

Electronic Supporting Information (ESI+)

Dynamics of the efficient cyclometalation of the undercoordinated organoplatinum complex [Pt(COD)(neoPh)]⁺ (neoPh = 2-methyl-2-phenylpropyl).

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contents:

- Fig. S1. 400 MHz ¹H NMR spectrum of the rearranged product [Pt(COD)(η²-neoPh)] acetone-d⁶.
- Fig. S2. 300 MHz ¹⁹⁵Pt/¹H HMBC spectrum of [Pt(COD)(η²-neoPh)] in acetone-d⁶.
- Fig. S3. View on the crystal structure of [Pt(COD)(η²-neoPh)] along the crystallographic *a* axis.
- Fig. S4. View on the crystal structure of [Pt(COD)(η²-neoPh)] along the crystallographic *b* axis.
- Fig. S5. C–H⋯π type intermolecular interaction in the crystal structure of [Pt(COD)(η²-neoPh)].
- Fig. S6. Optimised ground state geometry of [Pt(COD)(neoPh)Cl] obtained by DFT calculations.
- Fig. S7. Optimised ground state geometry of [Pt(COD)(neoPh)]⁺ obtained by DFT calculations.
- Fig. S8. Optimised ground state geometry of [Pt(COD)(η²-neoPh)] obtained by DFT calculations.
- Fig. S9. Snapshot along the MD trajectory at *n_H* = 0.46 which corresponds to a C–H bond length of 1.45 Å and a C–Pt bond length of 2.11 Å.
- Fig. S10. Relation between the coordination number *n_H* and the C–H distance.
- Table S1. Results of the structure refinement for [Pt(COD)(η²-neoPh)].
- Table S2. Selected structural data of doubly cyclometalated complexes.

References

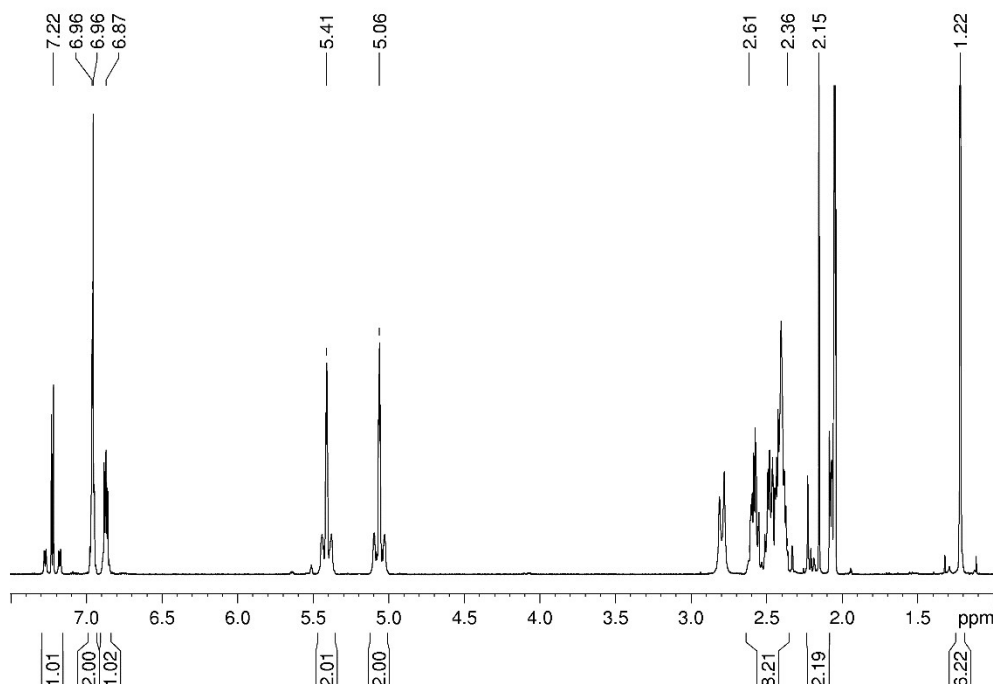


Fig. S1. 400 MHz ¹H NMR spectrum of the rearranged product [Pt(COD)(η²-neoPh)] acetone-d⁶.

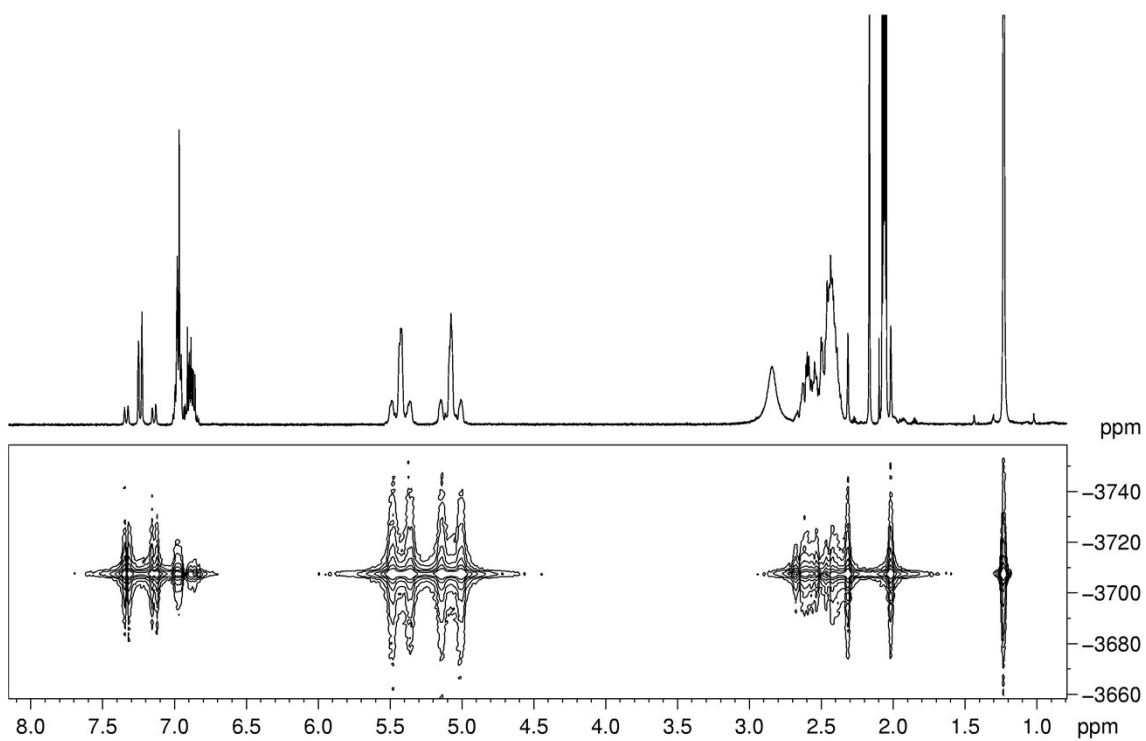


Fig. S2. 300 MHz $^{195}\text{Pt}^1\text{H}$ HMBC spectrum of $[\text{Pt}(\text{COD})(\eta^2\text{-neoPh})]$ in acetone- d_6 .

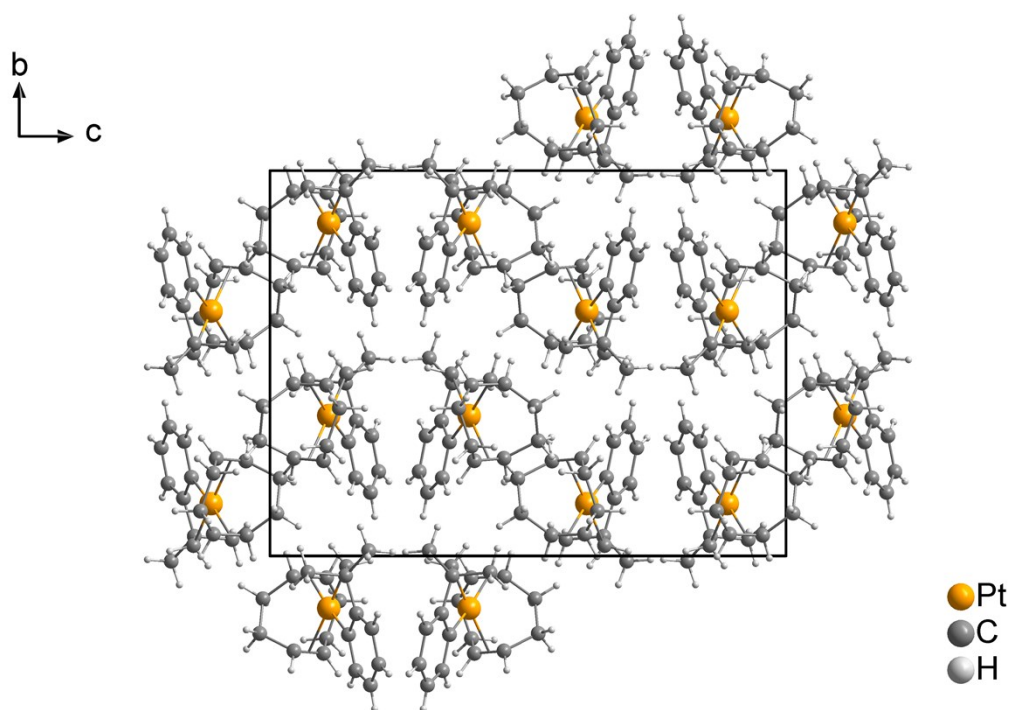


Fig. S3. View on the crystal structure of $[\text{Pt}(\text{COD})(\eta^2\text{-neoPh})]$ along the crystallographic a axis.

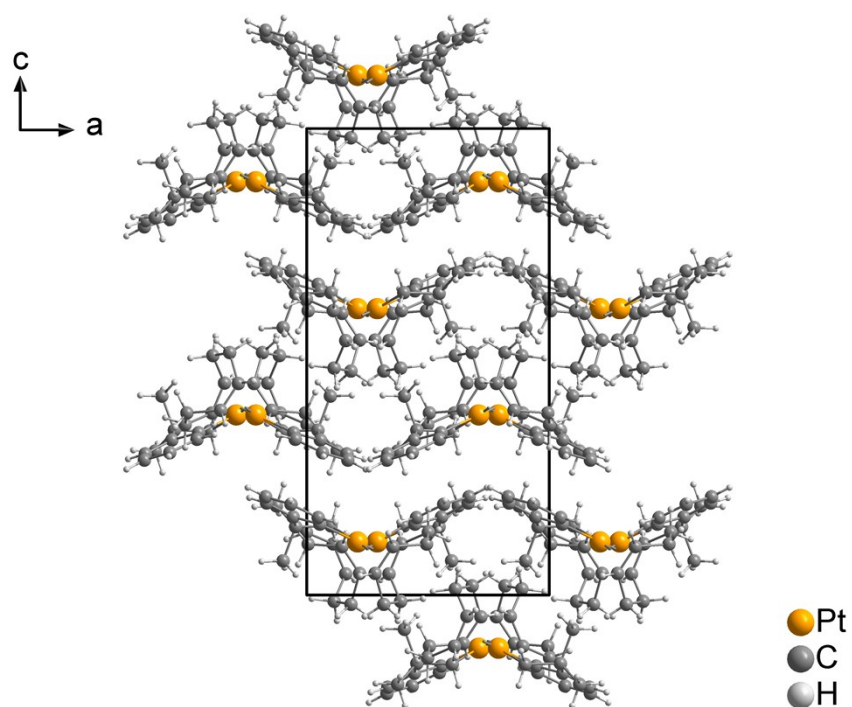


Fig. S4. View on the crystal structure of [Pt(COD)(η^2 -neoPh)] along the crystallographic *b* axis.

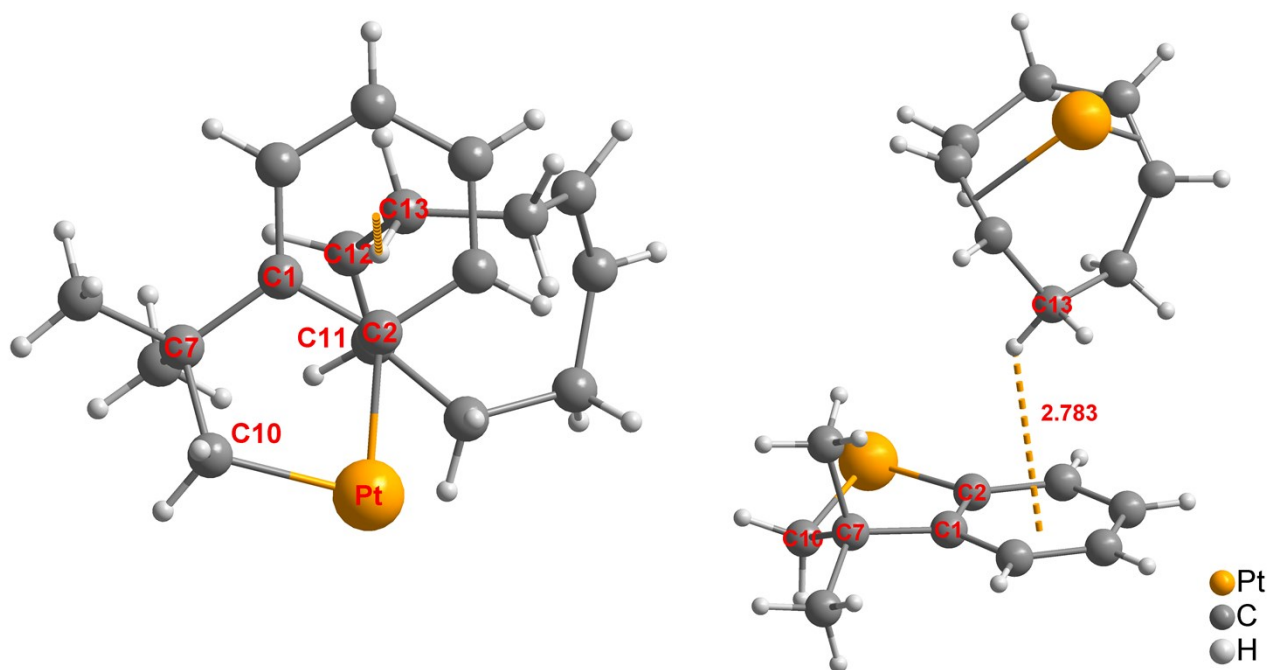


Fig. S5. C-H \cdots π type intermolecular interaction in the crystal structure of [Pt(COD)(η^2 -neoPh)]. Top view (left) and total view (right).

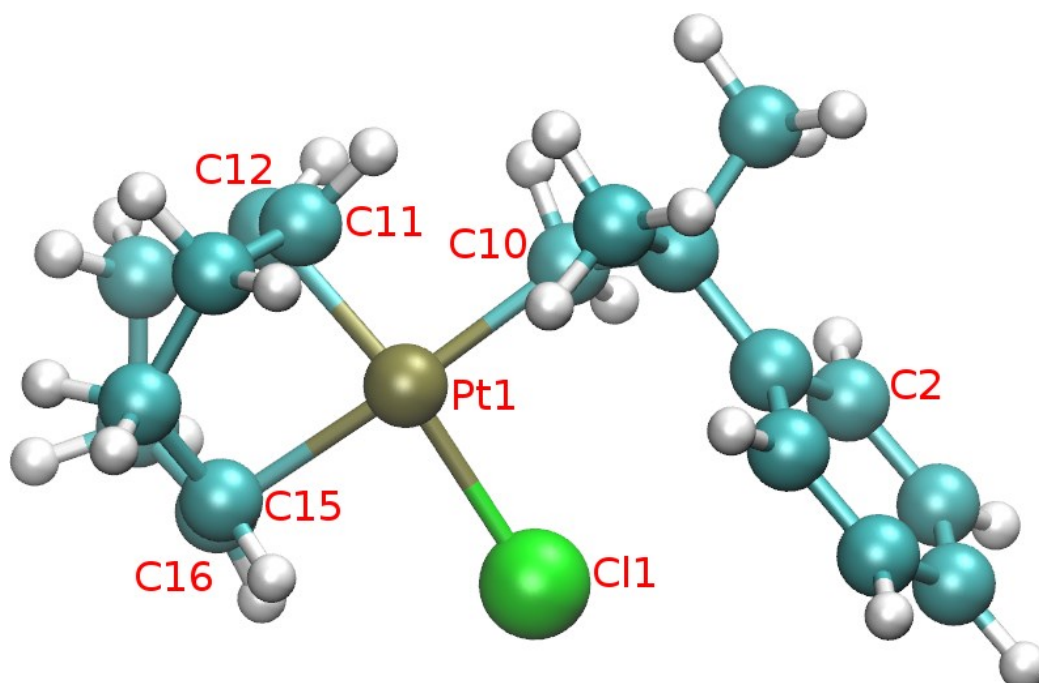


Fig. S6. Optimised ground state geometry of [Pt(COD)(neoPh)Cl] obtained by DFT calculations using the PBE0 functional and the SDD basis set.

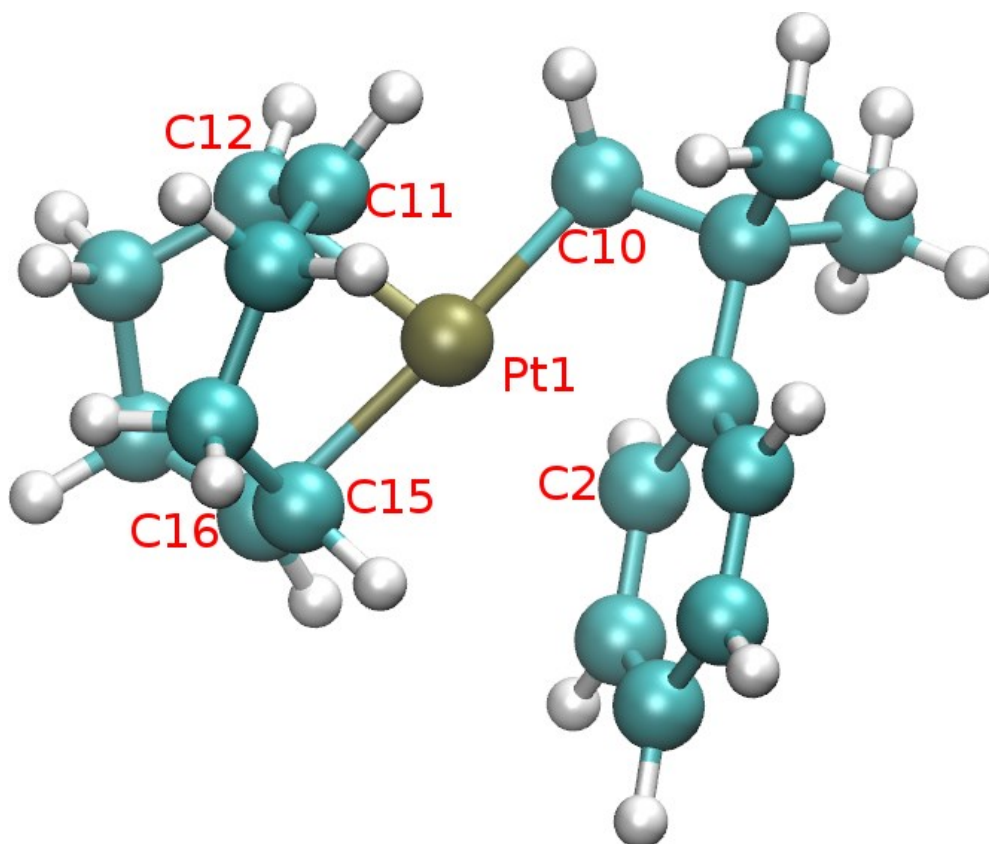


Fig. S7. Optimised ground state geometry of [Pt(COD)(neoPh)]⁺ obtained by DFT calculations using the PBE0 functional and the SDD basis set.

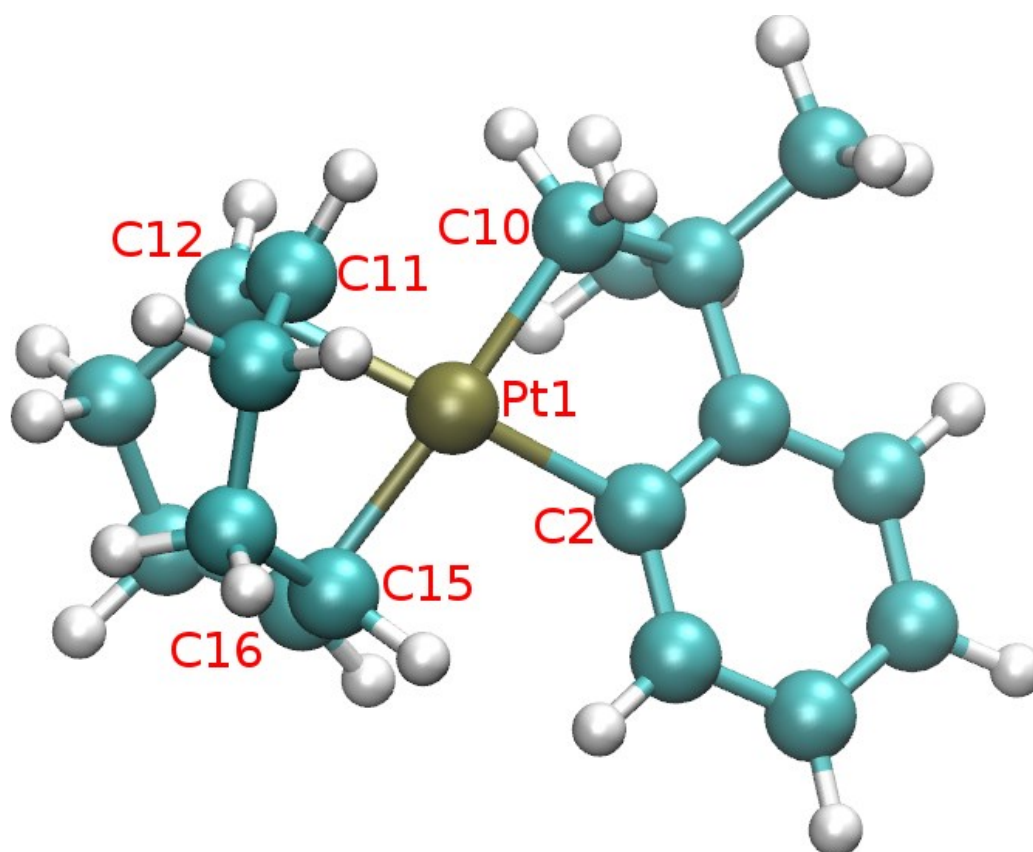


Fig. S8. Optimised ground state geometry of [Pt(COD)(η^2 -neoPh)] obtained by DFT calculations using the PBE0 functional and the SDD basis set.

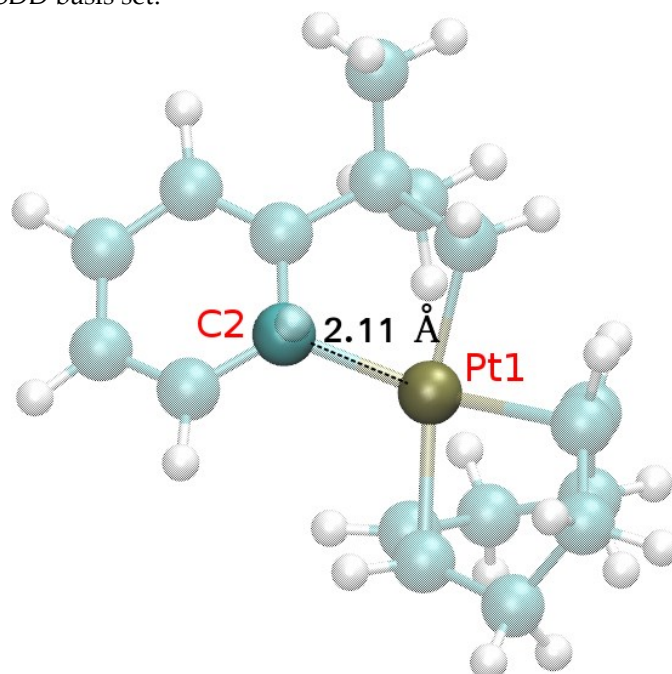


Fig. S9. Snapshot along the MD trajectory at $n_H = 0.46$ which corresponds to a C-H bond length of 1.45 Å and a C-Pt bond length of 2.11 Å.

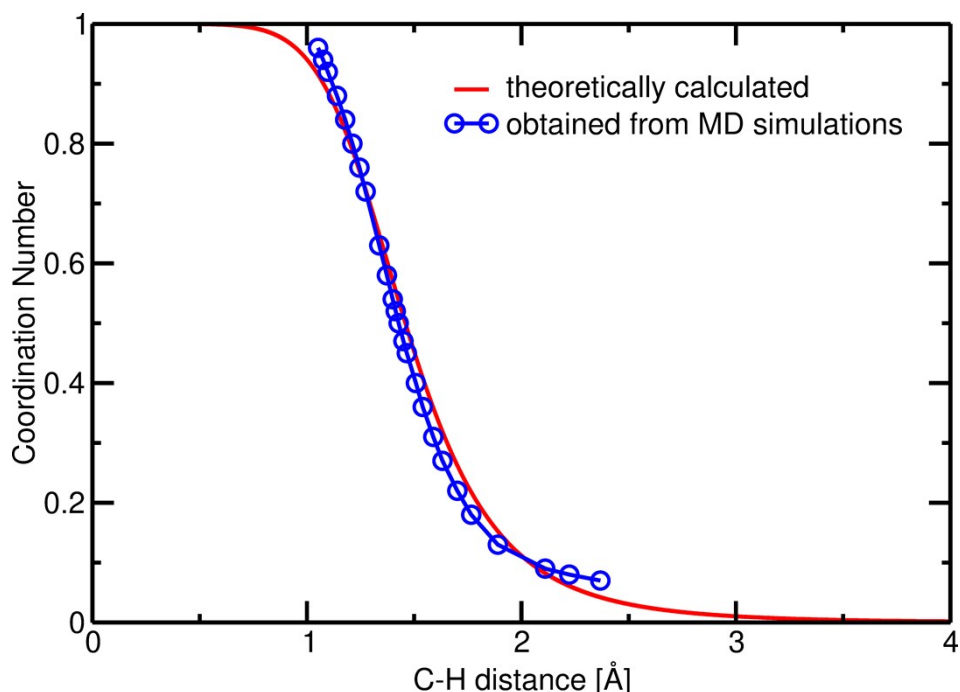


Fig. S10. Relation between the coordination number n_H and the C–H distance. Red line: Calculated using the formula implemented in CP2K (see Experimental Section 4.3) with only one H atom. Blue line: Values obtained from the MD simulations taking into account all H atoms.

Table S1. Results of the structure refinement for $[\text{Pt}(\text{COD})(\kappa^2\text{-neoPh})]$ ^a

empirical formula	$\text{C}_{18}\text{H}_{24}\text{Pt}$
formula mass g/mol	435.46
crystal system	orthorhombic
space group	$Pbca$
cell	$a = 10.2621(9) \text{ \AA}$
	$b = 14.7321(12) \text{ \AA}$
	$c = 19.7363(18) \text{ \AA}$
volume / Z	$2984.0(4) \text{ \AA}^3 / 8$
calc. density Mg/m^3	1.939
absorption coefficient mm^{-1}	9.389
F(000)	1680
crystal / colour	$0.3 \times 0.2 \times 0.1 \text{ mm}$ / colourless
T / wavelength	$170(2) \text{ K} / 0.71073 \text{ \AA}$
θ -range	2.06 to 27.42°
indices	$-13 < h < 13, -18 < k < 18, -25 < l < 25$
refl. measured / independent	32629 / 3333
R_{int}	0.0796
Completeness of to θ range	to $\theta = 25.242^\circ$: 100%
data / restraints / parameters	3333 / 0 / 173
goodness-of-Fit on F^2	1.024
final R values [$I > 2\sigma(I)$]	$R_1 = 0.0384, wR_2 = 0.0979$
R values (all data)	$R_1 = 0.0511, wR_2 = 0.1038$
largest diff. p. a.	1.933 and $-1.619 \text{ e \AA}^{-3}$
CCDC	1859573

^a Refinements: Full matrix least-squares on F^2 .

Table S2. Selected structural data of doubly cyclometalated Pt(II) complexes

	[Pt(COD) (κ^2 - neoPh)]	[Pd(COD) (κ^2 - neoPh)]	[Pt(COD) (bph)]	[Pt(phen Me ₄)(κ^2 - neoPh)] •CH ₂ Cl ₂ ^b	[Pt(PyM A-2- OH)(κ^2 - neoPh)] ^c	[Pt(PyM AH-2- OH)(κ^2 - neoPh)] ^c	[Pt(PyM AH-4- OH)(κ^2 - neoPh)] ^c	[Pt(Xyl- DAB)(κ^2 - neoPh)] ^d	[Pt(PPh ₃) ₂ (CH ₂) ₄]	[Pt(PPh ₂ - Ph- CH=NBN) (CH ₂) ₄]
reference	This work	Campora et al. <i>Inorg. Chem.</i> 2001, 40 , 4116	Chen et al. <i>J. Chem. Cryst.</i> 1996, 26 , 527	Puddephatt et al. <i>Organometallics</i> 2018, 37 , 3368	Puddephatt et al. <i>Eur. J. Chem.</i> 2019, 2899	Puddephatt et al. <i>Eur. J. Chem.</i> 2019, 2899	Puddephatt et al. <i>Eur. J. Chem.</i> 2019, 2899	Dahlenburg et al. <i>CDS Comm.</i> 1999	Biefeld et al. <i>Inorg. Chem.</i> 1973, 12 , 2166.	Lammertsma et al. <i>Dalton Trans.</i> 2014, 43 , 5546
CCDC	1859573	169528	1276686	1849222	1913418	1913416	1913417	104847	1275579	973798
bonds lengths (Å)										
C2-Pt	2.030(6)	2.023(3)	2.01(3)	1.98(1)	1.994(5)	1.995(1)	1.984(5)	2.01(1)	2.053(2)	2.052(6)
C10-Pt	2.070(7)	2.030(3)	2.02(3)	2.02(1)	2.034(6)	2.022(1)	2.036(6)	2.04(1)	2.117(2)	2.149(6)
Y1-Pt ^a	2.1155(3)	2.2310(6)	2.118(2)	2.099(9)	2.110(5)	2.105(1)	2.097(5)	2.08(1)	2.279(2)	2.244(1)
Y2-Pt ^a	2.1566(3)	2.1933(6)	2.149(2)	2.130(8)	2.124(4)	2.207(1)	2.205(5)	2.11(1)	2.284(2)	2.117(5)
C1-C2	1.419(9)	1.405(4)	1.36(3)	1.41(2)	1.417(7)	1.421(2)	1.424(7)	1.37(2)	1.480(1)	1.831(8)
C1-C7	1.513(8)	1.500(4)	1.41(4)	1.50(2)	1.510(8)	1.516(2)	1.506(8)	1.50(2)	1.458(2)	1.414(6)
C7-C10	1.539(9)	1.527(4)	1.47(4)	1.58(2)	1.543(9)	1.543(2)	1.555(7)	1.53(2)	1.570(2)	1.468(9)
C7-C8	1.542(9)	1.532(5)		1.52(2)	1.535(8)	1.535(2)	1.52(1)	1.52(3)		1.281(9)
angles (°)										
COD-bite Y1-Pt-Y2 ^a	85.7(1)	83.2(1)	85.03(6)	78.1(4)	77.3(1)	78.04(5)	79.6(2)	76.0(4)	98.80(4)	88.2(1)
				N1-Pt-N2	N1-Pt-N2	N1-Pt-NH	N1-Pt-NH	N1-Pt-N2	P1-Pt-P2	P-Pt-N
neoPh-bite C2-Pt-C10	80.5(3)	79.1(1)	79(1) bph	80.5(5)	80.1(2)	81.28(5)	80.6(3)	80.0(5)	81.04(4)	84.6(2)
									C ₄ H ₈	C ₄ H ₈
Y1-Pt-C2 ^a	175.4(2)	175.40(9)	98.1(8)	176.3(4)	173.3(2)	174.9(1)	173.2(2)	105.5(4)	93.74(5)	94.9(2)
					N1-Pt-C2	N1-Pt-C2	N1-Pt-C2	N2-Pt-C2	P1-Pt-C1	P1-Pt-C4
Y1-Pt-C10 ^a	94.9(3)	96.42(9)	177.3(7)	98.0(4)	99.7(2)	96.5(1)	98.7(2)	173.5(5)	173.39(5)	176.8(1)
					N1-Pt-C10	N1-Pt-C10	N1-Pt-C10	N2-Pt-C10	P1-Pt-C4	P1-Pt-C1
Y2-Pt-C2 ^a	98.8(2)	101.26(9)	176.4(8)	103.6(4)	103.0(1)	103.9(1)	101.2(2)	174.94(42)	167.36(6)	176.77(22)
					N2-Pt-C2	NH-Pt-C2	NH-Pt-C2	N1-Pt-C2	P2-Pt-C1	N1-Pt-C4
Y2-Pt-C10 ^a	177.9(2)	178.93(9)	97.6(7)	172.9(4)	176.3(2)	174.5(1)	176.6(2)	98.76(50)	86.56(4)	92.17(23)
					N2-Pt-C10	NH-Pt-C10	NH-Pt-C10	N1-Pt-C10	P2-Pt-C4	N1-Pt-C1
Pt-C2-C1	115.2(4)	115.6(2)	117(2)	116.2(8)	115.9(3)	116.2(1)	116.6(4)	116.7(8)	115.94(6)	104.16(35)
									Pt-C1-C2	Pt-C1-C2
Pt-C10-C7	110.0(4)	112.0(2)	116(2)	109.4(8)	111.3(4)	112.5(1)	111.4(4)	111.0(9)	104.55(6)	110.99(41)
									Pt-C3-C4	Pt-C4-C3
C2-C1-C7	115.3(5)	115.3(3)	114(2)	115.1(9)	115.2(5)	114.9(1)	114.7(5)	115(1)	107.18(7)	106.35(37)
									C1-C2-C3	C4-C3-C2
C1-C7-C10	106.4(5)	104.7(2)	112(2)	105.0(9)	104.9(5)	105.9(1)	105.0(4)	106(1)	110.58(8)	110.13(50)
									C2-C3-C4	C3-C2-C1
C1-C7-C8	108.1(5)	108.1(3)	-	109.6(9)	108.7(5)	108.4(1)	109.2(5)	109(1)	-	-
C-C-C-C torsion	28.6(7)	27.2(2)	2.3(33)	24.7(9)	25.8(6)	25.4(1)	28.1(7)	25.4(16)	47.6(1)	54.1(6)
Ph / coord. plane	~15	~16	~4	~25.5	~20.7	~13.9	~20.3	~18	-	~45

^a For the COD ligand, Y1: Centroid C11=C12 and Y2: Centroid C15=C16. ^b PhenMe₄ = 3,4,7,8-tetramethyl-1,10-phenanthroline. ^c PyMA-2-OH = κ^2 -N,N'-2-C₅H₄NCH=N-2-C₆H₄OH, PyMAH-2-OH = (κ^2 -N,N'-2-C₅H₄NCH-NH-2-C₆H₄OH, PyMAH-4-OH = (κ^2 -N,N'-2-C₅H₄NCH-NH-4-C₆H₄OH). ^d Xyl-DAB = N,N-bis(2,6-dimethylphenyl)-1,4-diazabuta-1,3-diene.

References

- J. Campora, J. A. Lopez, P. Palma, D. del Rio, and E. Carmona, Synthesis and Insertion Reactions of the Cyclometalated Palladium-Alkyl Complexes $\text{Pd}(\text{CH}_2\text{CMe}_2\text{-o-C}_6\text{H}_4)_2$. Observation of a Pentacoordinated Intermediate in the Insertion of SO_2 , *Inorg. Chem.* 2001, **40**, 4116–4126.
- Y. Chen, C. Woods, M. W. Perkovic, and D. P. Rillema, Crystal structure, physical and photophysical properties of a platinum(II) complex coordinated to the biphenyl dianion and cyclooctadiene, *J. Chem. Cryst.* 1996, **26**, 527–531.
- M. A. Fard, A. Behnia and R. J. Puddephatt, Cycloneophylplatinum Chemistry: A New Route to Platinum(II) Complexes and the Mechanism and Selectivity of Protonolysis of Platinum–Carbon Bonds, *Organometallics* 2018, **37**, 3368–3377.
- A. Behnia, M. A. Fard, P. D. Boyle and R. J. Puddephatt, Complexes Containing a Phenol–Platinum(II) Hydrogen Bond: Synthons for Supramolecular Self-Assembly and Precursors for Hydridoplatinum(IV) Complexes, *Eur. J. Inorg. Chem.* 2019, **2019**, 2899–2906.
- L. Dahlenburg, C. Becker, J. Hock, S. Kohlbrandt CDS Comm. 1999.
- C. Biefeld, H. A. Eick, and R. H. Grubbs, Crystal Structure of Bis(triphenylphosphine)tetramethyleneplatinum(II), *Inorg. Chem.* 1973, **12**, 2166–2170.
- T. Mahamo, J. R. Moss, S. F. Mapolie, G. S. Smith, J. C. Sloopweg, and K. Lammertsma, Platinacycloalkane complexes containing [P,N] bidentate ligands: synthesis and decomposition studies, *DaltonTrans.* 2014, **43**, 5546–5557.