Supporting Information:

Strong Cytotoxicity of Organometallic Platinum Complexes with Alkynyl Ligands

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Supplementary Figures (Figures S1–S25)

Supplementary Tables (Tables S1–S46)

Table S9. Hydrogen coordinates ($x\ 10^{-4}$) and isotropic displacement parameters ($Å^2\ x\ 10^{-3}$) for [(COD)Pt(C≡C(2Me)Ph)$_2$].

Table S10. Bond lengths [Å] for [(COD)Pt(C≡C(2Me)Ph)$_2$].

Table S11. Bond angles [°] for [(COD)Pt(C≡C(2Me)Ph)$_2$].

Table S12. Anisotropic displacement parameters ($Å^2\ x\ 10^{-3}$) for [(COD)Pt(C≡C(2Me)Ph)$_2$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2\cdot[h^2\cdot a^*2\cdot U_{11} + ... + 2\cdot h\cdot k\cdot a^*\cdot b^*\cdot U_{12}]$.

Table S13. Crystal data and structure refinement for [(COD)Pt(C≡C(3Me)Ph)$_2$].

Table S14. Atomic coordinates [$x\ 10^{-4}$] and equivalent isotropic displacement parameters [$Å^2\ x\ 10^{-3}$] for [(COD)Pt(C≡C(3Me)Ph)$_2$]. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table S15. Hydrogen coordinates ($x\ 10^{-4}$) and isotropic displacement parameters ($Å^2\ x\ 10^{-3}$) for [(COD)Pt(C≡C(3Me)Ph)$_2$].

Table S16. Bond lengths [Å] for [(COD)Pt(C≡C(3Me)Ph)$_2$].

Table S17. Bond angles [°] for [(COD)Pt(C≡C(3Me)Ph)$_2$].

Table S18. Anisotropic displacement parameters ($Å^2\ x\ 10^{-3}$) for [(COD)Pt(C≡C(3Me)Ph)$_2$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2\cdot[h^2\cdot a^*2\cdot U_{11} + ... + 2\cdot h\cdot k\cdot a^*\cdot b^*\cdot U_{12}]$.

Table S19. Crystal data and structure refinement for [(COD)Pt(C≡C(4Me)Ph)$_2$].

Table S20. Atomic coordinates [$x\ 10^{-4}$] and equivalent isotropic displacement parameters [$Å^2\ x\ 10^{-3}$] for [(COD)Pt(C≡C(4Me)Ph)$_2$]. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table S21. Hydrogen coordinates ($x\ 10^{-4}$) and isotropic displacement parameters ($Å^2\ x\ 10^{-3}$) for [(COD)Pt(C≡C(4Me)Ph)$_2$].

Table S22. Bond lengths [Å] for [(COD)Pt(C≡C(4Me)Ph)$_2$].

Table S23. Bond angles [°] for [(COD)Pt(C≡C(4Me)Ph)$_2$].

Table S24. Anisotropic displacement parameters ($Å^2\ x\ 10^{-3}$) for [(COD)Pt(C≡C(3Me)Ph)$_2$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2\cdot[h^2\cdot a^*2\cdot U_{11} + ... + 2\cdot h\cdot k\cdot a^*\cdot b^*\cdot U_{12}]$.

Table S25. Crystal data and structure refinement for [(COD)Pt(C≡C(4F)Ph)$_2$].

Table S26. Atomic coordinates [$x\ 10^{-4}$] and equivalent isotropic displacement parameters [$Å^2\ x\ 10^{-3}$] for [(COD)Pt(C≡C(4F)Ph)$_2$]. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table S27. Hydrogen coordinates ($x\ 10^{-4}$) and isotropic displacement parameters ($Å^2\ x\ 10^{-3}$) for [(COD)Pt(C≡C(4F)Ph)$_2$].

Table S28. Bond lengths [Å] for [(COD)Pt(C≡C(4F)Ph)$_2$].

Table S29. Bond angles [°] for [(COD)Pt(C≡C(4F)Ph)$_2$].

Table S30. Anisotropic displacement parameters ($Å^2\ x\ 10^{-3}$) for [(COD)Pt(C≡C(4F)Ph)$_2$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2\cdot[h^2\cdot a^*2\cdot U_{11} + ... + 2\cdot h\cdot k\cdot a^*\cdot b^*\cdot U_{12}]$.

Table S31. Crystal data and structure refinement for [(COD)Pt(C≡C(4OMe)Ph)$_2$].

Table S32. Atomic coordinates [$x\ 10^{-4}$] and equivalent isotropic displacement parameters [$Å^2\ x\ 10^{-3}$] for [(COD)Pt(C≡C(4OMe)Ph)$_2$]. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table S33. Hydrogen coordinates (x 10^{-4}) and isotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(C≡C(4OMe)Ph)$_2$].

Table S34. Bond lengths [Å] for [(COD)Pt(C≡C(4F)Ph)$_2$].

Table S35. Angles [°] for [(COD)Pt(C≡C(4OMe)Ph)$_2$].

Table S36. Anisotropic displacement parameters ($Å^2$ x 10^{-3}) for [Pt(cod)(C≡C(4OMe)Ph)$_2$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2 \cdot [h^2 \cdot a^* 2 \cdot U_{11} + ... + 2 \cdot h \cdot k \cdot a^* \cdot b^* \cdot U_{12}]$.

Table S37. Crystal data and structure refinement for [(COD)Pt(Me)(C≡C(3Me)Ph)].

Table S38. Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [$Å^2$ x 10^{-3}] for [(COD)Pt(Me)(C≡C(3Me)Ph)]. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table S39. Hydrogen coordinates (x 10^{-4}) and isotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(Me)(C≡C(3Me)Ph)].

Table S40. Bond lengths [Å] for [(COD)Pt(Me)(C≡C(3Me)Ph)].

Table S41. Angles [°] for [(COD)Pt(Me)(C≡C(3Me)Ph)].

Table S42. Anisotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(Me)(C≡C(3Me)Ph)]. The anisotropic displacement factor exponent takes the form: $-2\pi^2 \cdot [h^2 \cdot a^* 2 \cdot U_{11} + ... + 2 \cdot h \cdot k \cdot a^* \cdot b^* \cdot U_{12}]$.

Table S43. Crystal data and structure refinement for [(COD)Pt(Me)(C≡C(4F)Ph)].

Table S44. Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [$Å^2$ x 10^{-3}] for [(COD)Pt(Me)(C≡C(4F)Ph)]. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table S45. Hydrogen coordinates (x 10^{-4}) and isotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(Me)(C≡C(4F)Ph)].

Table S46. Bond lengths [Å] for [(COD)Pt(Me)(C≡C(4F)Ph)].

Table S47. Angles [°] for [(COD)Pt(Me)(C≡C(4F)Ph)].

Table S48. Anisotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(Me)(C≡C(4F)Ph)]. The anisotropic displacement factor exponent takes the form: $-2\pi^2 \cdot [h^2 \cdot a^* 2 \cdot U_{11} + ... + 2 \cdot h \cdot k \cdot a^* \cdot b^* \cdot U_{12}]$.

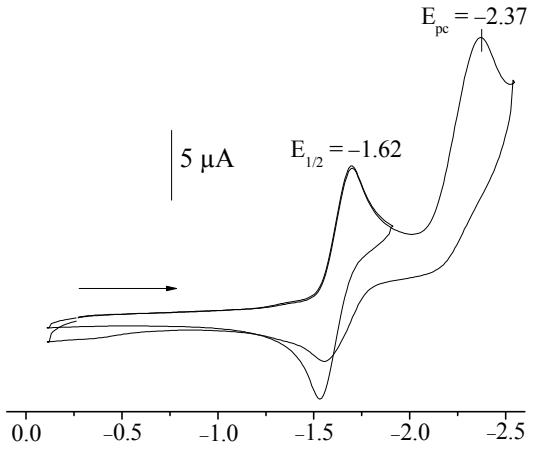

Figure S1. Cyclic voltammogramm of [(COD)Pt(C≡C(4NO_2)Ph)$_2$] in *n*-Bu_4NPF_6/CH_2Cl_2 at 298 K, sweep rate 100 mV/s.

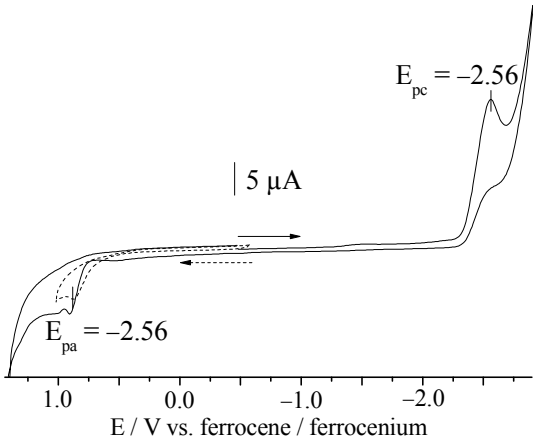

Figure S2. Cyclic voltammogramm of [(COD)Pt(C≡C(4Me)Ph)$_2$] in *n*-Bu_4NPF_6/CH_2Cl_2 at 298 K, sweep rate 100 mV/s.

Table S1. Redox potentials of the complexes [(COD)Pt(C≡CR)$_2$] and [(COD)Pt(Me)(C≡CR)] in *n*-Bu_4NPF_6/CH_2Cl_2 at 298 K, sweep rate 100 mV/s.

[(COD)Pt(C≡CR)$_2$]			R	[(COD)Pt(Me)(C≡CR)]		
E_1 [V]	E_2 [V]	E_3 [V]		E_1 [V]	E_2 [V]	E_3 [V]
0.96(irr.)	–	–	Ph	1.03(irr.)	–	–
0.94(irr.)	–	–2.44(irr.)	(2Me)Ph	0.93(irr.)	–	–
>1.2	–1.74(rev.)	–2.46(irr.)	(2NO_2)Ph	>1.2	–1.64(rev.)	–2.10(irr.)
1.04(irr.)	–	–	(3Me)Ph	0.95(irr.)	–	–
>1.2	–1.61(rev.)	–2.58(irr.)	(3NO_2)Ph	>1.2	–1.71(rev.)	–2.59(irr.)
0.87(irr.)	–	–2.56(irr.)	(4Me)Ph	0.85(irr.)	–	–
>1.2	–1.62(rev.)	–2.37(irr.)	(4NO_2)Ph	>1.2	–1.64(rev.)	–2.38(irr.)
1.06(irr.)	–	–2.43(irr.)	(4F)Ph	1.05(irr.)	–	–3.29*(irr.)
0.69(irr.)	–2.13(irr.)	–2.58(irr.)	(4OMe)Ph	0.69(irr.)	–	–2.18(irr.)
>1.2	–	–2.42(irr.)	2Py	>1.2	–	–

measured in [*n*-Bu_4N][PF_6]/CH_2Cl_2 vs ferrocene/ferrocenium; sweep rate 100 mV/s; for irreversible oxidations anodic peak potentials are given for irreversible reductions cathodic peak potentials are given and for reversible processes half step potentials are given; *measured in THF.

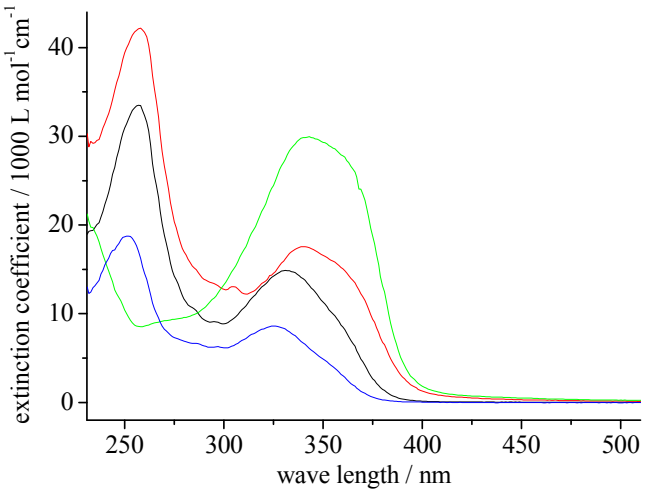

Figure S3. Absorption spectra of [(COD)Pt(C≡C(4NO_2)Ph)$_2$] (green), [(COD)Pt(C≡C(4Me)Ph)$_2$] (black), [(COD)Pt(C≡C(4F)Ph)$_2$] (blue) and [(COD)Pt(C≡C(4OMe)Ph)$_2$] (red) in THF at 298 K.

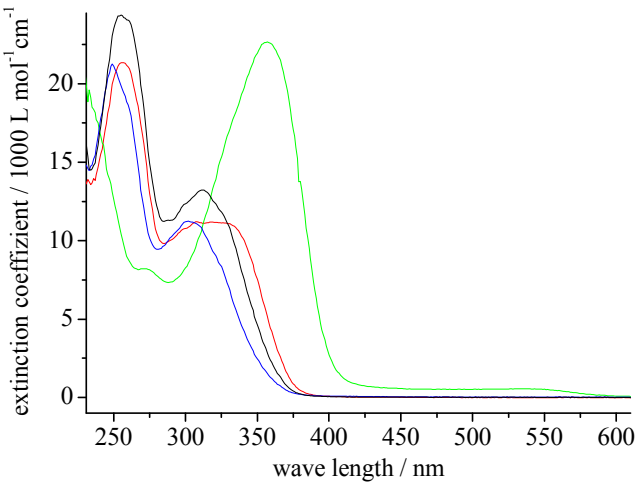

Figure S4. Absorption spectra of [(COD)Pt(Me)(C≡C(4NO_2)Ph)] (green), [(COD)Pt(Me)(C≡C(4Me)Ph)] (black), [(COD)Pt(Me)(C≡C(4F)Ph)] (blue) and [(COD)Pt(Me)(C≡C(4OMe)Ph)] (red) in THF at 298 K.

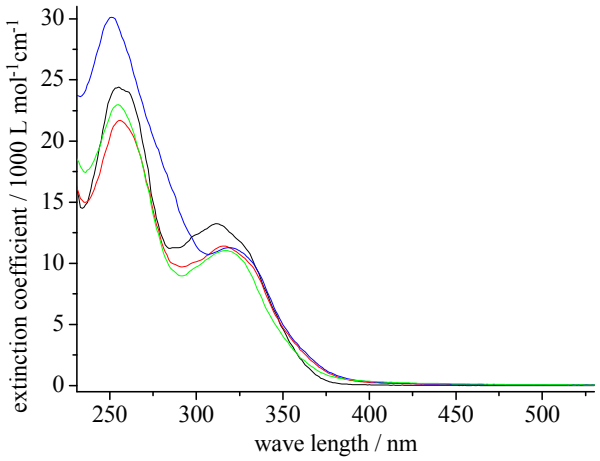

Figure S5. Absorption spectra of [(COD)Pt(Me)(C≡C(4Me)Ph)] (black), [(COD)Pt(neop)(C≡C(4Me)Ph)] (red), [(COD)Pt(bz)(C≡C(4Me)Ph)] (blue) and [(COD)Pt(neoSi)(C≡C(4Me)Ph)] (green) in THF at 298 K.

Table S2. Absorption maxima (nm) and extinction coefficients (1000 L mol^{-1} cm^{-1}) of the complexes [(COD)Pt(C≡CR)$_2$] measured in THF at 289 K.

R	λ_1, ε_1	λ_2, ε_2	λ_3, ε_3	λ_4, ε_4	λ_5, ε_5
Ph	357, *600*	328, *5200*	277, *3800*	256, *7000*	225, *13400*
(2Me)Ph	359, *3200*	331, *17100*	290, *7200*	257, *13600*	238, *27800*
(2NO_2)Ph	380, *2300*	358, *5000*	316, *10900*	272, *11900*	246, *33600*
(3Me)Ph	359, *2100*	331, *16000*	297, *6100*	257, *19500*	239, *25400*
(3NO_2)Ph	356, *700*	317, *14200*	276, *10400*	251, *40700*	
(4Me)Ph	360, *2800*	334, *12700*	297, *6100*	258, *12900*	246, *23300*
(4NO_2)Ph	369, *12700*	348, *17400*	325, *13000*	280, *9400*	231, *16100*
(4F)Ph	355, *1000*	326, *8300*	286, *5300*	252, *12700*	222, *13100*
(4OMe)Ph	368, *6500*	342, *11200*	297, *11800*	259, *18800*	242, *25100*
2Py		321, *13700*	288, *11800*	251, *7500*	242, *22400*
*t*Bu	310, *1500*	307, *4300*	290, *1000*	274, *3400*	253, *5500*

Table S3. Absorption maxima (nm) and extinction coefficients (1000 L mol^{-1} cm^{-1}) of the complexes [(COD)Pt(Me)(C≡CR)] measured in THF at 289 K.

R	λ_1, ε_1	λ_2, ε_2	λ_3, ε_3	λ_4, ε_4
Ph		308, *7300*		251, *14000*
(2Me)Ph		310, *8900*		250, *16200*
(2NO_2)Ph	421, *1900*	309*, *4900*		256, *19600*
(3Me)Ph		309, *11600*		257, *20300*
(3NO_2)Ph		305, *15500*		257, *31700*
(4Me)Ph		312, *13100*		255, *24300*
(4NO_2)Ph	538, *600*	358, *22700*	276, *8200*	229, *21900*
(4F)Ph		304, *11300*		250, *21200*
(4OMe)Ph		318, *11200*		257, *21400*
2Py		296, *9500*		251, *12400*

Table S4. Absorption maxima (nm) and extinction coefficients (1000 L mol^{-1} cm^{-1}) of the complexes [(COD)Pt(R`)(C≡C(4Me)Ph)] measured in tetrahydrofuran at 289 K.

R`	λ_2, ε_2	λ_4, ε_4
bz	321, *11300*	251, *30100*
neoSi	317, *11000*	255, *23000*
Me	312, *13100*	255, *24300*
neop	317, *11400*	257, *21600*

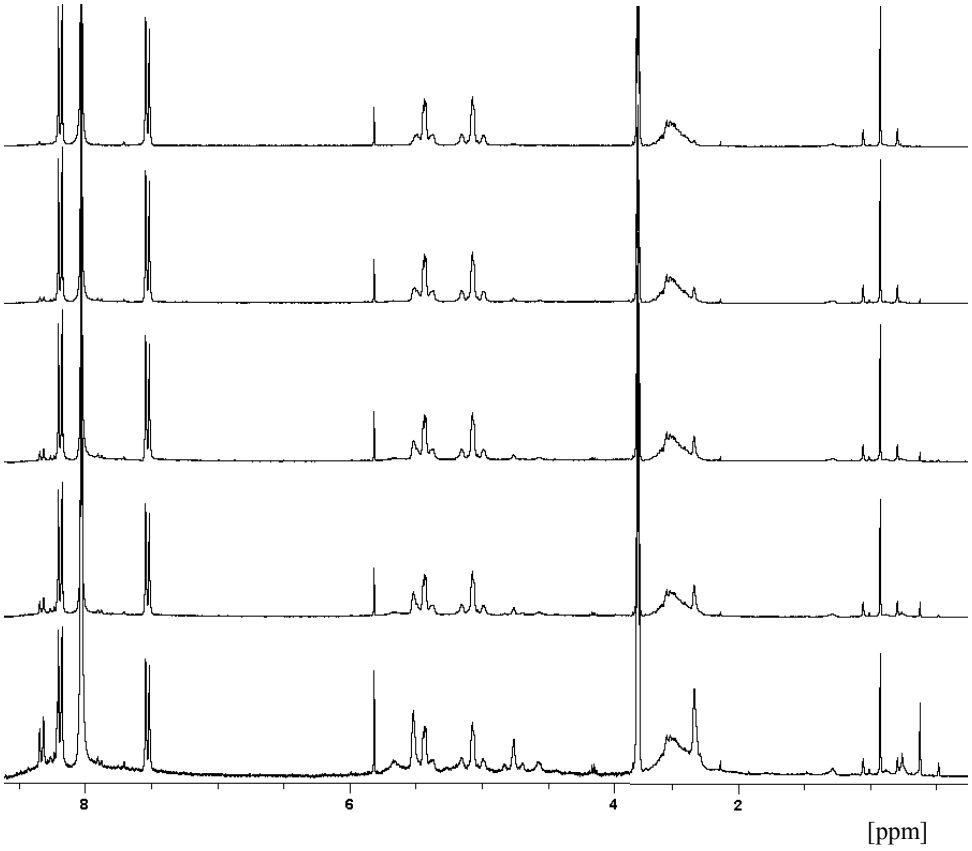

Figure S6. Time dependent ^{1}H-NMR-spectra of [(COD)Pt(Me)(C≡C(4NO$_2$)Ph)] in DMF-d^7.

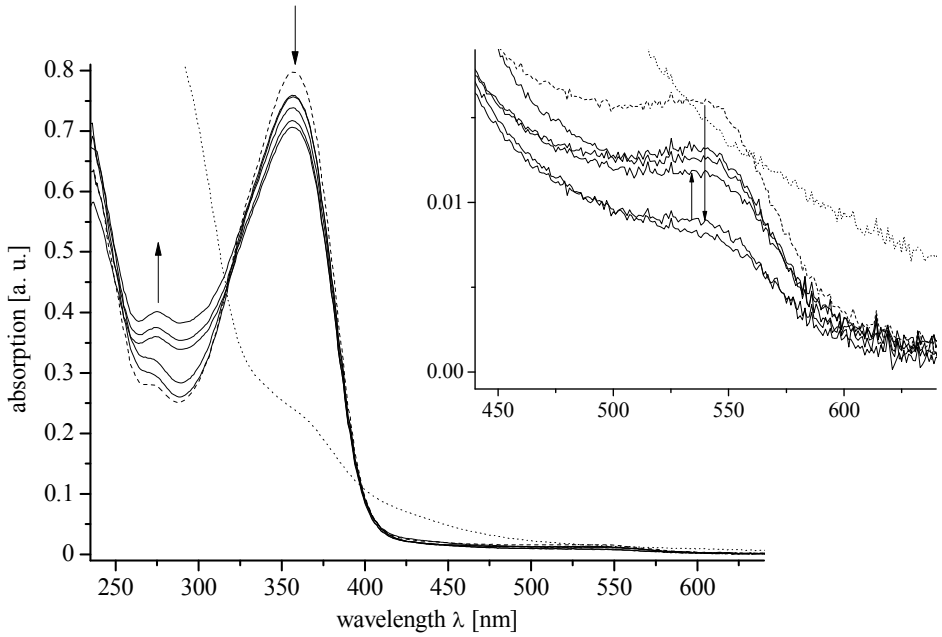

Figure S7. Absorption spectra of [(COD)Pt(C≡C(4Me)Ph)$_2$] in THF, addition of different amounts HBF_4 to set H+ concentration corresponding to pH = 6 to 1; absorption spectrum of [(COD)Pt(C≡C(4Me)Ph)$_2$] in THF: dashed graph, at pH values from 6 to 2: continuous graphs and at a pH = 1: dotted graph.

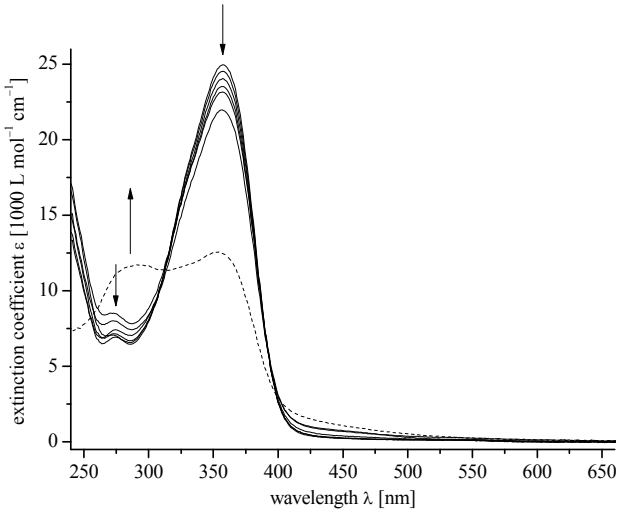

Figure S8. Absorption spectra of [(COD)Pt(Me)(C≡C(4NO_2)Ph)] in THF, addition of 0.5, 1, 1.5, 2, 5 equivalents of *n*-Bu_4NCl: continuous graph and addition of 5 equivalents *n*-Bu_4NCl after 18 hours: dotted graph.

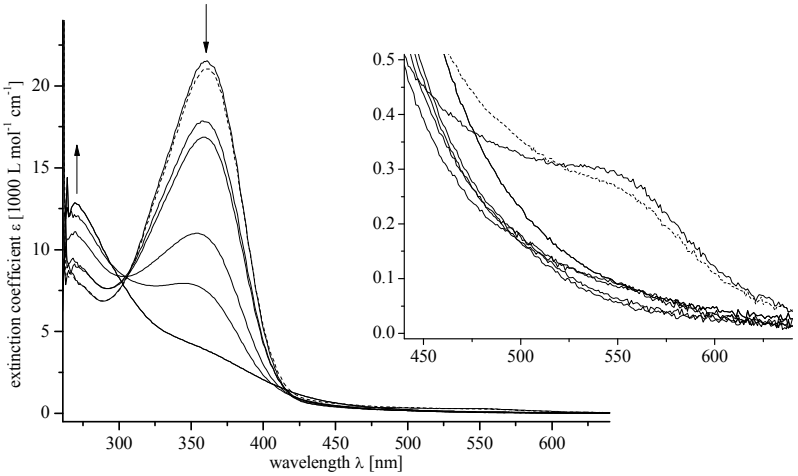

Figure S9. Absorption spectra of [(COD)Pt(Me)(C≡C(4NO_2)Ph)] in DMF, recorded after 0, 3, 4, 9, 12 and 30 days after stored at light: continuous graphs and after 3 days stored in the dark: dotted graph.

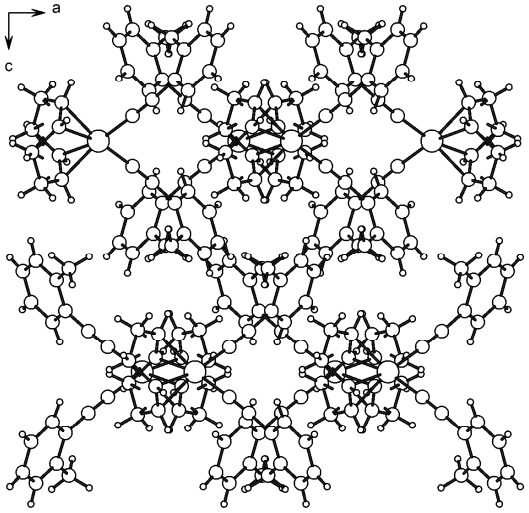

Figure S10. Crystal structure of [(COD)Pt(C≡C(2Me)Ph)$_2$].

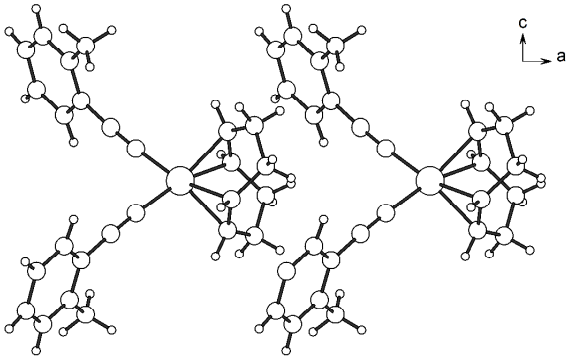

Figure S11. Detail of the crystal structure of [(COD)Pt(C≡C(2Me)Ph)$_2$] displaying the arrangement of two molecules.

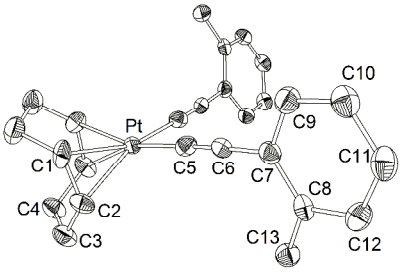

Figure S12. View of the complex molecule in the structure of [(COD)Pt(C≡C(2Me)Ph)$_2$] at 50% probability level (with numbering); protons were omitted for clarity.

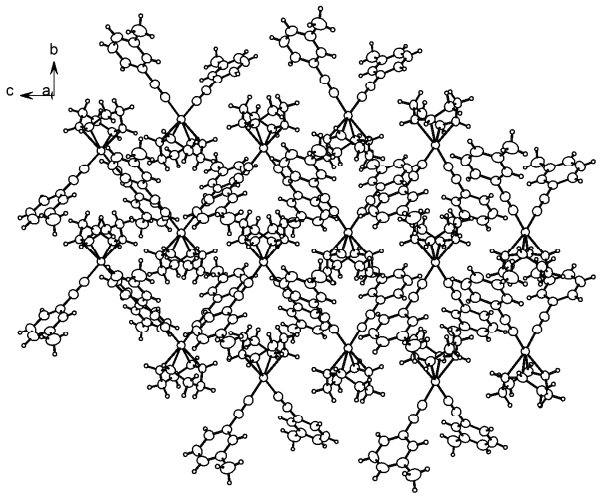

Figure S13. Crystal structure of [(COD)Pt(C≡C(3Me)Ph)$_2$].

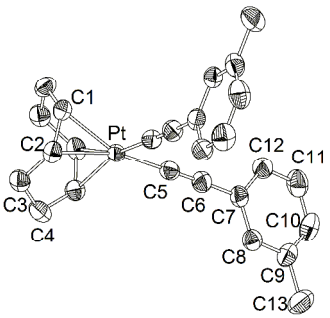

Figure S14. View of the complex molecule in the structure of [(COD)Pt(C≡C(3Me)Ph)$_2$] at 50% probability level (with numbering); protons were omitted for clarity.

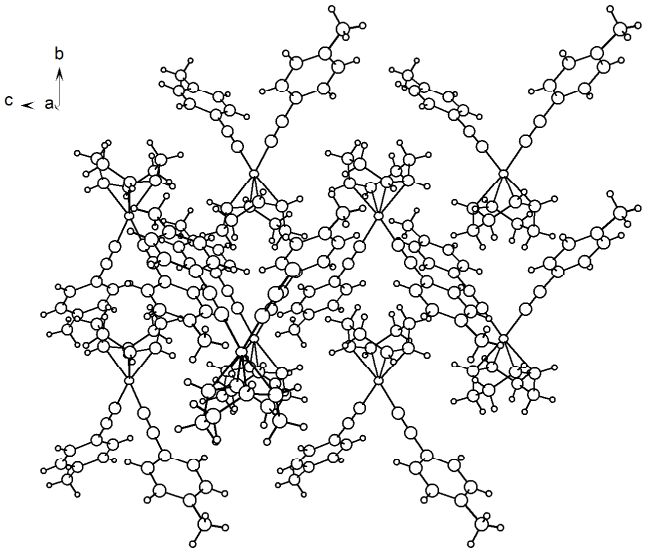

Figure S15. Crystal structure of [(COD)Pt(C≡C(4Me)Ph)$_2$].

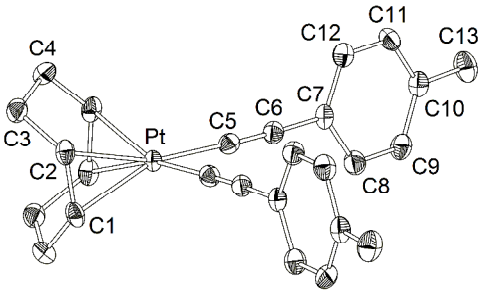

Figure S16. View of the complex molecule in the structure of [(COD)Pt(C≡C(4Me)Ph)$_2$] at 50% probability level (with numbering); protons were omitted for clarity.

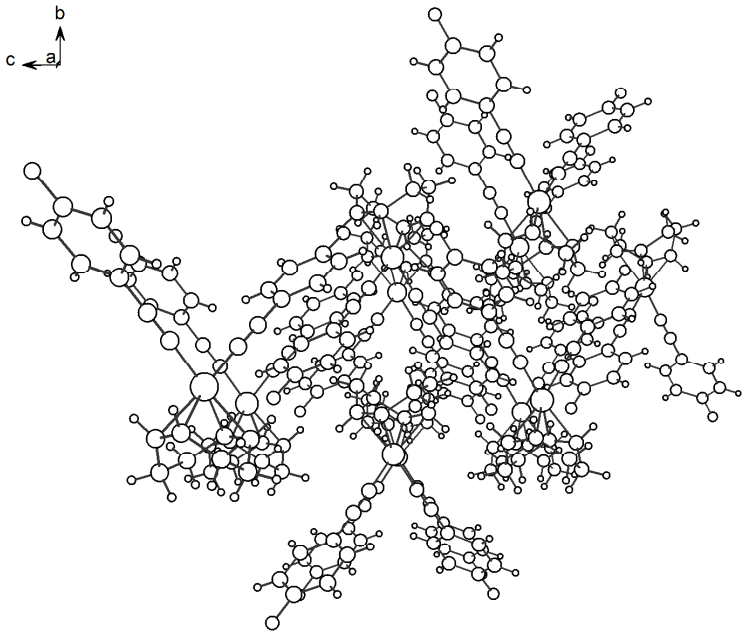

Figure S17. Crystal structure of [(COD)Pt(C≡C(4F)Ph)$_2$].

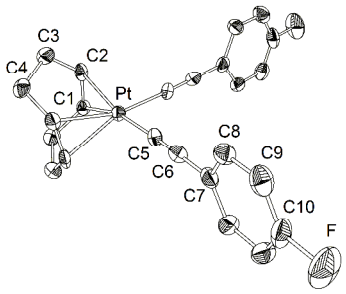

Figure S18. View of the complex molecule in the structure of [(COD)Pt(C≡C(4F)Ph)$_2$] at 50% probability level (with numbering); protons were omitted for clarity.

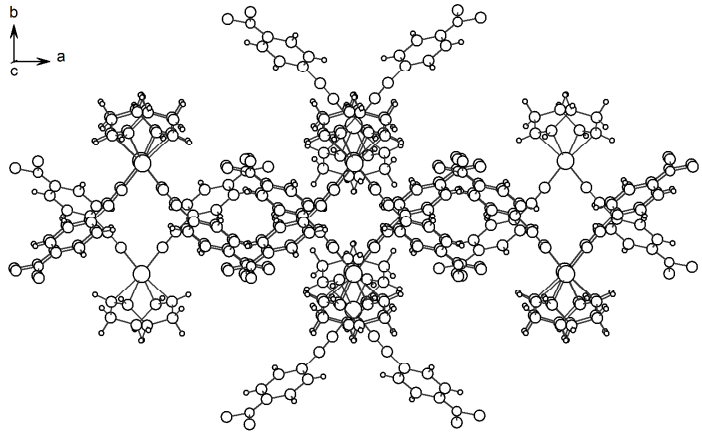

Figure S19. Crystal structure of [(COD)Pt(C≡C(4OMe)Ph)$_2$].

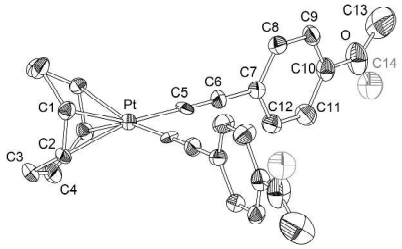

Figure S20. View of the complex molecule in the structure of [(COD)Pt(C≡C(4OMe)Ph)$_2$] at 30% probability level (with numbering); protons were omitted for clarity. Methyl groups are disordered.

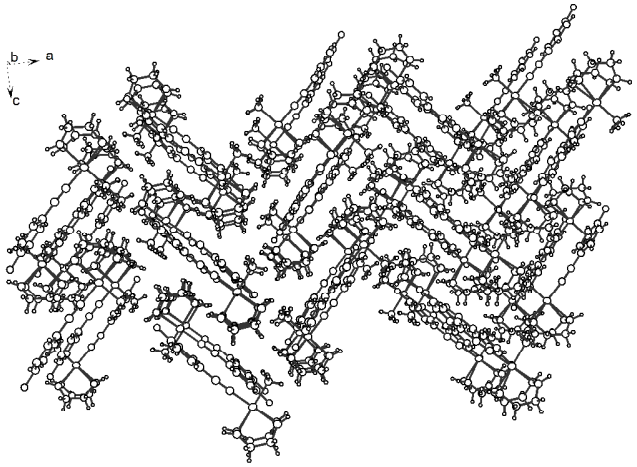

Figure S21. Crystal structure of [(COD)Pt(Me)(C≡C(4F)Ph)].

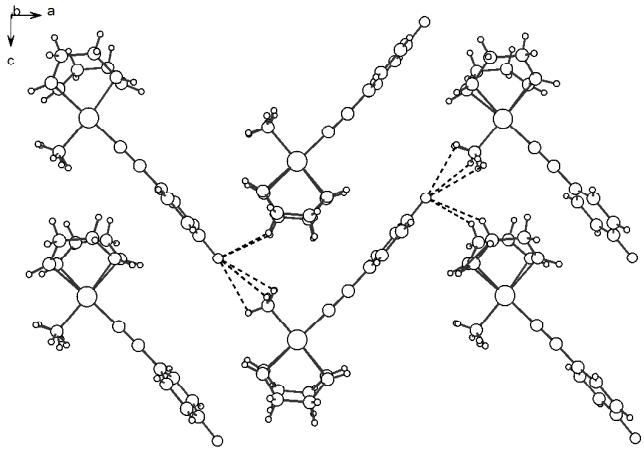

Figure S22. Detail of the crystal structure of [(COD)Pt(Me)(C≡C(4F)Ph)] displaying the F···H-interactions.

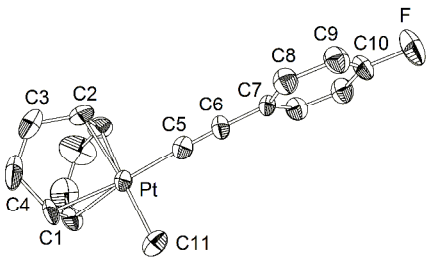

Figure S23. View of the complex molecule in the structure of [(COD)Pt(Me)(C≡C(4F)Ph)] at 50% probability level (with numbering); protons were omitted for clarity.

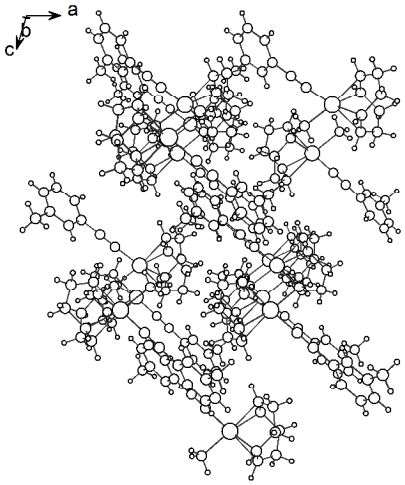

Figure S24. Crystal structure of [(COD)Pt(Me)(C≡C(3Me)Ph)].

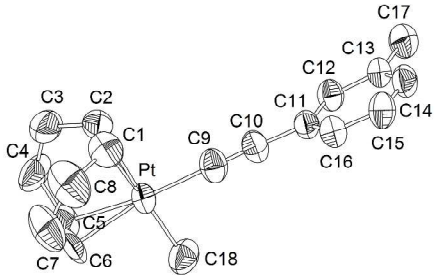

Figure S25. View of the complex molecule in the structure of [(COD)Pt(Me)(C≡C(3Me)Ph)] at 50% probability level (with numbering); protons were omitted for clarity.

Table S5. Parameter of crystal structure measurements and refinements of [(COD)Pt(C≡CR)$_2$][a]

R =	(2Me)Ph	(3Me)Ph	(4Me)Ph	(4F)Ph	(4OMe)Ph
Formula	$C_{26}H_{26}Pt_1$	$C_{26}H_{26}Pt_1$	$C_{26}H_{26}Pt_1$	$C_{24}H_{20}F_2Pt_1$	$C_{26}H_{26}O_2Pt_1$
Weigth [g/mol]	533.56	533.56	533.56	541.49	565.56
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*bna (No. 60)	*P*2/c (No. 13)	*P*2/c (No. 13)	*P*2/c (No. 13)	*P*2/c (No. 13)
T [K]	120(2)	293(2)	170(2)	293(2)	293(2)
cell:					
a [Å]	7.9541(8)	11.0258(14)	10.3303(11)	10.0746(17)	11.326(2)
b [Å]	13.0850(14)	7.9891(8)	7.9232(12)	7.8999(17)	7.8980(7)
c [Å]	18.9711(29)	11.8817(13)	11.9632(13)	11.7544(17)	12.0525(18)
β [°]	90	100.068(14)	90.055(8)	95.684(19)	93.06(2)
V [Å]^3 /Z	1974.50/4	1030.05/2	979.18/2	930.91/2	1076.59/2
ρ_{calc} [g/cm^3]	1.795	1.20	1.810	1.932	1.745
μ [mm^{-1}]	7.11	6.82	7.17	7.56	6.54
Limiting indices	–10<h<10, –16<k<16, –24<l<24	–14<h<14, –10<k<10, –15<l<15	–13<h<13, –10<k<10, –13<l<15	–13<h<13, –9<k<9, –15<l<15	–15<h<14, –10<k<10, –15<l<15
Refl.coll./uniq.	21569/2209	9578/2503	12624/2144	8579/2108	9981/2610
R_{int}	0.0862	0.0547	0.0679	0.0878	0.1536
Data/restr./param.	2209/0/144	2503/0/124	2144/0/124	2108/0/124	2610/0/142
Goof. on F^2	0.947	1.180	1.172	0.863	1.051
Final R_1, wR_2 [I>2σ(I)]	0.0323/0.0827	0.0274/0.0629	0.0242/0.0630	0.0339/0.0541	0.0614/0.1255
R_1, wR_2 (all data)	0.0483/0.0926	0.0346/0.0648	0.0270/0.0638	0.0654/0.0594	0.1028/0.1429
$\Delta\rho_{min/max}$ [10^{-6} e/pm^3]	–1.361/0.187	–1.216/0.908	–1.638/0.944	–2.201/1.885	–2.422/2.338

[a] Radiation wavelength λ = 0.71073 Å; Refinement method: Full-matrix least-squares on F^2.

Table S6. Parameter of crystal structure measurements and refinements of [(COD)Pt(Me)(C≡CR)] [a]

R =	(3Me)Ph)	(4F)Ph
formula	$C_{18}H_{22}Pt_1$	$C_{17}H_{22}F_1Pt_1$
weight [g/mol]	433.45	440.44
crystal system	monoclinic	orthorhombic
space group	$P2_1$/c (No. 14)	*P*nma (No. 62)
T [K]	293(2)	293(2)
cell:		
a [Å]	11.0258(14)	18.893(5)
b [Å]	7.9891(8)	9.615(5)
c [Å]	11.8817(13)	8.14(5)
β [°]	100.068(14)	90
V [Å]^3 /Z	1030.05/2	1974.50/4
ρ_{calc} [g/cm^3]	1.867	1.978
μ [mm^{-1}]	6.82	9.52
Limiting indices	–10<h<10, –13<k<13, –23<l<23	–15<h<15, –13<k<13, –14<l<16
Refl.coll./uniq.	16227/3336	14660/3067
R_{int}	0.0547	0.0564
Data/restr./param.	3336/0/175	3067/0/125
Goof. on F^2	1.180	1.077
Final R_1, wR_2 [I>2σ(I)]	0.0274/0.0629	0.0331/0.0601
R_1, wR_2 (all data)	0.0346/0.0648	0.0545/0.0641
$\Delta\rho_{min/max}$ [10^{-6} e/pm^3]	–1.216/0.908	–1.224/0.149

[a] Radiation wavelength λ = 0.71073 Å; Refinement method: Full-matrix least-squares on F^2.

Table S7. Crystal data and structure refinement for [(COD)Pt(C≡C(2Me)Ph)$_2$].

CCDC	929268
Empirical formula / Formula weight [g mol^{-1}]	$C_{26}H_{26}Pt_1$ / 533.57
Temperature [K] / Wavelength [Å]	120(2) / 0.71073
Radiation type / source	MoKα / fine-focus sealed tube
Monochromator / method	graphite / *Wycoff* scans
Crystal system / Space group	orthorhombic / *P*bna (Nr. 60)
Unit cell dimensions [Å]	a = 7.9541(8) b = 13.0850(14) c = 18.9711(29)
Volume [Å^3] / Z	1974.50 / 4
Density (calculated) [g/cm^3]	1.795
Absorption coefficient [mm^{-1}] / F(000)	7.11 / 1040.0
Crystal size [mm] / colour	0.3/0.2/0.2 / colourless
θ range for data collection [°]	2.15–27.34
Limiting indices h; k; l	–10/10; –16/16; –24/24
Reflections collected / independent	21569 / 2209
R_{int}	0.0862
Completeness to θ = 27.34°	98.7%
Absorption correction	shxabs
Refinement method	Full-matrix least-squares on F^2 [1,2,3]
Data / restraints / parameters	2209/0/144
Goodness-of-fit on F^2	0.947
Final R indices [I>2σ(I)]	R_1 = 0.0323, wR_2 = 0.0827
R indices (all data)	R_1 = 0.0483, wR_2 = 0.0926
$\Delta\rho_{min/max}$ [10^{-6} e/pm^3]	–1.361/0.187

1 G. M. Sheldrick. *SHELXTL-Plus. An Integrated System for Solving. Refining and Displaying Crystal Structures from Diffraction Data*. Siemens Analytical X-Ray Instruments Inc.. 1989.

2 G. M. Sheldrick. *SHELXL-93. Program for Crystal Structure Determination*. University of Göttingen. 1993.

3 International Tables for Crystallography; Vol. C. International Union of Crystallography; Kluwer Academic Publishers; Dortrecht. The Netherlands. 1992; Vol. C. Tables 9.5.1.1 and 9.6.3.3.

Table S8. Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [Å^2 x 10^{-3}] for [(COD)Pt(C≡C(2Me)Ph)$_2$].U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	x/a	y/b	z/c	U_{eq}
Pt(1)	3631(1)	2500	0	24(1)
C(2)	5529(7)	2125(5)	825(3)	34(1)
C(5)	1861(8)	1762(4)	542(3)	29(1)
C(3)	6597(8)	3069(6)	918(3)	40(2)
C(7)	–331(6)	765(4)	1329(3)	27(1)
C(8)	–794(6)	1155(4)	1989(3)	28(1)
C(4)	7061(8)	3620(5)	244(4)	42(1)
C(9)	–1862(7)	580(4)	2412(3)	31(1)
C(1)	5673(7)	1403(4)	309(3)	34(1)
C(6)	849(7)	1308(4)	887(3)	26(1)
C(13)	–158(8)	2171(4)	2246(3)	31(1)
C(12)	–1010(8)	–158(4)	1089(3)	33(1)
C(10)	–2540(7)	–340(4)	2178(3)	33(1)
C(11)	–2114(7)	–705(4)	1517(3)	34(1)

Table S9. Hydrogen coordinates (x 10^{-4}) and isotropic displacement parameters (Å^2 x 10^{-3}) for [(COD)Pt(C≡C(2Me)Ph)$_2$].

Atom	x/a	y/b	z/c	U
H(2)	5041	1867	1265	40
H(3A)	7625	2875	1158	48
H(3B)	6000	3542	1221	48
H(4A)	8065	3310	48	50
H(4B)	7324	4326	355	50
H(9)	–2128	814	2862	37

H(1)	5263	725	446	41
H(11)	–2567	–1318	1358	41
H(10)	–3210(70)	–700(40)	2490(30)	26(14)
H(13A)	–1050(60)	2500(30)	2540(30)	17(16)
H(13B)	890(90)	2070(60)	2510(40)	60(20)
H(13C)	20(80)	2680(40)	1890(40)	39(17)
H(12)	–630(80)	–460(50)	650(40)	54(19)

Table S10. Bond lengths [Å] for [(COD)Pt(C≡C(2Me)Ph)$_2$].

Atoms	Bond length	Atoms	Bond length	Atoms	Bond length
Pt(1)–C(5)#1	1,992(6)	C(2)–C(3)	1.509(10)	C(8)–C(13)	1.504(7)
Pt(1)–C(5)	1.992(6)	C(5)–C(6)	1.196(8)	C(4)–C(1)#1	1.523(10)
Pt(1)–C(2)	2.230(5)	C(3)–C(4)	1.513(9)	C(9)–C(10)	1.392(7)
Pt(1)–C(2)#1	2.230(5)	C(7)–C(12)	1.398(7)	C(1)–C(4)#1	1.523(10)
Pt(1)–C(1)#1	2.246(5)	C(7)–C(8)	1.401(7)	C(12)–C(11)	1.394(8)
Pt(1)–C(1)	2.246(5)	C(7)–C(6)	1.445(7)	C(10)–C(11)	1.383(8)
C(2)–C(1)	1.367(8)	C(8)–C(9)	1.391(7)		

Table S11. Bond angles [°] for [(COD)Pt(C≡C(2Me)Ph)$_2$].

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(5)#1–Pt(1)–C(5)	90.1(3)	C(2)–Pt(1)–C(1)	35.6(2)	C(9)–C(8)–C(13)	119.7(5)
C(5)#1–Pt(1)–C(2)	161.3(2)	C(2)#1–Pt(1)–C(1)	80.4(2)	C(7)–C(8)–C(13)	121.6(5)
C(5)–Pt(1)–C(2)	90.5(2)	C(1)#1–Pt(1)–C(1)	87.3(3)	C(3)–C(4)–C(1)#1	113.3(5)
C(5)#1–Pt(1)–C(2)#1	90.5(2)	C(1)–C(2)–C(3)	127.0(6)	C(8)–C(9)–C(10)	121.3(5)
C(5)–Pt(1)–C(2)#1	161.3(2)	C(1)–C(2)–Pt(1)	72.9(3)	C(2)–C(1)–C(4)#1	124.7(6)
C(2)–Pt(1)–C(2)#1	94.8(3)	C(3)–C(2)–Pt(1)	106.4(4)	C(2)–C(1)–Pt(1)	71.6(3)
C(5)#1–Pt(1)–C(1)#1	93.8(2)	C(6)–C(5)–Pt(1)	177.2(5)	C(4)#1–C(1)–Pt(1)	110.9(4)
C(5)–Pt(1)–C(1)#1	162.8(2)	C(2)–C(3)–C(4)	115.5(5)	C(5)–C(6)–C(7)	177.8(6)
C(2)–Pt(1)–C(1)#1	80.4(2)	C(12)–C(7)–C(8)	120.2(5)	C(11)–C(12)–C(7)	119.8(5)
C(2)#1–Pt(1)–C(1)#1	35.6(2)	C(12)–C(7)–C(6)	119.2(5)	C(11)–C(10)–C(9)	119.5(5)
C(5)#1–Pt(1)–C(1)	162.8(2)	C(8)–C(7)–C(6)	120.6(5)	C(10)–C(11)–C(12)	120.3(5)
C(5)–Pt(1)–C(1)	93.8(2)	C(9)–C(8)–C(7)	118.7(5)		

Table S12. Anisotropic displacement parameters (Å^2 x 10^{-3}) for [(COD)Pt(C≡C(2Me)Ph)$_2$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2\cdot[h^2\cdot a^*2\cdot U_{11} + ... + 2\cdot h\cdot k\cdot a^*\cdot b^*\cdot U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	23(1)	29(1)	20(1)	0(1)	0	0
C(2)	38(3)	40(3)	23(3)	7(2)	–13(2)	3(3)
C(5)	33(3)	34(3)	21(3)	1(2)	–3(3)	8(2)
C(3)	35(3)	54(4)	31(3)	6(3)	–9(3)	–7(3)
C(7)	23(3)	31(3)	26(3)	2(2)	–3(2)	1(2)
C(8)	18(3)	31(2)	36(3)	2(2)	0(2)	0(2)
C(4)	35(4)	49(4)	41(3)	2(3)	–8(3)	–12(3)
C(9)	33(3)	30(3)	29(3)	4(2)	5(3)	4(2)
C(1)	30(3)	32(3)	39(3)	14(3)	3(3)	19(3)
C(6)	24(3)	30(2)	24(3)	–1(2)	–4(2)	0(2)
C(13)	34(3)	26(2)	31(3)	–2(2)	0(3)	–1(2)
C(12)	31(3)	37(3)	30(3)	0(2)	2(3)	1(2)
C(10)	30(3)	28(3)	42(3)	7(2)	8(3)	–2(2)
C(11)	30(3)	25(3)	46(3)	2(2)	1(3)	–1(2)

Table S13. Crystal data and structure refinement for [(COD)Pt(C≡C(3Me)Ph)$_2$].

CCDC	929269
Empirical formula / Formula weight [g mol^{-1}]	$C_{26}H_{26}Pt_1$ / 533.57
Temperature [K] / Wavelength [Å]	293(2) / 0.71073
Radiation type / source	MoKα / fine-focus sealed tube
Monochromator / method	graphite / *Wycoff* scans
Crystal system / Space group	monoclinic / *P*2/c (Nr. 13)
Unit cell dimensions [Å]	a [Å] = 11.0258(14)
	b [Å] = 7.9891(8)
	c [Å] = 11.8817(13)

	β [°] = 100.068(14)
Volume [Å^3] / Z	1030.05 / 2
Density (calculated) [g/cm^3]	1.720
Absorption coefficient [mm^{-1}] / F(000)	6.82 / 520.0
Crystal size [mm] / colour	0.3 / 0.2 / 0.2 / colourless
θ range for data collection [°]	2.55–28.14
Limiting indices h; k; l	–14/14; –10/10; –15/15
Reflections collected / independent	9578 / 2503
R_{int}	0.0547
Completeness to θ = 28.14°	99.0%
Absorption correction	shxabs
Refinement method	Full-matrix least-squares on F^2 [1,2,3]
Data / restraints / parameters	2503/0/124
Goodness-of-fit on F^2	1.180
Final R indices [I>2σ(I)]	R_1 = 0.0274, wR_2 = 0.0629
R indices (all data)	R_1 = 0.0346, wR_2 = 0.0648
$\Delta\rho_{min/max}$ [10^{-6} e/pm^3]	–1.216/0.908

Table S14. Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [Å^2 x 10^{-3}] for [(COD)Pt(C≡C(3Me)Ph)$_2$]. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	x/a	y/b	z/c	U_{eq}
Pt(1)	5000	8691(1)	2500	32(1)
C(3)	4771(5)	12115(6)	3713(4)	45(1)
C(2)	5726(4)	10745(5)	3736(4)	40(1)
C(4)	6507(5)	11604(6)	1899(4)	49(1)
C(7)	2546(4)	4656(5)	469(4)	40(1)
C(12)	2765(5)	4074(6)	–588(4)	46(1)
C(13)	–401(6)	2320(7)	738(7)	70(2)
C(9)	697(5)	2940(6)	267(5)	48(1)
C(8)	1510(4)	4068(5)	883(4)	43(1)
C(1)	6507(4)	10573(5)	2955(4)	40(1)
C(11)	1951(6)	2965(7)	–1206(5)	59(1)
C(5)	3976(4)	6927(6)	1646(4)	41(1)
C(6)	3339(5)	5875(6)	1108(4)	44(1)
C(10)	924(6)	2417(6)	–787(5)	60(2)

Table S15. Hydrogen coordinates (x 10^{-4}) and isotropic displacement parameters (Å^2 x 10^{-3}) for [(COD)Pt(C≡C(3Me)Ph)$_2$].

Atom	x/a	y/b	z/c	U
H(3A)	5036	13091	3336	55
H(3B)	4722	12429	4492	55
H(2)	6073	10346	4505	47
H(4A)	6909	10971	1372	58
H(4B)	6989	12607	2107	58
H(12)	3456	4432	–871	56
H(13A)	–407	2823	1471	105
H(13B)	–355	1125	820	105
H(13C)	–1142	2616	225	105
H(8)	1363	4443	1588	51
H(1)	7310	10085	3273	48
H(11)	2092	2581	–1911	71
H(10)	377	1683	–1222	72

Table S16. Bond lengths [Å] for [(COD)Pt(C≡C(3Me)Ph)$_2$].

Atoms	Bond lengths	Atoms	Bond lengths	Atoms	Bond lengths
Pt(1)–C(5)	1.972(5)	C(3)–C(4)#1	1.523(7)	C(12)–C(11)	1.378(8)
Pt(1)–C(5)#1	1.972(5)	C(2)–C(1)	1.378(6)	C(13)–C(9)	1.504(8)
Pt(1)–C(1)	2.236(4)	C(4)–C(1)	1.500(7)	C(9)–C(10)	1.383(8)
Pt(1)–C(1)#1	2.236(4)	C(4)–C(3)#1	1.523(7)	C(9)–C(8)	1.386(7)
Pt(1)–C(2)	2.253(4)	C(7)–C(12)	1.400(7)	C(11)–C(10)	1.386(9)
Pt(1)–C(2)#1	2.253(4)	C(7)–C(8)	1.401(7)	C(5)–C(6)	1.204(7)

C(3)–C(2)	1.516(7)	C(7)–C(6)	1.435(7)		

Table S17. Bond angles [°] for [(COD)Pt(C≡C(3Me)Ph)$_2$].

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(5)–Pt(1)–C(5)#1	88.8(3)	C(5)#1–Pt(1)–C(2)#1	164.11(17)	C(8)–C(7)–C(6)	120.1(4)
C(5)–Pt(1)–C(1)	159.91(18)	C(1)–Pt(1)–C(2)#1	80.35(17)	C(11)–C(12)–C(7)	119.5(5)
C(5)#1–Pt(1)–C(1)	91.24(19)	C(1)#1–Pt(1)–C(2)#1	35.76(17)	C(10)–C(9)–C(8)	118.2(5)
C(5)–Pt(1)–C(1)#1	91.24(19)	C(2)–Pt(1)–C(2)#1	86.6(2)	C(10)–C(9)–C(13)	121.5(5)
C(5)#1–Pt(1)–C(1)#1	159.91(18)	C(2)–C(3)–C(4)#1	113.4(4)	C(8)–C(9)–C(13)	120.4(6)
C(1)–Pt(1)–C(1)#1	95.5(2)	C(1)–C(2)–C(3)	125.0(4)	C(9)–C(8)–C(7)	121.6(5)
C(5)–Pt(1)–C(2)	164.11(17)	C(1)–C(2)–Pt(1)	71.4(3)	C(2)–C(1)–C(4)	126.8(4)
C(5)#1–Pt(1)–C(2)	94.50(18)	C(3)–C(2)–Pt(1)	110.3(3)	C(2)–C(1)–Pt(1)	72.8(3)
C(1)–Pt(1)–C(2)	35.76(17)	C(1)–C(4)–C(3)#1	114.3(4)	C(4)–C(1)–Pt(1)	106.0(3)
C(1)#1–Pt(1)–C(2)	80.35(17)	C(12)–C(7)–C(8)	118.9(4)	C(12)–C(11)–C(10)	120.6(5)
C(5)–Pt(1)–C(2)#1	94.50(18)	C(12)–C(7)–C(6)	121.0(4)	C(6)–C(5)–Pt(1)	178.6(5)
C(5)–C(6)–C(7)	178.1(5)	C(9)–C(10)–C(11)	121.2(5)		

Table S18. Anisotropic displacement parameters (Å^2 x 10^{-3}) for [(COD)Pt(C≡C(3Me)Ph)$_2$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2\cdot[h^2\cdot a^{*2}\cdot U_{11} + ... + 2\cdot h\cdot k\cdot a^*\cdot b^*\cdot U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	37(1)	30(1)	31(1)	0	9(1)	0
C(3)	65(3)	43(2)	32(2)	–2(2)	19(2)	–1(2)
C(2)	54(3)	36(2)	28(2)	–1(2)	5(2)	–5(2)
C(4)	57(3)	47(2)	46(3)	–4(2)	19(2)	–15(2)
C(7)	45(3)	32(2)	41(2)	1(2)	7(2)	4(2)
C(12)	54(3)	42(2)	46(3)	–2(2)	15(2)	–2(2)
C(13)	56(4)	61(3)	94(5)	14(3)	18(3)	–12(3)
C(9)	45(3)	39(2)	56(3)	6(2)	1(2)	–5(2)
C(8)	49(3)	37(2)	42(2)	4(2)	7(2)	4(2)
C(1)	39(2)	37(2)	43(3)	–6(2)	7(2)	–5(2)
C(11)	80(4)	52(3)	43(3)	–13(2)	8(3)	–3(3)
C(5)	43(2)	40(2)	41(2)	2(2)	15(2)	3(2)
C(6)	49(3)	40(2)	42(2)	–4(2)	11(2)	–2(2)
C(10)	68(4)	43(2)	64(4)	–6(3)	–3(3)	–17(2)

Table S19. Crystal data and structure refinement for [(COD)Pt(C≡C(4Me)Ph)$_2$].

CCDC	929270
Empirical formula / Formula weight [g mol^{-1}]	$C_{26}H_{26}Pt_1$ / 533.57
Temperature [K] / Wavelength [Å]	170(2) / 0.71073
Radiation type / source	MoKα / fine-focus sealed tube
Monochromator / method	graphite / *Wycoff* scans
Crystal system / Space group	monoclinic / *P*2/c (Nr. 13)
Unit cell dimensions [Å]	a [Å] = 10.3303(11) b [Å] = 7.9232 (12) c [Å] = 11.9632(13) β [°] = 90.055(8)
Volume [Å^3] / Z / Density (calculated) [g/cm^3]	979.18 / 2 / 1.810
Absorption coefficient [mm^{-1}] / F(000)	7.17 / 520.0
Crystal size [mm] / colour	0.3 / 0.2 / 0.2 / colourless
θ range for data collection [°]	1.97–27.23
Limiting indices h; k; l	–13/13; –10/10; –13/15
Reflections collected / independent	12624 / 2144
R_{int}	0.0679
Completeness to θ = 27.23°	97.6%
Absorption correction	shxabs
Refinement method	Full-matrix least-squares on F$^{2\ 1,2,3}$
Data / restraints / parameters	2144/0/124
Goodness-of-fit on F^2	1.172
Final R indices [I>2σ(I)]	R_1 = 0.0242, wR_2 = 0.0630
R indices (all data)	R_1 = 0.0270, wR_2 = 0.0638
$\Delta\rho_{min/max}$ [10^{-6} e/pm^3]	–1.638/0.944

Table S20. Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [$Å^2$ x 10^{-3}] for [(COD)Pt(C≡C(4Me)Ph)$_2$]. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	x/a	y/b	z/c	U_{eq}
Pt(1)	5000	1290(1)	2500	18(1)
C(2)	4266(4)	–774(5)	3630(3)	23(1)
C(7)	2420(4)	5302(5)	4203(4)	22(1)
C(9)	8185(4)	3022(5)	4190(4)	27(1)
C(4)	6617(4)	–1657(6)	3306(4)	28(1)
C(3)	5273(4)	–2165(5)	3744(4)	26(1)
C(10)	9363(4)	2570(5)	4691(4)	26(1)
C(13)	10354(5)	1530(6)	4062(5)	35(1)
C(1)	3421(4)	–599(5)	2742(4)	23(1)
C(5)	3945(4)	3084(5)	3218(3)	22(1)
C(8)	7315(4)	4070(5)	4722(4)	27(1)
C(12)	1271(4)	5798(5)	3689(4)	26(1)
C(6)	3276(4)	4123(5)	3660(3)	23(1)
C(11)	9596(4)	3151(5)	5767(4)	28(1)

Table S21. Hydrogen coordinates (x 10^{-4}) and isotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(C≡C(4Me)Ph)$_2$].

Atom	x/a	y/b	z/c	U
H(2)	3922	–369	4345	28
H(9)	7986	2606	3484	33
H(4A)	7066	–1030	3886	33
H(4B)	7112	–2672	3158	33
H(3A)	4977	–3151	3337	31
H(3B)	5348	–2476	4526	31
H(13A)	10018	1244	3338	52
H(13B)	10535	516	4472	52
H(13C)	11136	2172	3978	52
H(1)	2584	–102	2945	28
H(8)	6547	4364	4367	33
H(12)	1083	5419	2971	31
H(11)	10352	2828	6132	33

Table S22. Bond lengths [Å] for [(COD)Pt(C≡C(4Me)Ph)$_2$].

Atoms	Bond length	Atoms	Bond length	Atoms	Bond length
Pt(1)–C(5)	1.986(4)	C(9)–C(8)	1.380(7)	C(13)–H(13B)	0.9600
Pt(1)–C(5)#1	1.986(4)	C(9)–C(10)	1.402(6)	C(13)–H(13C)	0.9600
Pt(1)–C(1)	2.234(4)	C(9)–H(9)	0.9300	C(1)–C(4)#1	1.509(6)
Pt(1)–C(1)#1	2.234(4)	C(4)–C(1)#1	1.509(6)	C(1)–H(1)	0.9800
Pt(1)–C(2)#1	2.254(4)	C(4)–C(3)	1.538(7)	C(5)–C(6)	1.198(6)
Pt(1)–C(2)	2.254(4)	C(4)–H(4A)	0.9700	C(8)–C(7)#2	1.405(6)
C(2)–C(1)	1.382(6)	C(4)–H(4B)	0.9700	C(8)–H(8)	0.9300
C(2)–C(3)	1.521(6)	C(3)–H(3A)	0.9700	C(12)–C(11)#2	1.385(7)
C(2)–H(2)	0.9800	C(3)–H(3B)	0.9700	C(12)–H(12)	0.9300
C(7)–C(12)	1.393(6)	C(10)–C(11)	1.389(7)	C(11)–C(12)#2	1.385(7)
C(7)–C(8)#2	1.405(6)	C(10)–C(13)	1.515(7)	C(11)–H(11)	0.9300
C(7)–C(6)	1.442(6)	C(13)–H(13A)	0.9600		

Table S23. Bond angles [°] for [(COD)Pt(C≡C(4Me)Ph)$_2$].

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(5)–Pt(1)–C(5)#1	88.7(2)	Pt(1)–C(2)–H(2)	114.1	C(11)–C(10)–C(13)	121.6(4)
C(5)–Pt(1)–C(1)	91.29(16)	C(12)–C(7)–C(8)#2	118.0(4)	C(9)–C(10)–C(13)	120.9(4)
C(5)#1–Pt(1)–C(1)	159.50(16)	C(12)–C(7)–C(6)	120.5(4)	C(10)–C(13)–H(13A)	109.5
C(5)–Pt(1)–C(1)#1	159.50(16)	C(8)#2–C(7)–C(6)	121.5(4)	C(10)–C(13)–H(13B)	109.5
C(5)#1–Pt(1)–C(1)#1	91.29(16)	C(8)–C(9)–C(10)	121.4(4)	H(13A)–C(13)–H(13B)	109.5
C(1)–Pt(1)–C(1)#1	95.8(2)	C(8)–C(9)–H(9)	119.3	C(10)–C(13)–H(13C)	109.5
C(5)–Pt(1)–C(2)#1	164.46(15)	C(10)–C(9)–H(9)	119.3	H(13A)–C(13)–H(13C)	109.5
C(5)#1–Pt(1)–C(2)#1	94.29(16)	C(1)#1–C(4)–C(3)	114.0(3)	H(13B)–C(13)–H(13C)	109.5
C(1)–Pt(1)–C(2)#1	80.64(16)	C(1)#1–C(4)–H(4A)	108.8	C(2)–C(1)–C(4)#1	126.8(4)

C(1)#1–Pt(1)–C(2)#1	35.86(15)	C(3)–C(4)–H(4A)	108.8	C(2)–C(1)–Pt(1)	72.9(2)
C(5)–Pt(1)–C(2)	94.29(16)	C(1)#1–C(4)–H(4B)	108.8	C(4)#1–C(1)–Pt(1)	106.4(3)
C(5)#1–Pt(1)–C(2)	164.46(15)	C(3)–C(4)–H(4B)	108.8	C(2)–C(1)–H(1)	114.0
C(1)–Pt(1)–C(2)	35.86(15)	H(4A)–C(4)–H(4B)	107.7	C(4)#1–C(1)–H(1)	114.0
C(1)#1–Pt(1)–C(2)	80.64(15)	C(2)–C(3)–C(4)	113.4(3)	Pt(1)–C(1)–H(1)	114.0
C(2)#1–Pt(1)–C(2)	86.9(2)	C(2)–C(3)–H(3A)	108.9	C(6)–C(5)–Pt(1)	177.7(4)
C(1)–C(2)–C(3)	125.0(4)	C(4)–C(3)–H(3A)	108.9	C(9)–C(8)–C(7)#2	120.6(4)
C(1)–C(2)–Pt(1)	71.3(2)	C(2)–C(3)–H(3B)	108.9	C(9)–C(8)–H(8)	119.7
C(3)–C(2)–Pt(1)	110.4(3)	C(4)–C(3)–H(3B)	108.9	C(7)#2–C(8)–H(8)	119.7
C(1)–C(2)–H(2)	114.1	H(3A)–C(3)–H(3B)	107.7	C(11)#2–C(12)–C(7)	120.9(4)
C(3)–C(2)–H(2)	114.1	C(11)–C(10)–C(9)	117.5(4)	C(11)#2–C(12)–H(12)	119.6
C(12)#2–C(11)–H(11)	119.2	C(5)–C(6)–C(7)	176.9(5)	C(7)–C(12)–H(12)	119.6
C(10)–C(11)–H(11)	119.2	C(12)#2–C(11)–C(10)	121.5(4)		

Table S24. Anisotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(C≡C(4Me)Ph)$_2$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2\cdot[h^2\cdot a^{*2}\cdot U_{11} + ... + 2\cdot h\cdot k\cdot a^*\cdot b^*\cdot U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	20(1)	15(1)	20(1)	0	2(1)	0
C(2)	29(2)	19(2)	20(2)	3(2)	8(2)	–4(2)
C(7)	26(2)	16(2)	25(2)	–1(2)	3(2)	0(1)
C(9)	34(2)	24(2)	23(2)	–5(2)	4(2)	0(2)
C(4)	28(2)	26(2)	29(2)	3(2)	–5(2)	5(2)
C(3)	35(2)	22(2)	22(2)	2(2)	–2(2)	–1(2)
C(10)	28(2)	20(2)	30(2)	–1(2)	4(2)	–1(2)
C(13)	34(3)	29(2)	41(3)	–2(2)	10(2)	8(2)
C(1)	20(2)	19(2)	31(2)	1(2)	6(2)	–5(1)
C(5)	23(2)	21(2)	21(2)	0(2)	0(2)	–2(2)
C(8)	28(2)	23(2)	31(2)	1(2)	–1(2)	1(2)
C(12)	29(2)	23(2)	26(2)	–3(2)	2(2)	1(2)
C(6)	25(2)	21(2)	23(2)	0(2)	0(2)	–1(2)
C(11)	24(2)	24(2)	34(2)	2(2)	–3(2)	6(2)

Table S25. Crystal data and structure refinement for [(COD)Pt(C≡C(4F)Ph)$_2$].

CCDC	929271
Empirical formula / Formula weight [g mol^{-1}]	$C_{24}H_{20}F_2Pt_1$ / 541.49
Temperature [K] / Wavelength [Å]	293(2) / 0.71073
Radiation type / source	MoKα / fine-focus sealed tube
Monochromator / method	graphite / *Wycoff* scans
Crystal system / Space group	monoclinic / *P*2/c (Nr. 13)
Unit cell dimensions	a [Å] = 10.0746(17) b [Å] = 7.8999(17) c [Å] = 11.7544(17) β [°] = 95.684(19)
Volume [$Å^3$] / Z	930.91 / 2
Density (calculated) [g/cm^3]	1.932
Absorption coefficient [mm^{-1}] / F(000)	7.56 / 520.0
Crystal size [mm] / colour	0.1 / 0.1 / 0.1 / colourless
θ range for data collection [°]	3.11–28.11
Limiting indices h; k; l	–13/13; –9/9; –15/15
Reflections collected / independent	8579 / 2108
R_{int}	0.0878
Completeness to θ = 28.11°	92.8%
Absorption correction	shxabs
Refinement method	Full-matrix least-squares on $F^{2\ 1,2,3}$
Data / restraints / parameters	2108 / 0 / 124
Goodness-of-fit on F^2	0.863
Final R indices [I>2σ(I)]	R_1 = 0.0339, wR_2 = 0.0541
R indices (all data)	R_1 = 0.0654, wR_2 = 0.0594
$\Delta\rho_{min/max}$ [10^{-6} e/pm^3]	–2.201/1.885

Table S26. Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [$Å^2$ x 10^{-3}] for [(COD)Pt(C≡C(4F)Ph)$_2$]. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	x/a	y/b	z/c	U_{eq}
Pt(1)	0	1311(1)	2500	23(1)
F(1)	5245(5)	8817(8)	6059(3)	74(1)
C(9)	4659(8)	7147(10)	4430(6)	44(2)
C(4)	–231(7)	–2147(9)	3748(5)	32(2)
C(10)	4392(8)	7686(9)	5481(6)	42(2)
C(5)	1127(7)	3105(8)	3281(5)	28(2)
C(3)	–1634(6)	–1640(9)	3215(5)	34(2)
C(8)	3825(7)	5978(9)	3868(5)	34(2)
C(7)	2713(7)	5364(8)	4361(5)	30(2)
C(2)	–1648(7)	–601(8)	2142(5)	29(2)
C(11)	3332(8)	7127(9)	6015(5)	41(2)
C(6)	1841(7)	4123(9)	3769(5)	31(2)
C(12)	2485(7)	5976(9)	5439(5)	34(2)
C(1)	–792(6)	–779(8)	1307(5)	26(2)

Table S27. Hydrogen coordinates (x 10^{-4}) and isotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(C≡C(4F)Ph)$_2$].

Atom	x/a	y/b	z/c	U
H(9)	5393	7562	4097	52
H(4A)	–281	–2453	4542	38
H(4B)	58	–3141	3355	38
H(3A)	–2150	–2661	3043	40
H(3B)	–2072	–1003	3776	40
H(8)	4002	5591	3151	41
H(2)	–2294	240	2033	35
H(11)	3186	7510	6740	49
H(12)	1743	5596	5777	40
H(1)	–854	22	724	32

Table S28. Bond lengths [Å] for [(COD)Pt(C≡C(4F)Ph)$_2$].

Atoms	Bond length	Atoms	Bond length	Atoms	Bond length
Pt(1)–C(5)#1	1.984(7)	C(4)–C(1)#1	1.499(9)	C(8)–H(8)	0.9300
Pt(1)–C(5)	1.984(7)	C(4)–C(3)	1.541(9)	C(7)–C(12)	1.397(8)
Pt(1)–C(2)	2.253(6)	C(4)–H(4A)	0.9700	C(7)–C(6)	1.447(9)
Pt(1)–C(2)#1	2.253(6)	C(4)–H(4B)	0.9700	C(2)–C(1)	1.376(8)
Pt(1)–C(1)	2.260(6)	C(10)–C(11)	1.365(10)	C(2)–H(2)	0.9300
Pt(1)–C(1)#1	2.260(6)	C(5)–C(6)	1.188(8)	C(11)–C(12)	1.378(9)
F(1)–C(10)	1.372(8)	C(3)–C(2)	1.504(8)	C(11)–H(11)	0.9300
C(9)–C(10)	1.359(10)	C(3)–H(3A)	0.9700	C(12)–H(12)	0.9300
C(9)–C(8)	1.373(9)	C(3)–H(3B)	0.9700	C(1)–C(4)#1	1.499(9)
C(9)–H(9)	0.9300	C(8)–C(7)	1.398(9)	C(1)–H(1)	0.9300

Table S29. Bond angles [°] for [(COD)Pt(C≡C(4F)Ph)$_2$].

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(5)#1–Pt(1)–C(5)	88.8(4)	C(1)#1–C(4)–C(3)	113.7(5)	C(7)–C(8)–H(8)	119.6
C(5)#1–Pt(1)–C(2)	90.9(2)	C(1)#1–C(4)–H(4A)	108.8	C(12)–C(7)–C(8)	117.8(6)
C(5)–Pt(1)–C(2)	160.5(2)	C(3)–C(4)–H(4A)	108.8	C(12)–C(7)–C(6)	121.6(6)
C(5)#1–Pt(1)–C(2)#1	160.5(2)	C(1)#1–C(4)–H(4B)	108.8	C(8)–C(7)–C(6)	120.6(5)
C(5)–Pt(1)–C(2)#1	90.9(2)	C(3)–C(4)–H(4B)	108.8	C(1)–C(2)–C(3)	126.0(6)
C(2)–Pt(1)–C(2)#1	95.8(3)	H(4A)–C(4)–H(4B)	107.7	C(1)–C(2)–Pt(1)	72.5(4)
C(5)#1–Pt(1)–C(1)	94.8(2)	C(9)–C(10)–C(11)	123.4(7)	C(3)–C(2)–Pt(1)	105.3(4)
C(5)–Pt(1)–C(1)	163.7(2)	C(9)–C(10)–F(1)	118.9(7)	C(1)–C(2)–H(2)	117.0
C(2)–Pt(1)–C(1)	35.5(2)	C(11)–C(10)–F(1)	117.6(6)	C(3)–C(2)–H(2)	117.0
C(2)#1–Pt(1)–C(1)	80.5(2)	C(6)–C(5)–Pt(1)	177.0(6)	Pt(1)–C(2)–H(2)	92.3
C(5)#1–Pt(1)–C(1)#1	163.7(2)	C(2)–C(3)–C(4)	114.5(5)	C(10)–C(11)–C(12)	117.5(6)
C(5)–Pt(1)–C(1)#1	94.8(2)	C(2)–C(3)–H(3A)	108.6	C(10)–C(11)–H(11)	121.2
C(2)–Pt(1)–C(1)#1	80.5(2)	C(4)–C(3)–H(3A)	108.6	C(12)–C(11)–H(11)	121.2
C(2)#1–Pt(1)–C(1)#1	35.5(2)	C(2)–C(3)–H(3B)	108.6	C(5)–C(6)–C(7)	179.8(7)

C(1)–Pt(1)–C(1)#1	86.1(3)	C(4)–C(3)–H(3B)	108.6	C(11)–C(12)–C(7)	121.6(6)
C(10)–C(9)–C(8)	118.8(7)	H(3A)–C(3)–H(3B)	107.6	C(11)–C(12)–H(12)	119.2
C(10)–C(9)–H(9)	120.6	C(9)–C(8)–C(7)	120.7(6)	C(7)–C(12)–H(12)	119.2
C(8)–C(9)–H(9)	120.6	C(9)–C(8)–H(8)	119.6	C(2)–C(1)–C(4)#1	125.9(5)
C(2)–C(1)–H(1)	117.0	Pt(1)–C(1)–H(1)	87.4	C(2)–C(1)–Pt(1)	72.0(3)
C(4)#1–C(1)–H(1)	117.0	C(4)#1–C(1)–Pt(1)	110.6(4)		

Table S30. Anisotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(C≡C(4F)Ph)$_2$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2 \cdot [h^2 \cdot a^* 2 \cdot U_{11} + ... + 2 \cdot h \cdot k \cdot a^* \cdot b^* \cdot U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	24(1)	21(1)	25(1)	0	1(1)	0
F(1)	73(3)	55(4)	87(3)	–13(3)	–25(2)	–27(4)
C(9)	28(4)	41(5)	61(5)	10(4)	0(4)	–4(4)
C(4)	45(5)	32(4)	20(3)	5(2)	9(3)	1(3)
C(10)	46(5)	25(5)	51(4)	–2(3)	–12(4)	–7(4)
C(5)	33(4)	19(4)	31(3)	–3(2)	3(3)	2(3)
C(3)	32(4)	32(5)	39(3)	1(3)	7(3)	–5(3)
C(8)	33(4)	33(6)	37(3)	4(3)	6(3)	–2(3)
C(7)	30(4)	24(4)	36(3)	2(3)	1(3)	7(3)
C(2)	30(4)	15(4)	40(3)	–5(3)	–8(3)	–4(3)
C(11)	51(5)	33(5)	38(4)	–9(3)	–1(3)	3(4)
C(6)	29(4)	31(5)	35(3)	–2(3)	7(3)	5(3)
C(12)	36(4)	32(5)	34(3)	–1(3)	10(3)	3(3)
C(1)	27(4)	23(5)	28(3)	–1(2)	–1(3)	–2(3)

Table S31. Crystal data and structure refinement for [(COD)Pt(C≡C(4OMe)Ph)$_2$].

CCDC	929272
Empirical formula / Formula weight [g mol^{-1}]	$C_{26}H_{26}O_2Pt_1$ / 565.56
Temperature [K] / Wavelength [Å]	293(2) / 0.71073
Radiation type / source	MoKα / fine-focus sealed tube
Monochromator / method	graphite / *Wycoff* scans
Crystal system / Space group	monoclinic / *P*2/c (Nr. 13)
Unit cell dimensions	a [Å] = 11.326(2) b [Å] = 7.8980(7) c [Å] = 12.0525(18) β [°] = 93.06(2)
Volume [$Å^3$] / Z	1076.59 / 2
Density (calculated) [g/cm^3]	1.745
Absorption coefficient [mm^{-1}] / F(000)	6.54 / 552.0
Crystal size [mm] / colour	0.2 / 0.2 / 0.3 / colourless
θ range for data collection [°]	2.85–28.22
Limiting indices h; k; l	–15/14; –10/10; –15/15
Reflections collected / independent	9981 / 2610
R_{int}	0.1536
Completeness to θ = 28.22°	98.4%
Absorption correction	shxabs
Refinement method	Full-matrix least-squares on F^2 [1,2,3]
Data / restraints / parameters	2610 / 0 / 142
Goodness-of-fit on F^2	1.051
Final R indices [I>2σ(I)]	R_1 = 0.0614, wR_2 = 0.1255
R indices (all data)	R_1 = 0.1028, wR_2 = 0.1429
$\Delta\rho_{min/max}$ [10^{-6} e/pm^3]	–2.422/2.338

Table S32. Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [$Å^2$ x 10^{-3}] for [(COD)Pt(C≡C(4OMe)Ph)$_2$]. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	x/a	y/b	z/c	U_{eq}
Pt(1)	5000	8738(1)	2500	39(1)
O(1)	90(13)	1903(14)	5631(13)	97(4)
C(6)	3392(12)	5953(13)	3571(10)	50(3)
C(5)	4017(12)	6988(14)	3157(9)	44(3)
C(11)	662(13)	3441(17)	4034(13)	67(4)

C(2)	5666(11)	10830(12)	1425(9)	44(3)
C(3)	4759(12)	12191(14)	1257(10)	51(3)
C(10)	906(13)	2797(16)	5103(12)	56(3)
C(9)	2011(12)	3125(14)	5629(11)	52(3)
C(7)	2574(11)	4803(14)	4070(10)	47(3)
C(8)	2839(12)	4110(14)	5122(10)	52(3)
C(1)	6430(11)	10639(13)	2336(10)	45(3)
C(4)	3548(13)	11706(15)	1620(13)	64(4)
C(12)	1484(13)	4434(17)	3546(12)	61(3)
C(13)	90(50)	1140(70)	6530(40)	140(20)
C(14)	–990(30)	1610(50)	5280(30)	84(11)

Table S33. Hydrogen coordinates (x 10^{-4}) and isotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(C≡C(4OMe)Ph)$_2$].

Atom	x/a	y/b	z/c	U[$Å^2$ 10^{-3}]
H(11)	–54	3197	3655	80
H(2)	5985	10426	733	52
H(3A)	4695	12490	475	61
H(3B)	5026	13189	1667	61
H(9)	2194	2676	6331	63
H(8)	3572	4310	5481	62
H(1)	7197	10152	2173	54
H(4A)	3136	11085	1023	77
H(4B)	3102	12730	1745	77
H(12)	1304	4873	2841	73

Table S34. Bond lengths [Å] for [(COD)Pt(C≡C(4F)Ph)$_2$].

Atoms	Bond length	Atoms	Bond length	Atoms	Bond length
Pt(1)–C(5)#1	1.967(13)	C(11)–C(12)	1.374(19)	C(9)–H(9)	0.9300
Pt(1)–C(5)	1.967(13)	C(11)–C(10)	1.40(2)	C(7)–C(12)	1.387(18)
Pt(1)–C(1)	2.225(11)	C(11)–H(11)	0.9300	C(7)–C(8)	1.399(16)
Pt(1)–C(1)#1	2.225(11)	C(2)–C(1)	1.370(17)	C(8)–H(8)	0.9300
Pt(1)–C(2)	2.254(9)	C(2)–C(3)	1.494(16)	C(1)–C(4)#1	1.513(17)
Pt(1)–C(2)#1	2.254(9)	C(2)–H(2)	0.9800	C(1)–H(1)	0.9800
O(1)–C(13)	1.24(6)	C(3)–C(4)	1.51(2)	C(4)–C(1)#1	1.513(17)
O(1)–C(14)	1.29(4)	C(3)–H(3A)	0.9700	C(4)–H(4A)	0.9700
O(1)–C(10)	1.349(16)	C(3)–H(3B)	0.9700	C(4)–H(4B)	0.9700
C(6)–C(5)	1.207(17)	C(10)–C(9)	1.40(2)	C(12)–H(12)	0.9300
C(6)–C(7)	1.451(17)	C(9)–C(8)	1.385(18	C(13)–C(14)	1.92(7)

Table S35. Angles [°] for [(COD)Pt(C≡C(4OMe)Ph)$_2$].

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(5)#1–Pt(1)–C(5)	90.8(7)	C(12)–C(11)–C(10)	119.8(13)	C(10)–C(9)–H(9)	119.5
C(5)#1–Pt(1)–C(1)	90.5(5)	C(12)–C(11)–H(11)	120.1	C(12)–C(7)–C(8)	118.2(12)
C(5)–Pt(1)–C(1)	160.0(4)	C(10)–C(11)–H(11)	120.1	C(12)–C(7)–C(6)	121.0(11)
C(5)#1–Pt(1)–C(1)#1	160.0(4)	C(1)–C(2)–C(3)	126.0(10)	C(8)–C(7)–C(6)	120.6(11)
C(5)–Pt(1)–C(1)#1	90.5(5)	C(1)–C(2)–Pt(1)	71.0(6)	C(9)–C(8)–C(7)	120.2(12)
C(1)–Pt(1)–C(1)#1	95.1(6)	C(3)–C(2)–Pt(1)	110.9(8)	C(9)–C(8)–H(8)	119.9
C(5)#1–Pt(1)–C(2)	94.0(5)	C(1)–C(2)–H(2)	113.6	C(7)–C(8)–H(8)	119.9
C(5)–Pt(1)–C(2)	163.8(4)	C(3)–C(2)–H(2)	113.6	C(2)–C(1)–C(4)#1	125.9(11)
C(1)–Pt(1)–C(2)	35.6(4)	Pt(1)–C(2)–H(2)	113.6	C(2)–C(1)–Pt(1)	73.4(7)
C(1)#1–Pt(1)–C(2)	79.9(4)	C(2)–C(3)–C(4)	114.0(9)	C(4)#1–C(1)–Pt(1)	106.4(8)
C(5)#1–Pt(1)–C(2)#1	163.8(4)	C(2)–C(3)–H(3A)	108.8	C(2)–C(1)–H(1)	114.2
C(5)–Pt(1)–C(2)#1	94.0(5)	C(4)–C(3)–H(3A)	108.8	C(4)#1–C(1)–H(1)	114.2
C(1)–Pt(1)–C(2)#1	79.9(4)	C(2)–C(3)–H(3B)	108.8	Pt(1)–C(1)–H(1)	114.2
C(1)#1–Pt(1)–C(2)#1	35.6(4)	C(4)–C(3)–H(3B)	108.8	C(3)–C(4)–C(1)#1	114.1(11)
C(2)–Pt(1)–C(2)#1	85.8(6)	H(3A)–C(3)–H(3B)	107.7	C(3)–C(4)–H(4A)	108.7
C(13)–O(1)–C(14)	99(3)	O(1)–C(10)–C(9)	120.2(14)	C(1)#1–C(4)–H(4A)	108.7
C(13)–O(1)–C(10)	134(3)	O(1)–C(10)–C(11)	121.2(14)	C(3)–C(4)–H(4B)	108.7
C(14)–O(1)–C(10)	127(2)	C(9)–C(10)–C(11)	118.6(12)	C(1)#1–C(4)–H(4B)	108.7
C(5)–C(6)–C(7)	175.8(13)	C(8)–C(9)–C(10)	121.0(12)	H(4A)–C(4)–H(4B)	107.6

C(6)–C(5)–Pt(1)	178.0(11)	C(8)–C(9)–H(9)	119.5	C(11)–C(12)–C(7)	122.1(13)
C(11)–C(12)–H(12)	119.0	O(1)–C(13)–C(14)	42(2)		
C(7)–C(12)–H(12)	119.0	O(1)–C(14)–C(13)	39.7(18)		

Table S36. Anisotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(C≡C(4OMe)Ph)$_2$]. The anisotropic displacement factor exponent takes the form: $–2\pi^2·[h^2·a^*2·U_{11} + ... + 2·h·k·a^*·b^*·U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	46(1)	34(1)	37(1)	0	–2(1)	0
O(1)	104(10)	71(6)	120(11)	14(7)	59(9)	–10(7)
C(6)	76(8)	35(6)	40(6)	4(5)	6(5)	–9(5)
C(5)	61(8)	45(5)	25(6)	10(4)	–12(5)	8(5)
C(11)	60(8)	67(9)	72(9)	14(7)	–12(7)	–13(7)
C(2)	68(8)	37(5)	27(5)	9(4)	12(5)	–8(5)
C(3)	68(8)	41(5)	44(6)	16(5)	0(6)	0(5)
C(10)	60(8)	48(6)	60(8)	2(6)	23(6)	–6(6)
C(9)	71(9)	41(5)	46(7)	7(5)	12(6)	1(5)
C(7)	56(7)	43(5)	41(6)	2(5)	–4(5)	–6(5)
C(8)	58(7)	48(6)	48(6)	–2(5)	–5(5)	1(5)
C(1)	52(7)	43(5)	42(6)	–6(5)	11(5)	–5(5)
C(4)	74(9)	45(6)	71(9)	14(6)	–14(7)	14(6)
C(12)	66(9)	60(7)	56(8)	9(6)	–9(7)	–13(6)
C(13)	140(40)	160(40)	120(40)	–10(40)	40(30)	–80(40)
C(14)	54(17)	100(30)	100(30)	10(20)	23(16)	–30(18)

Table S37. Crystal data and structure refinement for [(COD)Pt(Me)(C≡C(3Me)Ph)].

CCDC	929274
Empirical formula / Formula weight [g mol^{-1}]	$C_{18}H_{22}Pt_1$ / 433.45
Temperature [K] / Wavelength [Å]	293(2) / 0.71073
Radiation type / source	MoKα / fine-focus sealed tube
Monochromator / method	graphite / *Wycoff* scans
Crystal system / Space group	monoclinic / *P* 2_1/c (Nr. 14)
Unit cell dimensions	a [Å] = 8.2036(16) b [Å] = 10.3681(14) c [Å] = 18.997(3) β [°] = 107.414(14)
Volume [$Å^3$] / Z	1541.7 / 4
Density (calculated) [g/cm^3]	1.867
Absorption coefficient [mm^{-1}] / F(000)	9.09 / 832.0
Crystal size [mm] / colour	0.2 / 0.2 / 0.3 / colourless
θ range for data collection [°]	2.25–27.29
Limiting indices h; k; l	–10/10; –13/13; –23/23
Reflections collected / independent	16227 / 3336
R_{int}	0.1056
Completeness to θ = 27.29°	96.2%
Absorption correction	shxabs
Refinement method	Full-matrix least-squares on $F^{2\ 1,2,3}$
Data / restraints / parameters	3336 / 0 / 175
Goodness-of-fit on F^2	0.845
Final R indices [I>2σ(I)]	R_1 = 0.0323, wR_2 = 0.0582
R indices (all data)	R_1 = 0.0859, wR_2 = 0.0704
$\Delta\rho_{min/max}$ [10^{-6} e/pm^3]	–2.298/0.152

Table S38. Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [$Å^2$ x 10^{-3}] for [(COD)Pt(Me)(C≡C(3Me)Ph)]. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	x/a	y/b	z/c	U_{eq}
Pt(1)	–46(1)	–4481(1)	–3130(1)	52(1)
C(17)	–7525(11)	495(9)	–4627(5)	80(2)
C(12)	–5533(10)	–1408(8)	–4427(4)	56(2)
C(8)	2192(18)	–5644(13)	–3997(7)	122(4)
C(11)	–4999(10)	–2601(7)	–4604(4)	53(2)
C(10)	–3429(11)	–3163(9)	–4137(5)	64(2)

C(5)	2403(11)	–4880(10)	–2277(5)	72(3)
C(1)	1250(12)	–4421(11)	–4029(5)	79(3)
C(9)	–2159(11)	–3631(8)	–3745(5)	64(2)
C(3)	3477(13)	–3228(11)	–3012(5)	91(3)
C(15)	–7490(11)	–2669(9)	–5661(5)	69(2)
C(4)	3676(12)	–3889(12)	–2330(5)	98(4)
C(6)	1960(12)	–5960(10)	–2710(6)	81(3)
C(13)	–7006(10)	–807(8)	–4852(4)	55(2)
C(2)	1751(11)	–3347(10)	–3601(4)	66(2)
C(7)	2761(17)	–6319(12)	–3305(7)	119(5)
C(16)	–6004(10)	–3220(8)	–5225(4)	59(2)
C(14)	–7981(11)	–1468(10)	–5470(5)	68(2)
C(18)	–1516(11)	–5026(10)	–2447(5)	77(3)

Table S39. Hydrogen coordinates ($x\ 10^{-4}$) and isotropic displacement parameters ($Å^2\ x\ 10^{-3}$) for [(COD)Pt(Me)(C≡C(3Me)Ph)].

Atom	x/a	y/b	z/c	U
H(17A)	–8205	944	–5056	120
H(17B)	–6521	990	–4393	120
H(17C)	–8178	374	–4288	120
H(12)	–4872	–992	–4004	68
H(8A)	1470	–6226	–4357	146
H(8B)	3189	–5465	–4155	146
H(5)	2304	–4987	–1779	86
H(1)	462	–4221	–4517	95
H(3A)	4348	–3540	–3220	109
H(3B)	3699	–2319	–2903	109
H(15)	–8159	–3096	–6078	82
H(4A)	3713	–3240	–1958	118
H(4B)	4787	–4304	–2194	118
H(6)	1609	–6698	–2467	98
H(2)	1289	–2537	–3846	79
H(7A)	3985	–6195	–3106	143
H(7B)	2569	–7233	–3406	143
H(16)	–5672	–4023	–5352	71
H(14)	–8987	–1099	–5765	82
H(18A)	–783	–5372	–1994	116
H(18B)	–2331	–5669	–2692	116
H(18C)	–2108	–4286	–2342	116

Table S40. Bond lengths [Å] for [(COD)Pt(Me)(C≡C(3Me)Ph)].

Atoms	Bond length	Atoms	Bond length	Atoms	Bond length
Pt(1)–C(9)	1.984(9)	C(8)–H(8A)	0.9700	C(15)–C(14)	1.389(12)
Pt(1)–C(18)	2.096(8)	C(8)–H(8B)	0.9700	C(15)–H(15)	0.9300
Pt(1)–C(5)	2.210(8)	C(11)–C(16)	1.379(10)	C(4)–H(4A)	0.9700
Pt(1)–C(6)	2.216(8)	C(11)–C(10)	1.450(11)	C(4)–H(4B)	0.9700
Pt(1)–C(1)	2.267(7)	C(10)–C(9)	1.188(11)	C(6)–C(7)	1.515(14)
Pt(1)–C(2)	2.269(8)	C(5)–C(6)	1.372(13)	C(6)–H(6)	0.9800
C(17)–C(13)	1.515(11)	C(5)–C(4)	1.490(13)	C(13)–C(14)	1.388(11)
C(17)–H(17A)	0.9600	C(5)–H(5)	0.9800	C(2)–H(2)	0.9800
C(17)–H(17B)	0.9600	C(1)–C(2)	1.368(12)	C(7)–H(7A)	0.9700
C(17)–H(17C)	0.9600	C(1)–H(1)	0.9801	C(7)–H(7B)	0.9700
C(12)–C(13)	1.384(10)	C(3)–C(4)	1.430(12)	C(16)–H(16)	0.9300
C(12)–C(11)	1.387(10)	C(3)–C(2)	1.524(12)	C(14)–H(14)	0.9300
C(12)–H(12)	0.9300	C(3)–H(3A)	0.9700	C(18)–H(18A)	0.9600
C(8)–C(7)	1.438(14)	C(3)–H(3B)	0.9700	C(18)–H(18B)	0.9600
C(8)–C(1)	1.476(14)	C(15)–C(16)	1.376(11)	C(18)–H(18C)	0.9600

Table S41. Angles [°] for [(COD)Pt(Me)(C≡C(3Me)Ph)].

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(9)–Pt(1)–C(18)	85.5(4)	C(13)–C(12)–C(11)	122.9(7)	C(8)–C(1)–Pt(1)	107.6(7)

C(9)–Pt(1)–C(5)	163.2(4)	C(13)–C(12)–H(12)	118.5	C(2)–C(1)–H(1)	112.7
C(18)–Pt(1)–C(5)	93.5(3)	C(11)–C(12)–H(12)	118.5	C(8)–C(1)–H(1)	114.2
C(9)–Pt(1)–C(6)	160.6(4)	C(7)–C(8)–C(1)	118.6(9)	Pt(1)–C(1)–H(1)	113.1
C(18)–Pt(1)–C(6)	95.4(4)	C(7)–C(8)–H(8A)	107.7	C(10)–C(9)–Pt(1)	177.1(8)
C(5)–Pt(1)–C(6)	36.1(3)	C(1)–C(8)–H(8A)	107.7	C(4)–C(3)–C(2)	117.1(8)
C(9)–Pt(1)–C(1)	93.9(3)	C(7)–C(8)–H(8B)	107.7	C(4)–C(3)–H(3A)	108.0
C(18)–Pt(1)–C(1)	163.8(4)	C(1)–C(8)–H(8B)	107.7	C(2)–C(3)–H(3A)	108.0
C(5)–Pt(1)–C(1)	91.7(3)	H(8A)–C(8)–H(8B)	107.1	C(4)–C(3)–H(3B)	108.0
C(6)–Pt(1)–C(1)	79.9(4)	C(16)–C(11)–C(12)	118.1(7)	C(2)–C(3)–H(3B)	108.0
C(9)–Pt(1)–C(2)	95.4(3)	C(16)–C(11)–C(10)	122.1(7)	H(3A)–C(3)–H(3B)	107.3
C(18)–Pt(1)–C(2)	161.1(4)	C(12)–C(11)–C(10)	119.8(7)	C(16)–C(15)–C(14)	119.3(8)
C(5)–Pt(1)–C(2)	80.3(3)	C(9)–C(10)–C(11)	178.7(10)	C(16)–C(15)–H(15)	120.3
C(6)–Pt(1)–C(2)	90.0(4)	C(6)–C(5)–C(4)	125.9(10)	C(14)–C(15)–H(15)	120.3
C(1)–Pt(1)–C(2)	35.1(3)	C(6)–C(5)–Pt(1)	72.2(5)	C(3)–C(4)–C(5)	120.0(8)
C(13)–C(17)–H(17A)	109.5	C(4)–C(5)–Pt(1)	108.8(6)	C(3)–C(4)–H(4A)	107.3
C(13)–C(17)–H(17B)	109.5	C(6)–C(5)–H(5)	113.7	C(5)–C(4)–H(4A)	107.3
H(17A)–C(17)–H(17B)	109.5	C(4)–C(5)–H(5)	114.0	C(3)–C(4)–H(4B)	107.3
C(13)–C(17)–H(17C)	109.5	Pt(1)–C(5)–H(5)	114.2	C(5)–C(4)–H(4B)	107.3
H(17A)–C(17)–H(17C)	109.5	C(2)–C(1)–C(8)	127.8(10)	H(4A)–C(4)–H(4B)	106.9
H(17B)–C(17)–H(17C)	109.5	C(2)–C(1)–Pt(1)	72.5(5)	C(5)–C(6)–C(7)	123.5(10)
C(5)–C(6)–Pt(1)	71.7(5)	C(1)–C(2)–H(2)	114.2	C(11)–C(16)–H(16)	119.5
C(7)–C(6)–Pt(1)	110.0(6)	C(3)–C(2)–H(2)	114.9	C(13)–C(14)–C(15)	121.6(8)
C(5)–C(6)–H(6)	114.7	Pt(1)–C(2)–H(2)	115.3	C(13)–C(14)–H(14)	119.2
C(7)–C(6)–H(6)	114.4	C(8)–C(7)–C(6)	117.9(8)	C(15)–C(14)–H(14)	119.2
Pt(1)–C(6)–H(6)	114.7	C(8)–C(7)–H(7A)	107.8	Pt(1)–C(18)–H(18A)	109.5
C(12)–C(13)–C(14)	116.9(7)	C(6)–C(7)–H(7A)	107.8	Pt(1)–C(18)–H(18B)	109.5
C(12)–C(13)–C(17)	120.4(7)	C(8)–C(7)–H(7B)	107.8	H(18A)–C(18)–H(18B)	109.5
C(14)–C(13)–C(17)	122.7(7)	C(6)–C(7)–H(7B)	107.8	Pt(1)–C(18)–H(18C)	109.5
C(1)–C(2)–C(3)	123.4(9)	H(7A)–C(7)–H(7B)	107.2	H(18A)–C(18)–H(18C)	109.5
C(1)–C(2)–Pt(1)	72.4(5)	C(15)–C(16)–C(11)	121.1(8)	H(18B)–C(18)–H(18C)	109.5
C(3)–C(2)–Pt(1)	108.8(5)	C(15)–C(16)–H(16)	119.5		

Table S42. Anisotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(Me)(C≡C(3Me)Ph)]. The anisotropic displacement factor exponent takes the form: $-2\pi^2\cdot[h^2\cdot a^*2\cdot U_{11} + ... + 2\cdot h\cdot k\cdot a^*\cdot b^*\cdot U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	43(1)	58(1)	50(1)	–1(1)	6(1)	7(1)
C(17)	63(5)	75(6)	103(7)	5(6)	29(5)	14(6)
C(12)	49(5)	63(5)	52(4)	–5(4)	7(4)	3(4)
C(8)	146(12)	128(11)	103(9)	–8(9)	57(8)	56(10)
C(11)	44(4)	60(5)	53(5)	5(4)	11(4)	5(4)
C(10)	53(6)	65(6)	68(5)	2(4)	9(5)	11(4)
C(5)	49(5)	104(8)	50(5)	29(5)	–4(4)	13(5)
C(1)	89(7)	102(7)	57(5)	5(6)	37(5)	20(7)
C(9)	58(6)	64(6)	66(5)	–11(5)	12(5)	8(5)
C(3)	67(7)	104(8)	90(7)	22(6)	6(6)	–19(6)
C(15)	49(5)	88(7)	59(5)	–12(5)	1(4)	1(5)
C(4)	55(6)	154(11)	70(6)	18(6)	–5(5)	–44(6)
C(6)	64(6)	86(7)	82(7)	32(5)	3(5)	40(5)
C(13)	41(4)	60(6)	62(5)	4(4)	12(4)	6(4)
C(2)	64(6)	82(6)	54(5)	18(5)	18(4)	4(5)
C(7)	118(10)	113(10)	127(10)	1(8)	38(9)	70(8)
C(16)	53(5)	65(5)	57(5)	–3(4)	12(4)	8(4)
C(14)	45(5)	92(7)	60(5)	15(5)	6(4)	8(5)
C(18)	58(6)	107(8)	63(5)	4(5)	12(5)	–12(5)

Table S43. Crystal data and structure refinement for [(COD)Pt(Me)(C≡C(4F)Ph)].

CCDC	929273
Empirical formula / Formula weight [g mol^{-1}]	$C_{17}H_{22}F_1Pt_1$ / 440.44
Temperature [K] / Wavelength [Å]	293(2) / 0.71073
Radiation type / source	MoKα / fine-focus sealed tube
Monochromator / method	graphite / *Wycoff* scans

Crystal system / Space group	orthorhombic / *P* nma (Nr. 62)
Unit cell dimensions	a [Å] = 18.893(5)
	b [Å] = 9.615(5)
	c [Å] = 8.14(5)
Volume [$Å^3$] / Z / Density (calculated) [g/cm^3]	1478.7 / 4 / 1.978
Absorption coefficient [mm^{-1}] / F(000)	9.52 / 844.0
Crystal size [mm] / colour	0.3 / 0.2 / 0.2 / colourless
θ range for data collection [°]	2.72–28.05
Limiting indices h; k; l	–9/9; –12/12; –24/24
Reflections collected / independent	13467 / 1767
R_{int}	0.0564
Completeness to θ = 28.05°	93.0%
Absorption correction	shxabs
Refinement method	Full-matrix least-squares on F^2 [1,2,3]
Data / restraints / parameters	1767 / 0 / 99
Goodness-of-fit on F^2	1.080
Final R indices [I>2σ(I)]	R_1 = 0.0331, wR_2 = 0.0601
R indices (all data)	R_1 = 0.0545, wR_2 = 0.0641
$\Delta\rho_{min/max}$ [10^{-6} e/pm^3]	–1.233/0.728

Table S44. Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [$Å^2$ x 10^{-3}] for [(COD)Pt(Me)(C≡C(4F)Ph)]. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x/a	y/b	z/c	U_{eq}
Pt(1)	1207(1)	7500	1281(1)	33(1)
F(1)	–1902(4)	7500	9197(9)	75(2)
C(9)	–1239(4)	8745(6)	7266(8)	45(1)
C(6)	–19(4)	7500	3986(11)	38(2)
C(2)	491(4)	6801(7)	–787(9)	54(2)
C(11)	1909(6)	7500	3214(13)	52(3)
C(5)	446(5)	7500	2944(13)	39(2)
C(3)	921(6)	5896(13)	–1901(15)	101(4)
C(10)	–1448(5)	7500	7907(13)	44(2)
C(1)	2018(4)	6790(8)	–476(9)	53(2)
C(4)	1676(5)	5881(11)	–1760(11)	78(3)
C(7)	–537(4)	7500	5275(10)	34(2)
C(8)	–773(3)	8743(6)	5949(8)	43(2)

Table S45. Hydrogen coordinates (x 10^{-4}) and isotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(Me)(C≡C(4F)Ph)].

Atom	x/a	y/b	z/c	U
H(9)	–1405	9577	7702	54
H(2)	45	6391	–423	64
H(11A)	2372	7744	2823	78
H(11B)	1923	6591	3699	78
H(11C)	1759	8165	4022	78
H(3A)	758	4948	–1753	122
H(3B)	808	6159	–3021	122
H(1)	2426	6365	66	63
H(4A)	1871	6141	–2819	94
H(4B)	1820	4929	–1550	94
H(8)	–617	9583	5513	52

Table S46. Bond lengths [Å] for [(COD)Pt(Me)(C≡C(4F)Ph)].

Atoms	Bond length	Atoms	Bond length	Atoms	Bond length
Pt(1)–C(5)	1.976(10)	C(9)–C(10)	1.364(8)	C(10)–C(9)#1	1.364(8)
Pt(1)–C(11)	2.057(10)	C(9)–C(8)	1.387(9)	C(1)–C(1)#1	1.366(15)
Pt(1)–C(1)#1	2.204(6)	C(6)–C(5)	1.221(13)	C(1)–C(4)	1.508(11)
Pt(1)–C(1)	2.204(6)	C(6)–C(7)	1.436(11)	C(7)–C(8)	1.389(7)
Pt(1)–C(2)	2.262(7)	C(2)–C(2)#1	1.343(14)	C(7)–C(8)#1	1.389(7)
Pt(1)–C(2)#1	2.262(7)	C(2)–C(3)	1.496(11)		
F(1)–C(10)	1.355(11)	C(3)–C(4)	1.430(13)		

Table S47. Angles [°] for [(COD)Pt(Me)(C≡C(4F)Ph)].

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(5)–Pt(1)–C(11)	86.8(4)	C(11)–Pt(1)–C(2)#1	162.67(18)	F(1)–C(10)–C(9)#1	118.7(4)
C(5)–Pt(1)–C(1)#1	161.95(19)	C(1)#1–Pt(1)–C(2)#1	80.8(3)	F(1)–C(10)–C(9)	118.7(4)
C(11)–Pt(1)–C(1)#1	92.8(4)	C(1)–Pt(1)–C(2)#1	91.4(3)	C(9)#1–C(10)–C(9)	122.6(9)
C(5)–Pt(1)–C(1)	161.95(19)	C(2)–Pt(1)–C(2)#1	34.6(4)	C(1)#1–C(1)–C(4)	125.4(5)
C(11)–Pt(1)–C(1)	92.8(4)	C(10)–C(9)–C(8)	118.6(6)	C(1)#1–C(1)–Pt(1)	71.95(19)
C(1)#1–Pt(1)–C(1)	36.1(4)	C(5)–C(6)–C(7)	177.0(10)	C(4)–C(1)–Pt(1)	109.4(5)
C(5)–Pt(1)–C(2)	94.3(3)	C(2)#1–C(2)–C(3)	125.6(6)	C(3)–C(4)–C(1)	118.5(7)
C(11)–Pt(1)–C(2)	162.67(18)	C(2)#1–C(2)–Pt(1)	72.72(18)	C(8)–C(7)–C(8)#1	118.8(8)
C(1)#1–Pt(1)–C(2)	91.4(3)	C(3)–C(2)–Pt(1)	107.4(5)	C(8)–C(7)–C(6)	120.5(4)
C(1)–Pt(1)–C(2)	80.8(3)	C(6)–C(5)–Pt(1)	179.3(9)	C(8)#1–C(7)–C(6)	120.5(4)
C(5)–Pt(1)–C(2)#1	94.3(3)	C(4)–C(3)–C(2)	119.9(7)	C(9)–C(8)–C(7)	120.7(6)

Table S48. Anisotropic displacement parameters ($Å^2$ x 10^{-3}) for [(COD)Pt(Me)(C≡C(4F)Ph)]. The anisotropic displacement factor exponent takes the form: $-2\pi^2 \cdot [h^2 \cdot a^* 2 \cdot U_{11} + ... + 2 \cdot h \cdot k \cdot a^* \cdot b^* \cdot U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	36(1)	36(1)	26(1)	0	2(1)	0
F(1)	72(4)	85(4)	67(5)	0	45(4)	0
C(9)	50(3)	37(3)	47(4)	–7(2)	9(3)	7(3)
C(6)	42(5)	43(4)	30(6)	0	9(4)	0
C(2)	44(4)	74(4)	43(5)	–9(3)	–15(3)	–7(3)
C(11)	59(6)	60(6)	37(7)	0	–12(4)	0
C(5)	49(5)	33(4)	35(5)	0	0(4)	0
C(3)	87(7)	131(9)	87(9)	–76(7)	–7(6)	–4(6)
C(10)	33(4)	57(5)	42(5)	0	16(4)	0
C(1)	43(4)	79(4)	36(4)	–10(3)	21(3)	11(3)
C(4)	92(7)	96(6)	46(7)	–36(5)	13(4)	16(5)
C(7)	37(4)	45(4)	21(5)	0	3(3)	0
C(8)	48(3)	37(3)	45(4)	3(2)	5(3)	0(2)