.148982	2.090237	-0.344068
H	-0.344081	-1.450591	-0.519629
H	0.241144	-1.553657	0.992404
C	-2.546038	0.126227	0.213955
C	-1.743525	-0.968319	0.926557
C	-3.982659	0.180043	0.742991
H	-2.562633	-0.109311	-0.862980
C	-2.431434	-2.329066	0.808320
H	-1.654212	-0.692320	1.989912
C	-4.676508	-1.181368	0.631786
H	-3.953909	0.495776	1.801236
H	-4.543007	0.952665	0.193808
C	-3.868749	-2.275233	1.335824
H	-1.842823	-3.085381	1.351160
H	-2.437748	-2.629181	-0.254909
H	-5.689844	-1.116975	1.057873
H	-4.797732	-1.442323	-0.434106
H	-4.349540	-3.256694	1.202034
H	-3.850070	-2.077524	2.421874

T-coordination
$\kappa^1(O^1)$ D_{2d}-symmetrical (twisted) oxalate



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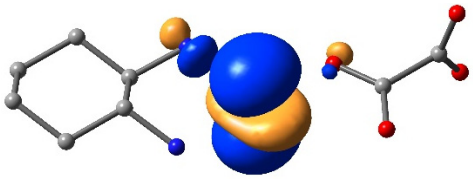

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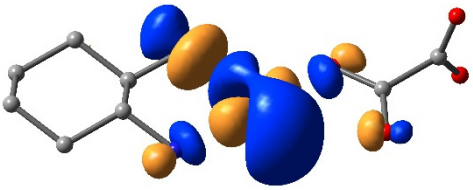
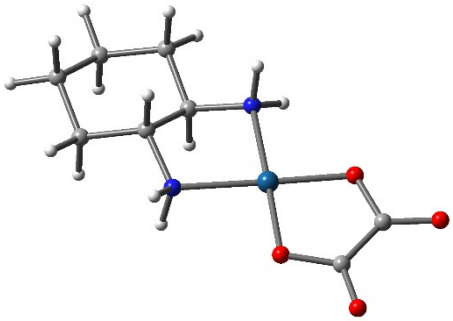


$^{3\text{-MLCT}}$[**1**]$_{\text{sq.-pl.}}$: E(TD-B3LYP) =-843.204685377 E_h

Pt	0.059464	1.467645	0.174682
O	0.327857	3.324848	-0.149066
C	1.705623	3.643845	-0.321999
O	1.955455	4.854196	-0.529590
O	2.043113	1.322732	0.014890
C	2.607079	2.539067	-0.228810
O	3.847353	2.624949	-0.354747
N	-2.025026	1.576750	0.361858
N	-0.302800	-0.560400	0.505266
H	-2.258098	1.960459	1.276949
H	-2.428991	2.210032	-0.324453
H	-0.150563	-1.050696	-0.377245
H	0.362753	-0.959399	1.164385
C	-2.603076	0.207857	0.211997
C	-1.707464	-0.763850	0.977863
C	-4.057016	0.101954	0.665713
H	-2.536498	-0.030936	-0.861136
C	-2.192293	-2.203567	0.832202
H	-1.711351	-0.479005	2.041697
C	-4.556325	-1.342163	0.527259
H	-4.129284	0.422605	1.719639
H	-4.680511	0.789579	0.073634
C	-3.654082	-2.324634	1.280986
H	-1.544744	-2.874011	1.418048
H	-2.101437	-2.505893	-0.225943
H	-5.590885	-1.411290	0.896629
H	-4.583212	-1.614980	-0.542011
H	-4.001289	-3.357964	1.128594
H	-3.718147	-2.125838	2.364844

Square-planar structure
$\kappa^2(O^1,O^2)$ planar oxalate



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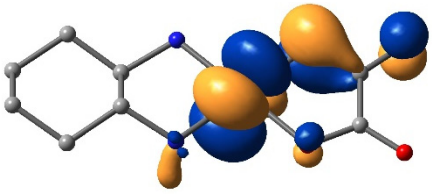

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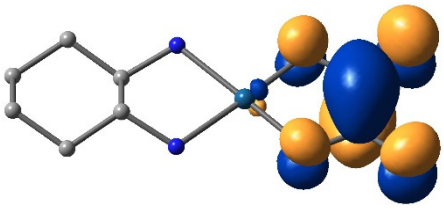
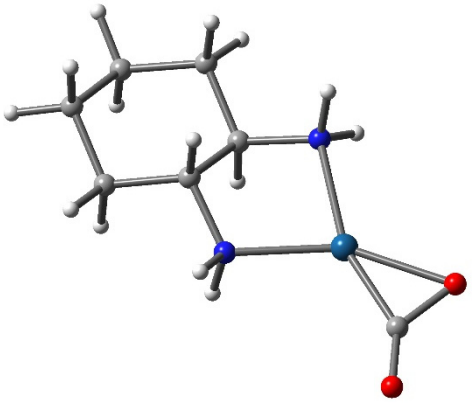


Optimized geometries of [Pt(chda)(CO_2)] – singlet/triplet states from restricted/unrestricted DFT

[**2**](S_0): E(RB3LYP) = -654.630620198 E_h

Pt	0.075283	1.557534	-0.069986
O	1.326201	3.252238	-0.386693
C	1.916103	2.101279	-0.339327
O	3.078555	1.759025	-0.443641
N	-2.212358	1.603765	0.186017
N	-0.379320	-0.459076	0.194408
H	-2.417885	2.021856	1.090152
H	-2.670989	2.184329	-0.507755
H	-0.342498	-0.915673	-0.715909
H	0.344696	-0.897702	0.756536
C	-2.728344	0.219923	0.133113
C	-1.711507	-0.692813	0.817895
C	-4.118129	0.045206	0.748989
H	-2.767869	-0.058430	-0.933385
C	-2.143348	-2.157478	0.768875
H	-1.614418	-0.373621	1.868115
C	-4.564236	-1.421223	0.717167
H	-4.085729	0.401415	1.794553
H	-4.837737	0.685789	0.215050
C	-3.534011	-2.334231	1.389691
H	-1.400102	-2.782222	1.289233
H	-2.162978	-2.488488	-0.284956
H	-5.545339	-1.524128	1.206850
H	-4.700910	-1.736187	-0.332373
H	-3.844465	-3.387904	1.312446
H	-3.482228	-2.098577	2.467190
H	-4.348344	-1.276141	-0.835308

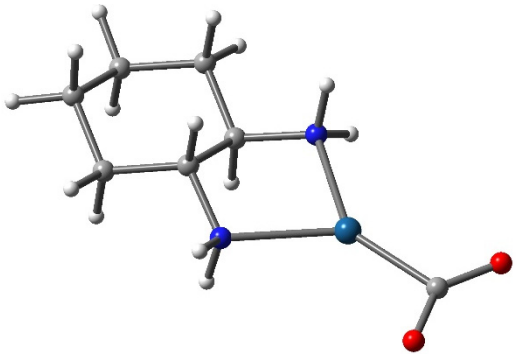
Trigonal / square-planar coordination
η^2(O,C) CO_2 neutral / carbonite dianion



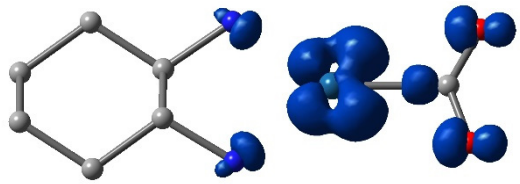
[**2**](T_1): E(UB3LYP) = -654.575075388 E_h

Pt	0.138960	1.488187	-0.062840
O	1.585928	3.858511	-0.525790
C	1.810177	2.649332	-0.401364
O	2.834087	1.950956	-0.435741
N	-2.084640	1.515940	0.199011
N	-0.361117	-0.675641	0.223587
H	-2.267751	1.938173	1.106303
H	-2.512952	2.119232	-0.495455
H	-0.333577	-1.122758	-0.689876
H	0.347631	-1.125846	0.793586
C	-2.658630	0.150241	0.136959
C	-1.701003	-0.818441	0.835233
C	-4.065222	0.064255	0.733914
H	-2.697003	-0.121039	-0.930927
C	-2.232928	-2.252573	0.796234
H	-1.597040	-0.498193	1.885011
C	-4.600298	-1.371821	0.702007
H	-4.024435	0.420252	1.779159
H	-4.737734	0.745262	0.188948
C	-3.639086	-2.339131	1.399031
H	-1.535093	-2.916206	1.330935
H	-2.258210	-2.591677	-0.254854
H	-5.594248	-1.408682	1.174818
H	-4.737887	-1.685544	-0.347718
H	-4.012613	-3.372626	1.327170
H	-3.588876	-2.095558	2.474914
H	-4.348344	-1.276141	-0.835308

Trigonal-planar coordination
η^1(C) carbon dioxide radical anion



Spin density

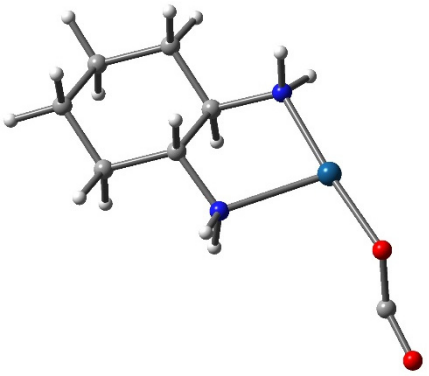


This is clearly a carbon dioxide radical anion that is ferromagnetically coupled to a platinum(I) center!

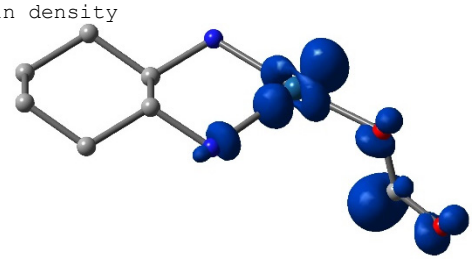
[**2**](T_2): E(RB3LYP) = -654.551846618 E_h

Pt	-0.461959	2.186667	0.225388
O	1.543657	2.737648	0.056298
C	2.183224	2.421675	-0.994250
O	3.340489	2.606008	-1.307804
N	-2.483135	1.772310	0.481339
N	-0.397385	-0.095213	0.321096
H	-2.746952	2.027435	1.432003
H	-3.057711	2.347346	-0.129181
H	-0.262231	-0.450921	-0.621729
H	0.373128	-0.437939	0.884926
C	-2.802224	0.333203	0.250557
C	-1.697911	-0.528390	0.870347
C	-4.182534	-0.050176	0.784256
H	-2.776498	0.186057	-0.841294
C	-1.983543	-2.018695	0.667030
H	-1.666487	-0.311544	1.950974
C	-4.464385	-1.542406	0.579621
H	-4.222914	0.188297	1.862373
H	-4.951798	0.565143	0.290844
C	-3.364873	-2.403941	1.207350
H	-1.192435	-2.609853	1.154905
H	-1.932106	-2.243510	-0.413437
H	-5.446768	-1.797563	1.006910
H	-4.524795	-1.756140	-0.502003
H	-3.556353	-3.471781	1.017600
H	-3.376700	-2.270787	2.303578

T-coordination
η^1(O) bent carbon dioxide radical anion



Spin density



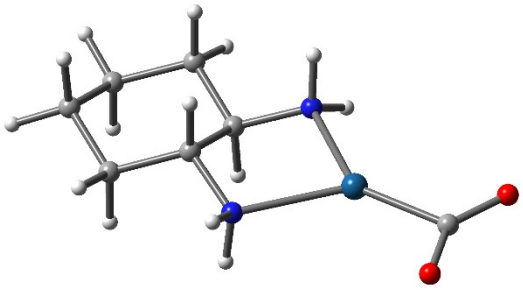
This is clearly a carbon dioxide radical anion that is ferromagnetically coupled to a platinum(I) center!

Optimized geometry of [Pt(chda)(CO_2)] – triplet states from TD-DFT with closed-shell reference

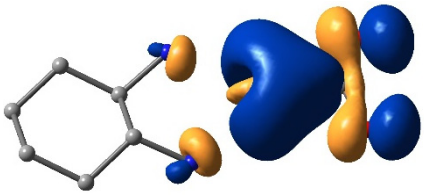
[**2**](T_0): E(TD-B3LYP) = -654.572972478 E_h

Pt	0.117664	1.498089	-0.059860
O	1.603032	3.847072	-0.566545
C	1.808194	2.638832	-0.420070
O	2.816764	1.917484	-0.438837
N	-2.084689	1.517536	0.213358
N	-0.360202	-0.662068	0.235013
H	-2.264640	1.932806	1.124517
H	-2.515676	2.126002	-0.474911
H	-0.324283	-1.111465	-0.676907
H	0.350894	-1.102483	0.809494
C	-2.659194	0.152207	0.143359
C	-1.701807	-0.815471	0.841727
C	-4.067388	0.063320	0.734509
H	-2.692967	-0.114639	-0.925684
C	-2.229010	-2.250683	0.794795
H	-1.603071	-0.498640	1.892977
C	-4.598947	-1.373782	0.694299
H	-4.031462	0.415246	1.781266
H	-4.738713	0.745294	0.189291
C	-3.638060	-2.342168	1.390800
H	-1.532436	-2.914668	1.330622
H	-2.248688	-2.586110	-0.257569
H	-5.594540	-1.415178	1.163108
H	-4.731803	-1.682946	-0.357380
H	-4.009508	-3.375905	1.312979
H	-3.593024	-2.103078	2.467908

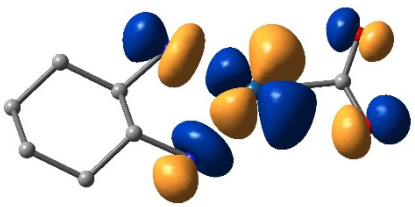
Trigonal-planar
η^1(C) carbon dioxide radical anion



HOTO



LUTO



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