

Supporting Information

for

Synthesis of Pt(II) phosphinocarboxylate complexes with auxiliary arylcarbene ligands and factors that control their stereochemistry

Filip Horký,^a Johannes Soellner,^b Jiří Schulz,^a Ivana Císařová,^a

Thomas Strassner*^b and Petr Štěpnička*

^a *Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030,
128 40 Prague, Czech Republic;* ^b *Physikalische Organische Chemie, Technische Universität Dresden,
Bergstrasse 66, 01069 Dresden, Germany*

X-ray crystallography

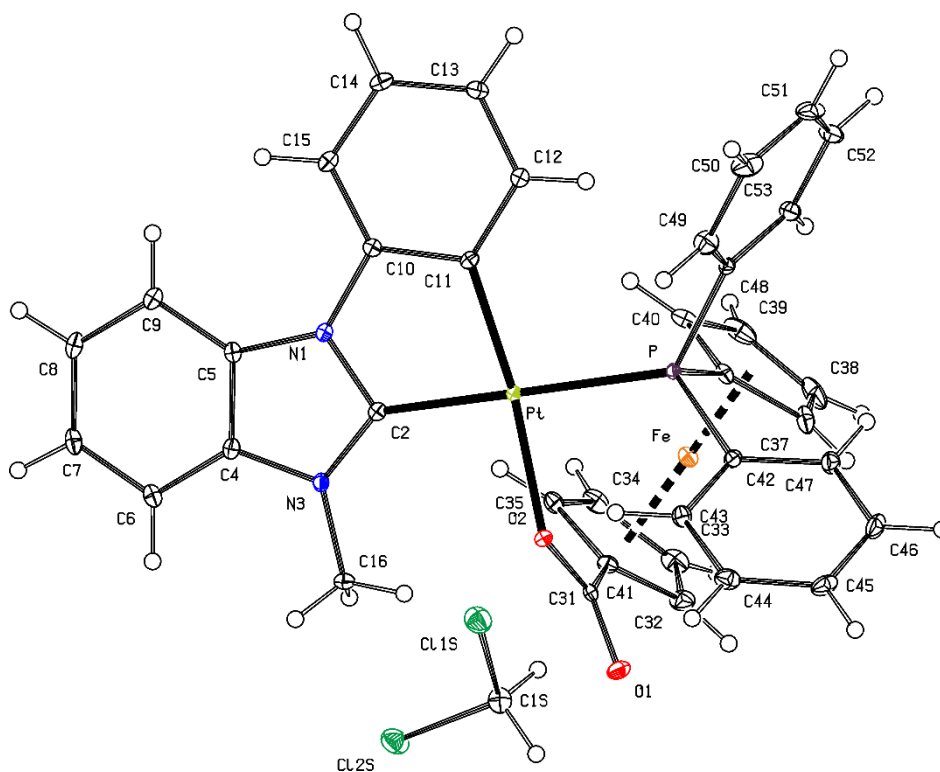


Figure S1. PLATON plot of the structure of $2^{\text{Me}} \cdot \text{CH}_2\text{Cl}_2$ showing 30% probability displacement ellipsoids.

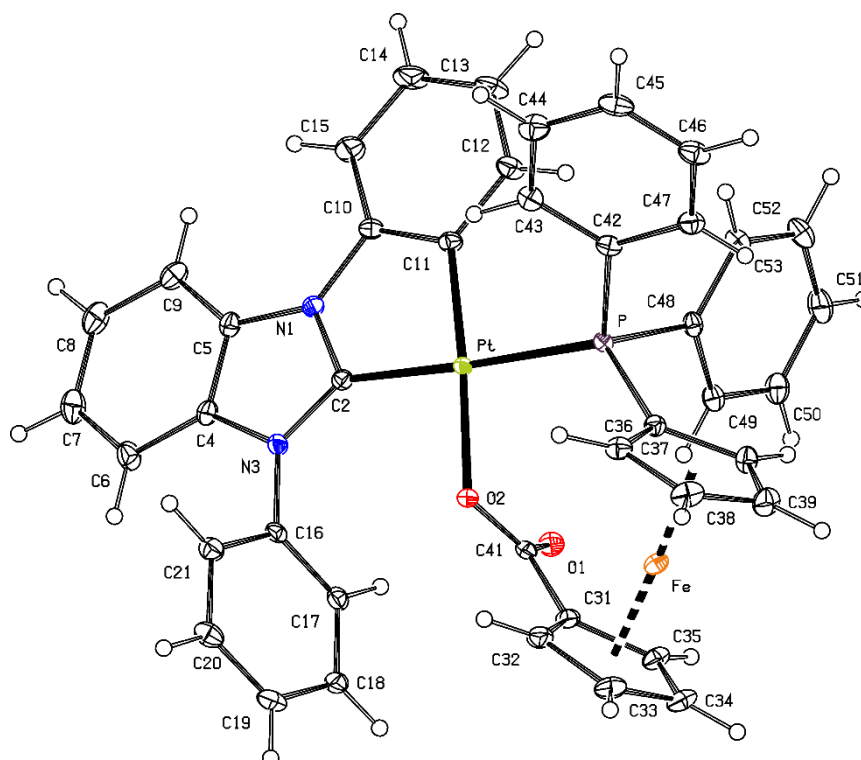


Figure S2. PLATON plot of the structure of $2^{\text{Ph}} \cdot \frac{1}{2} \text{AcOEt}$ showing 30% probability displacement ellipsoids. The solvent molecule was eliminated using PLATON/SQUEEZE (see main text).

Table S1. Selected crystallographic data and structure refinement parameters

Compound	2^{Me}·CH₂Cl₂	2^{Ph}·½AcOEt
Formula	C ₃₈ H ₃₁ Cl ₂ FeN ₂ O ₂ Ppt	C ₄₄ H ₃₅ FeN ₂ O ₃ Ppt
<i>M</i>	900.46	921.65
Crystal system	triclinic	monoclinic
Space group	<i>P</i> -1 (no. 2)	<i>C2/c</i> (no. 15)
<i>T</i> [K]	120(2)	150(2)
<i>a</i> [Å]	10.9275(7)	24.479(1)
<i>b</i> [Å]	12.1821(7)	11.2400(5)
<i>c</i> [Å]	13.5028(8)	26.612(1)
α [°]	90.484(2)	90
β [°]	92.307(2)	102.805(1)
γ [°]	115.888(2)	90
<i>V</i> [Å ³]	1615.1(2)	7140.1(5)
<i>Z</i>	2	8
μ (Mo K α) [mm ⁻¹]	5.030	4.411
Diffns collected	30790	46973
Independent diffns	7396	8231
Observed diffns ^[a]	7294	7746
<i>R</i> _{int} ^[b] [%]	1.97	2.54
No. of parameters	426	461
<i>R</i> ^[b] obsd diffns [%]	1.27	1.58
<i>R</i> , <i>wR</i> ^[b] all data [%]	1.30, 3.07	1.79, 3.63
$\Delta\rho$ [e Å ⁻³]	0.46, -0.69	0.68, -0.56
CCDC deposition number	2284526	2284527

[a] Diffractions with $I > 2\sigma(I)$. [b] Definitions: $R_{\text{int}} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma F_o^2$, where $F_o^2(\text{mean})$ is the average intensity of symmetry-equivalent diffractions. $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR = [\Sigma \{w(F_o^2 - F_c^2)^2\} / \Sigma w(F_o^2)^2]^{1/2}$.

Additional cyclic voltammograms

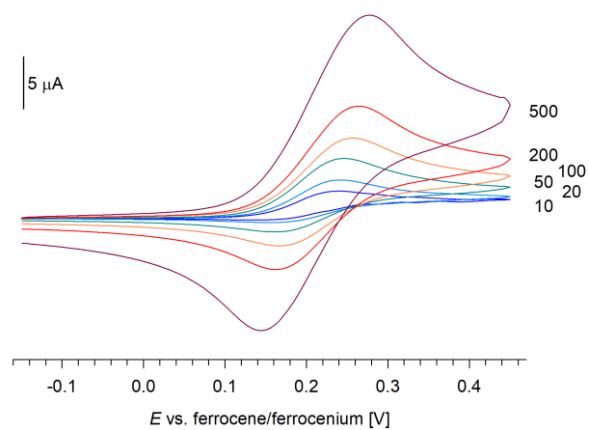


Figure S3 Cyclic voltammograms of **2^{Ph}** (≈ 0.1 mM) recorded at varying scan rates (given in mV s^{-1} in the Figure) at glassy carbon electrode in dichloromethane containing $\text{Bu}_4\text{N}[\text{PF}_6]$ (0.1 M) as the supporting electrolyte

Frontier orbitals and electron density difference on going from 2^{Ph} to 2^{Ph}

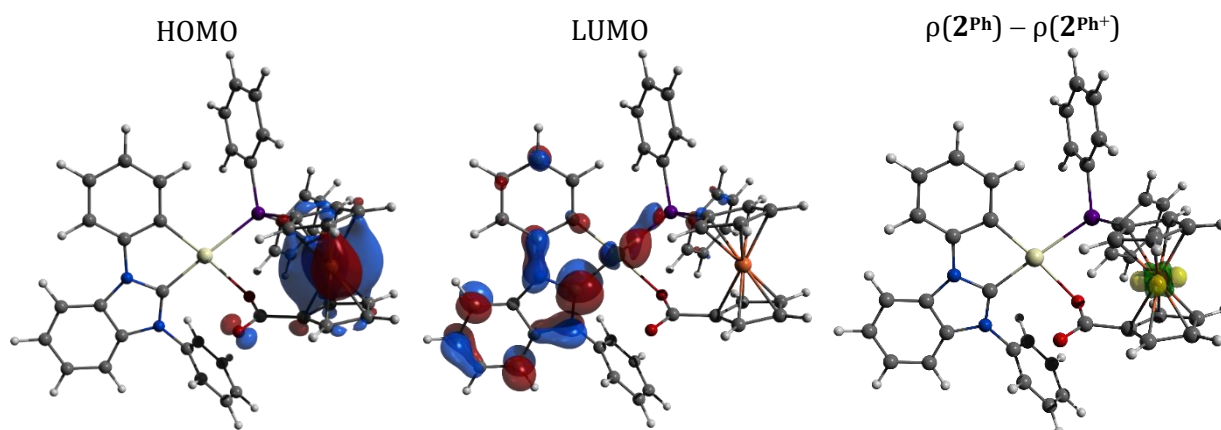


Figure S4 Frontier orbitals of 2^{Ph} (contour maps with isosurfaces at ± 0.04 a.u.) computed at the B3LYP(d3bj)/6-311+G(d,p):LanL2TZ(Pt) level of theory, and the electron difference map for $\rho(2^{\text{Ph}}) - \rho(2^{\text{Ph}^+})$ mapped at the equilibrium geometry of 2^{Ph} (isosurface at ± 0.02 a.u.)

Selected intrinsic bond orbitals (IBOs) for 2^{Me}, 3^{Me}, 2^{Ph}, and 3^{Ph}

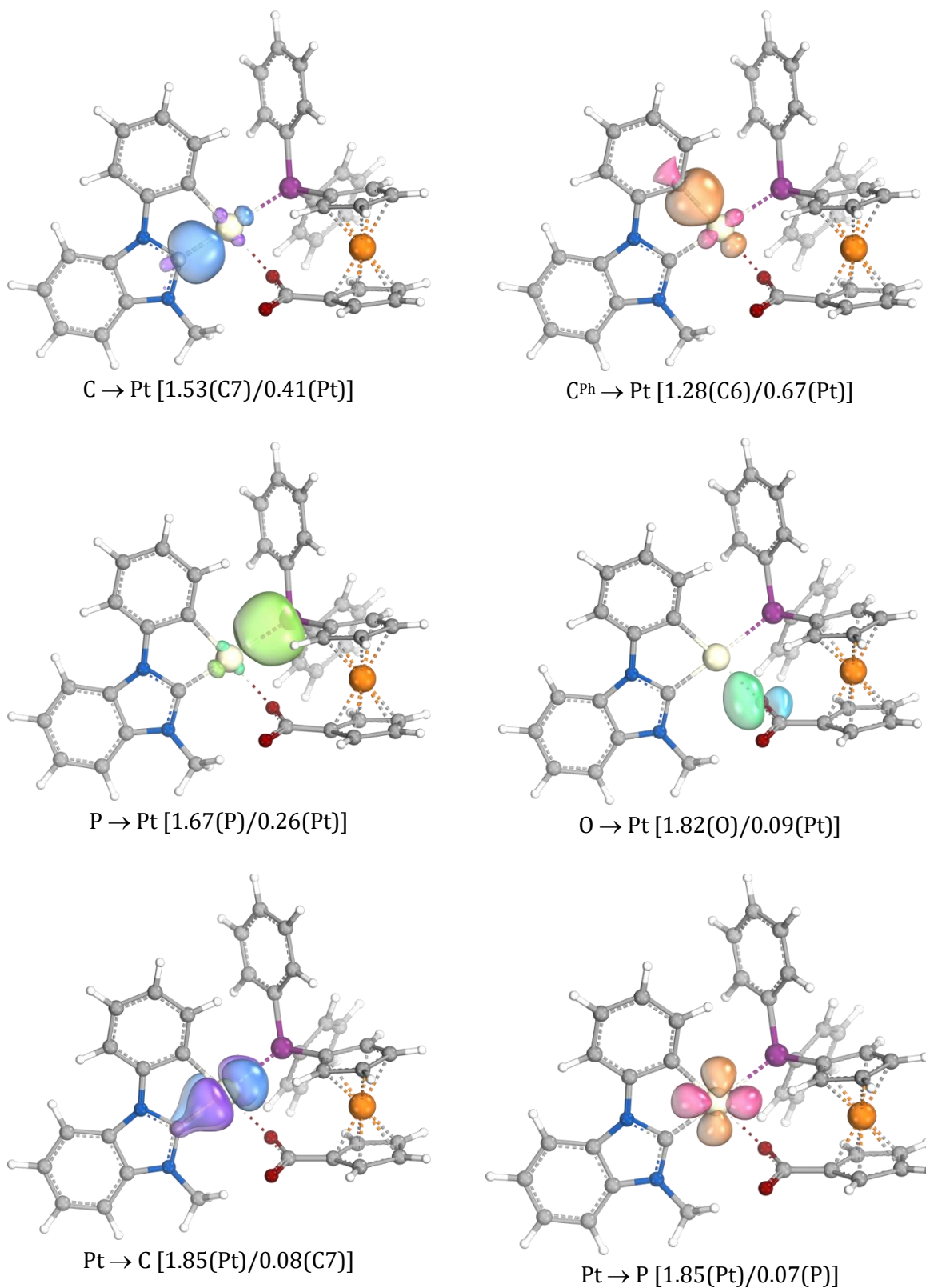
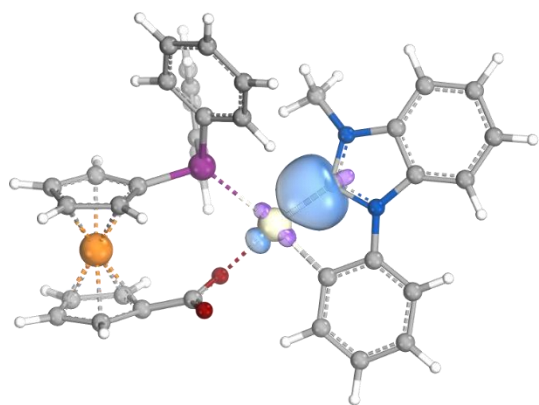
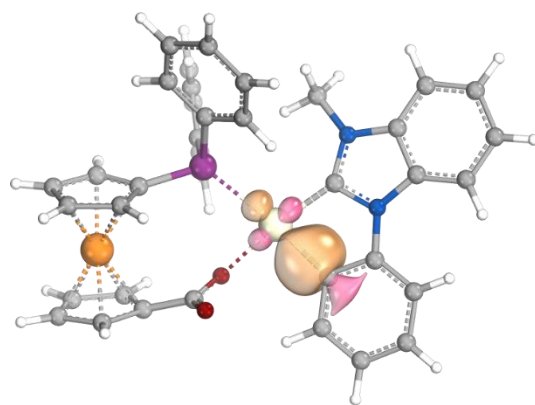


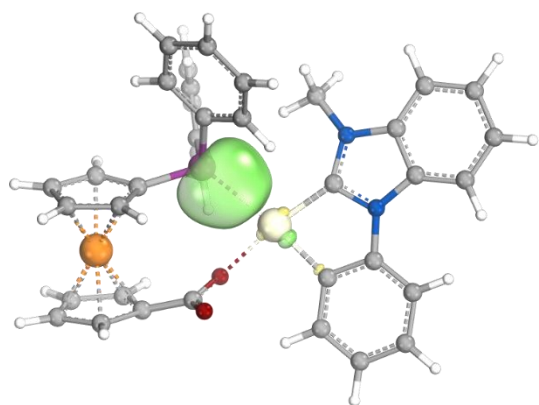
Figure S5 Selected intrinsic bond orbitals (IBOs) of 2^{Me}. Values in parentheses indicate the fraction of bonding electrons assigned to the individual atoms



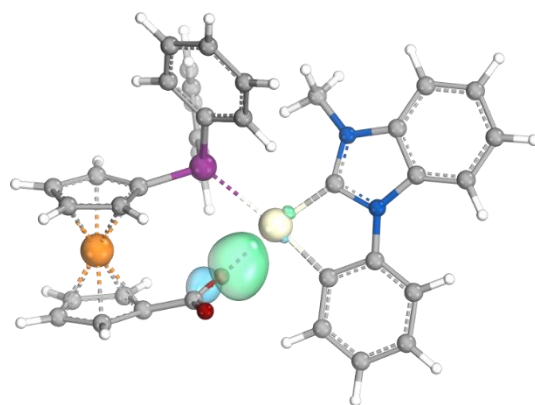
C → Pt [1.51(C7)/0.43(Pt)]



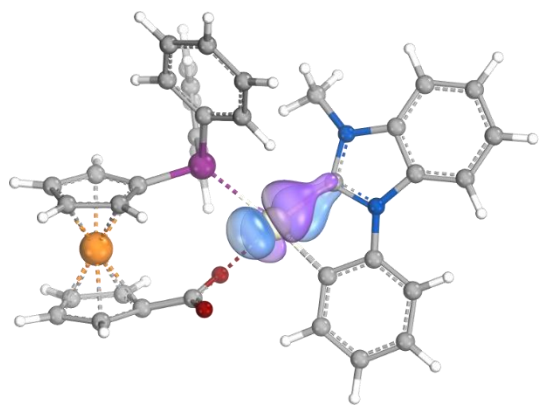
C^{Ph} → Pt [1.27(C6)/0.68(Pt)]



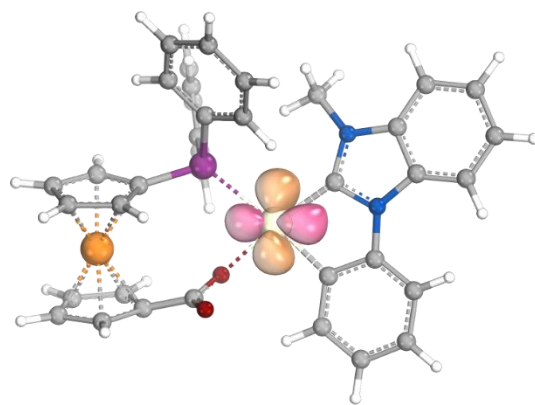
P → Pt [1.73(P)/0.18(Pt)]



O → Pt [1.72(O)/0.19(Pt)]



Pt → C [1.83(Pt)/0.12(C7)]



Pt → P [1.92(Pt)/0.02(P)]

Figure S6 Selected intrinsic bond orbitals (IBOs) of **3^{Me}**. Values in parentheses indicate the fraction of bonding electrons assigned to the individual atoms

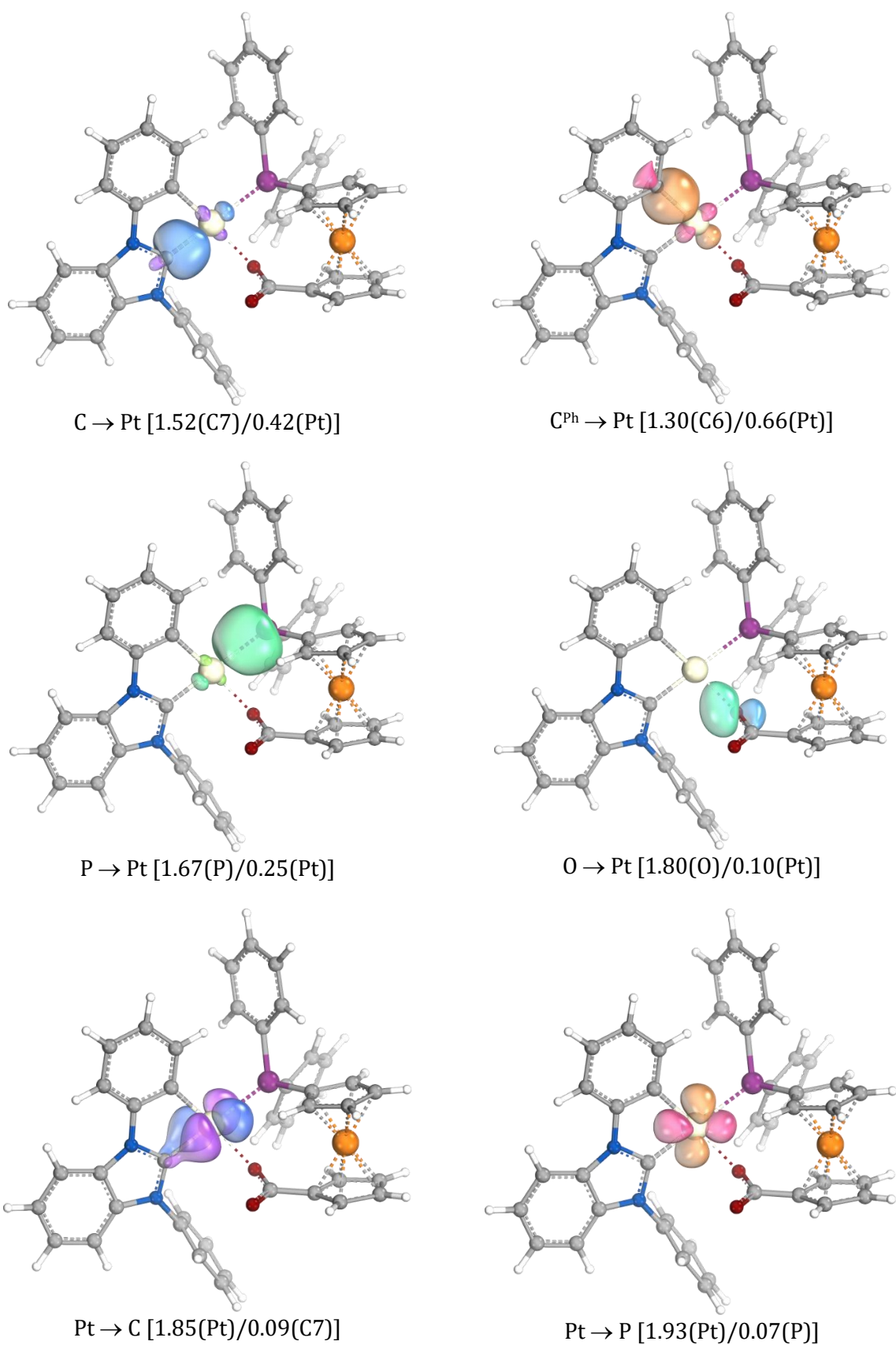
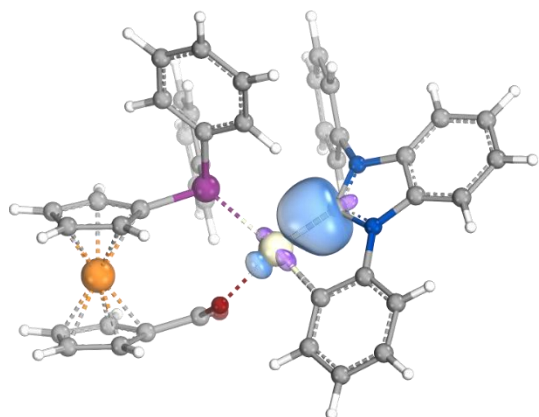
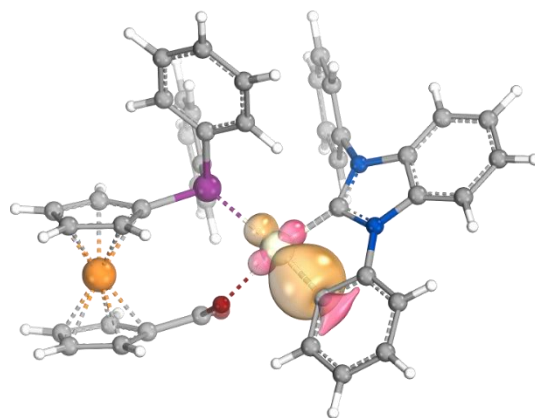


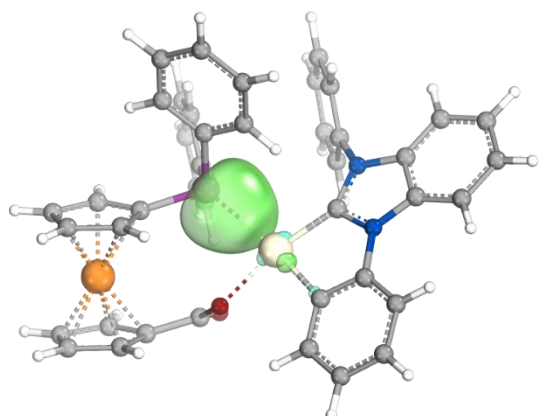
Figure S7 Selected intrinsic bond orbitals (IBOs) of **2^{Ph}**. Values in parentheses indicate the fraction of bonding electrons assigned to the individual atoms



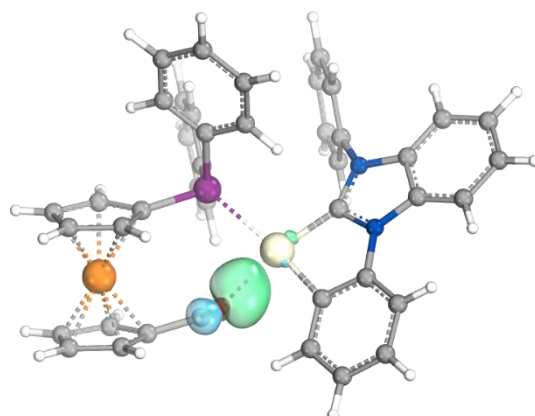
C → Pt [1.51(C7)/0.43(Pt)]



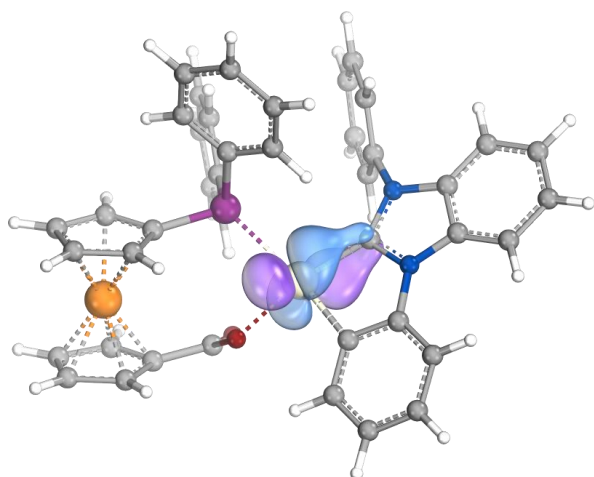
C^{Ph} → Pt [1.27(C^{Ph})/0.68(Pt)]



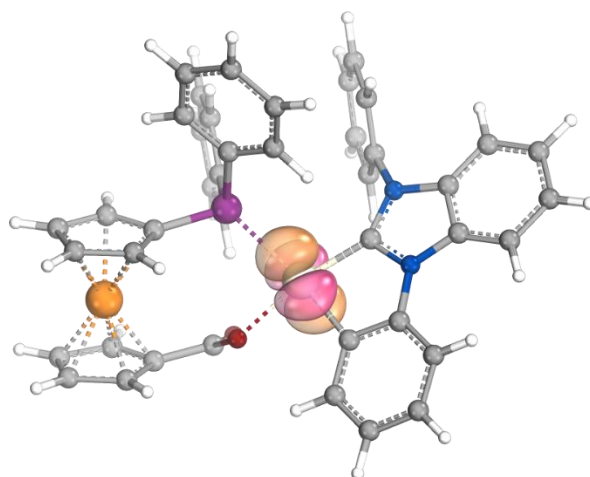
P → Pt [1.74(P)/0.17(Pt)]



O → Pt [1.72(O)/0.19(Pt)]



Pt → C [1.82(Pt)/0.13(C7)]



Pt → P [1.93(Pt)/0.00(P), 0.02(C6)]

Figure S8 Selected intrinsic bond orbitals (IBOs) of **3^{Ph}**. Values in parentheses indicate the fraction of bonding electrons assigned to the individual atoms

Copies of the NMR spectra

(Note: solvent signals in the NMR spectra are marked by an asterisk.)

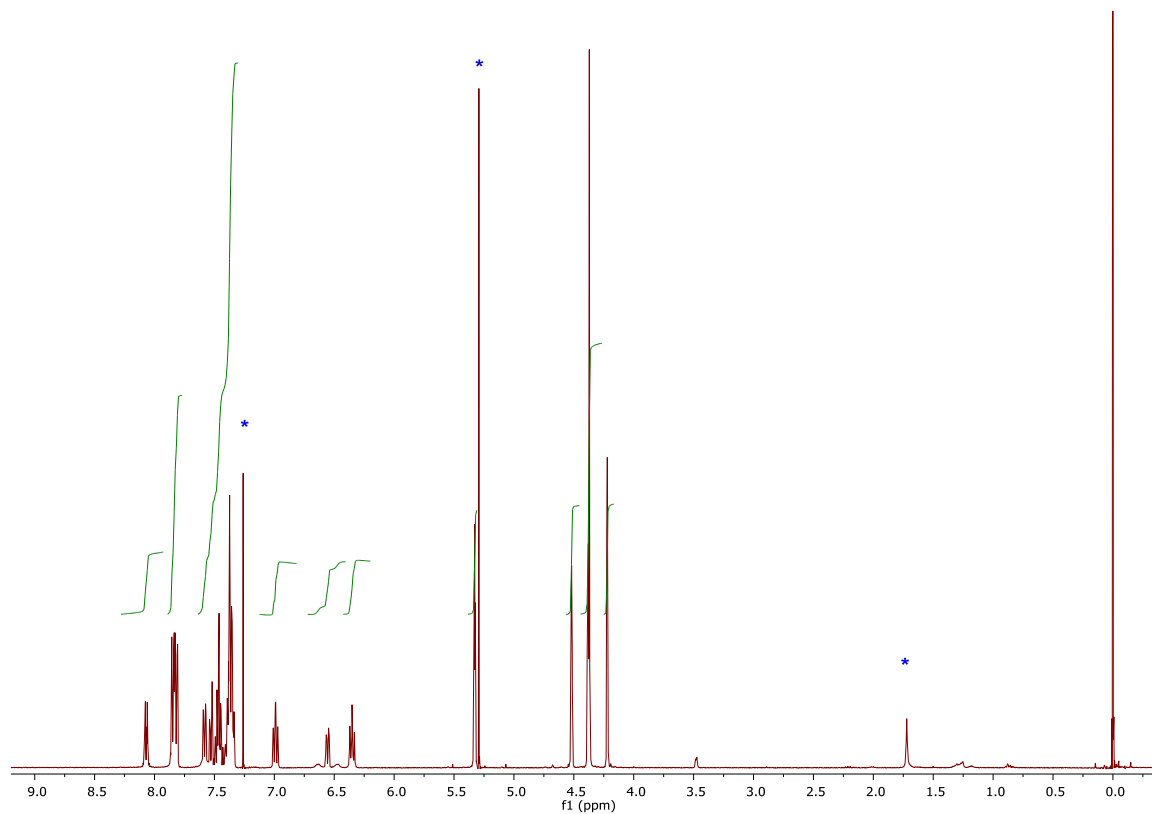


Figure S9 ^1H NMR spectrum (400 MHz, CDCl_3) of **2^{Me}**

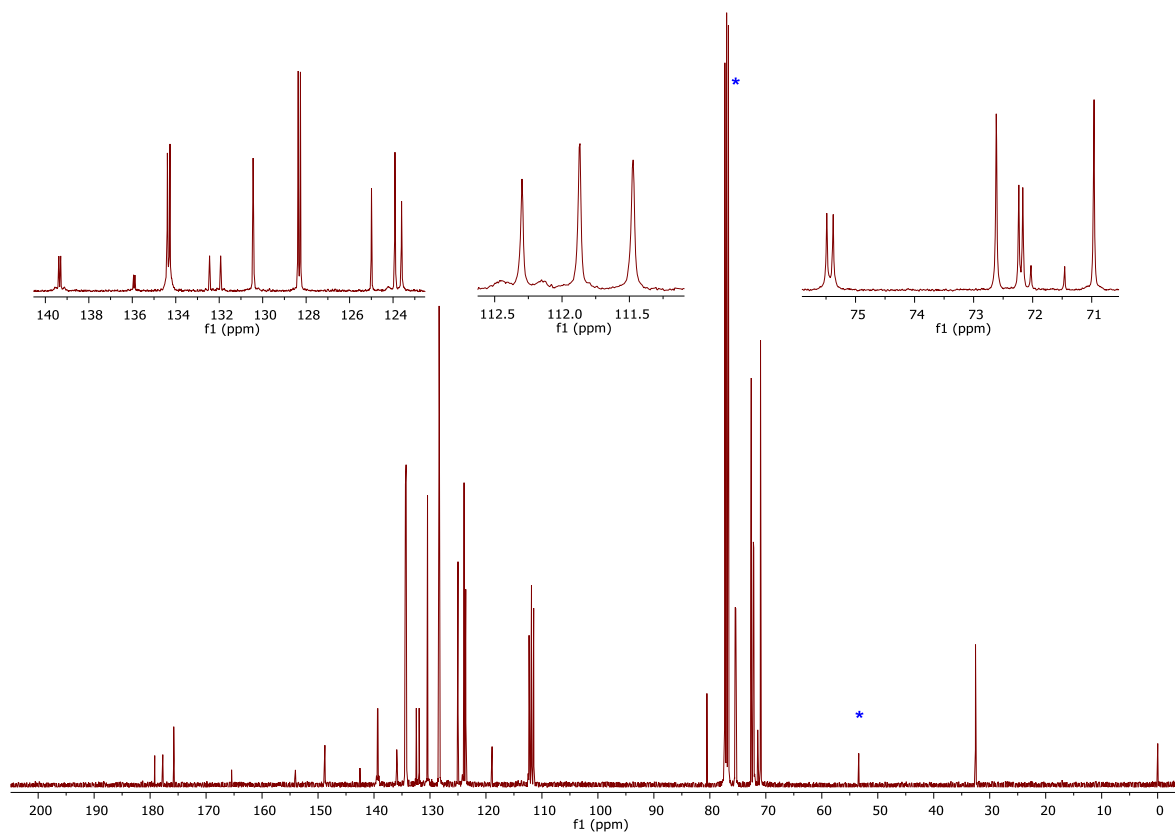


Figure S10 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **2^{Me}**

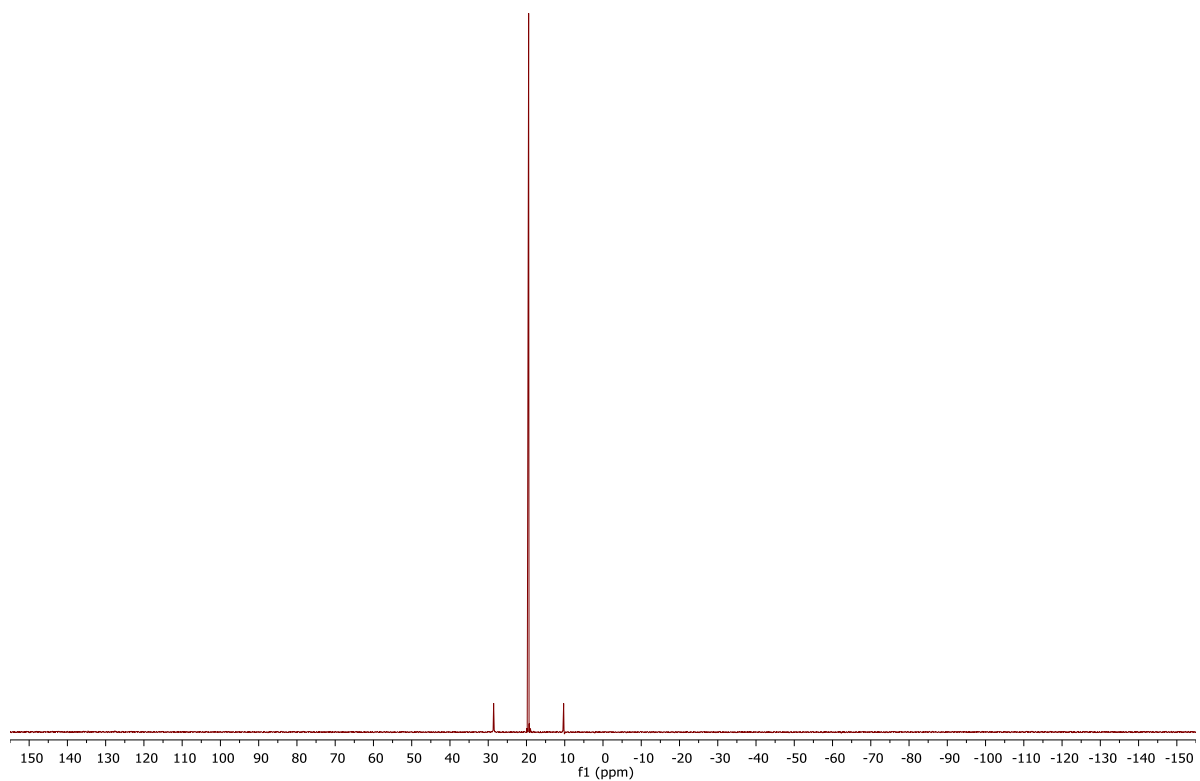


Figure S11 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3) of **2^{Me}**

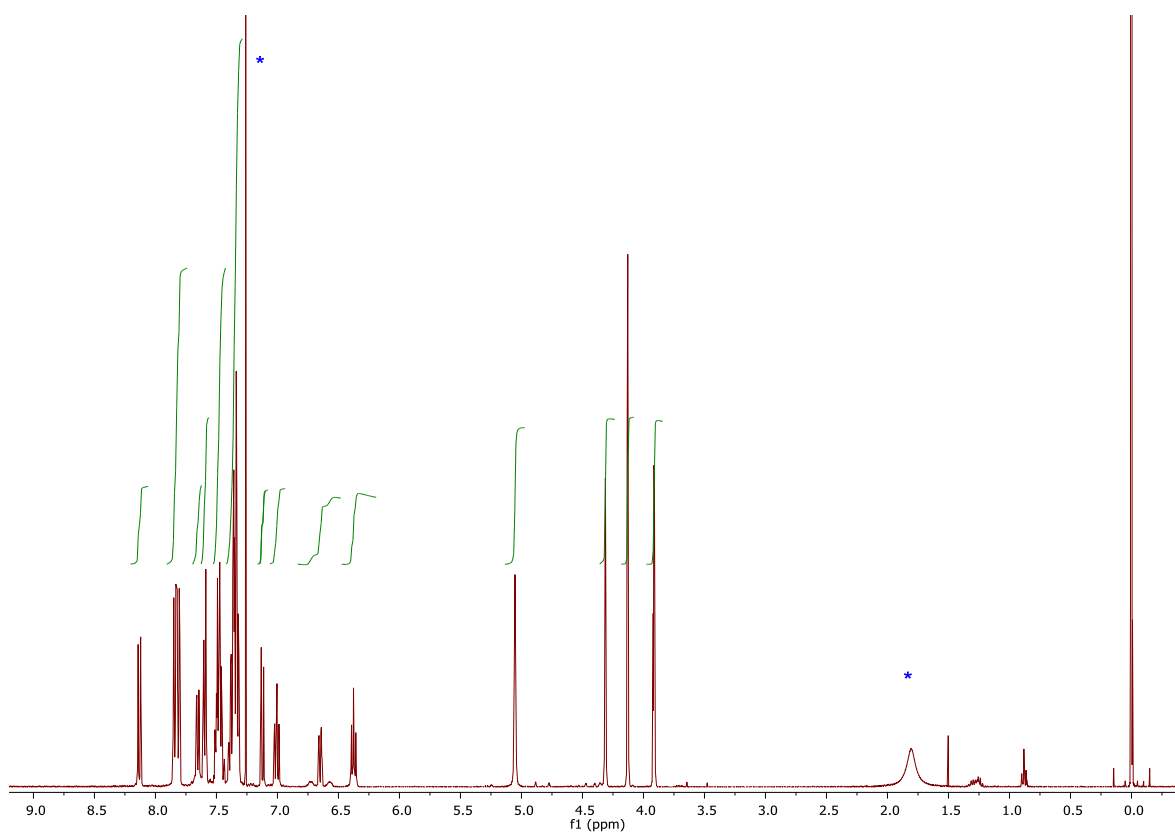


Figure S12 ^1H NMR spectrum (400 MHz, CDCl_3) of 2^{Ph}

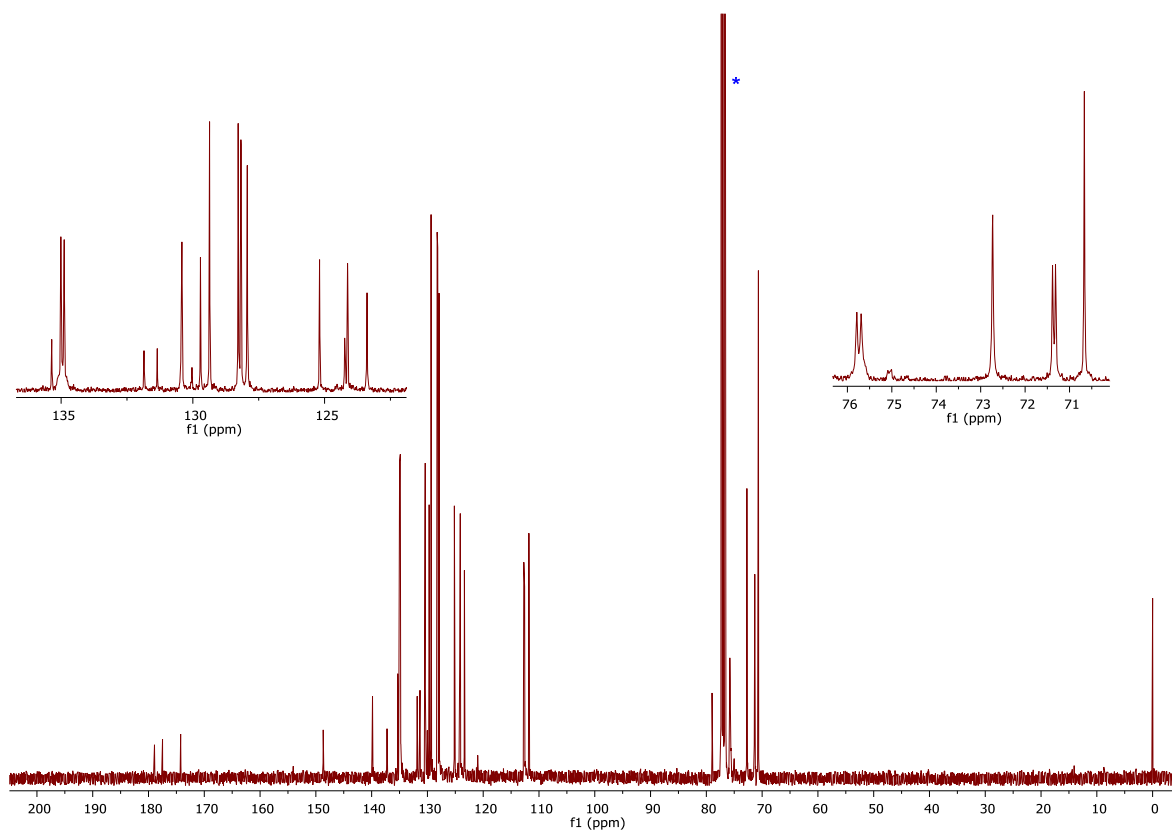


Figure S13 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of 2^{Ph}

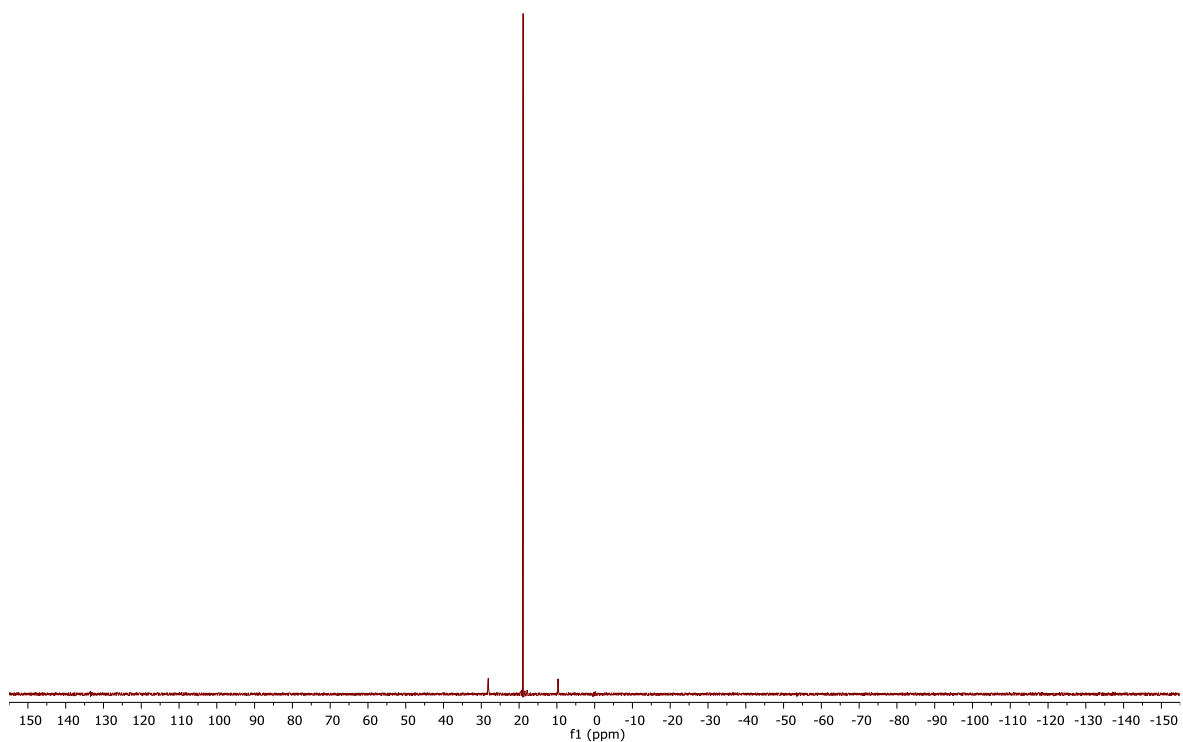


Figure S14 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, CDCl_3) of **2^{Ph}**

Cartesian coordinates of the DFT-optimised species

2^{Me}				H	-4.99150600	-3.89717600	-1.75713600
Pt	0.86497700	-0.03191700	-0.08903300	C	5.69965900	-2.65994900	0.78761800
N	3.73576000	0.14096000	-0.20317500	C	6.28878100	0.03159100	0.06857500
N	3.30826000	-1.92829200	0.36504000	C	7.00917000	-2.18883600	0.77431200
C	4.97446600	-0.43780000	0.06760200	H	7.81785000	-2.85651200	1.04619400
C	4.69267100	-1.76743000	0.43283200	C	7.29514000	-0.86274900	0.42410400
C	1.92330900	1.57412800	-0.72303100	H	8.32293700	-0.51982600	0.43307400
C	2.72925300	-0.76441900	-0.00136300	H	5.47749500	-3.68010500	1.07267400
C	3.32732200	1.41894700	-0.68200800	H	6.53654600	1.05203200	-0.17982900
C	3.70334600	3.56646200	-1.68696100	C	-0.59790200	-2.67868700	-0.45885600
H	4.38427000	4.32718000	-2.05070800	O	-0.23515000	-1.84061900	0.46745800
C	2.32900000	3.74221000	-1.77601100	O	0.11548100	-3.12577800	-1.35696200
H	1.92284400	4.64615500	-2.21665600	C	2.61633700	-3.18784200	0.64220100
C	1.45755000	2.75432700	-1.30443200	H	2.24765900	-3.20267600	1.66917000
H	0.39614100	2.92394500	-1.40541900	H	1.79047100	-3.29615000	-0.05672200
C	4.21216100	2.38429900	-1.14642300	H	3.32243000	-4.00429800	0.49619500
H	5.28039900	2.22801900	-1.12516200	2^{Ph}			
P	-1.34661700	0.93318900	0.25072000	Pt	0.62242500	0.53144900	-0.01792300
C	-1.93248200	0.68051900	1.99108100	N	3.38004700	1.25375200	-0.41632500
C	-1.27501100	-0.21432800	2.84314300	N	3.40202600	-0.84862200	0.19260700
C	-3.02545100	1.40802100	2.48420000	C	4.72807400	0.89071200	-0.36389700
C	-1.71112600	-0.38339300	4.15724600	C	4.73717100	-0.46016200	0.02400100
H	-0.44139500	-0.79204000	2.46975500	C	1.29752800	2.39484600	-0.45438000
C	-3.46374300	1.22921300	3.79383300	C	2.58432900	0.19615300	-0.08364400
H	-3.52659100	2.13349000	1.85467600	C	2.69440600	2.48064800	-0.66362900
C	-2.80616600	0.33239600	4.63485700	C	2.56687300	4.78394000	-1.33009700
H	-1.19050500	-1.07853600	4.80661300	H	3.05250100	5.69269500	-1.66618700
H	-4.31151000	1.79836000	4.15892600	C	1.19233600	4.74016100	-1.14096200
H	-3.14245500	0.19835800	5.65704700	H	0.58847200	5.62148600	-1.32834100
C	-1.56674000	2.76294600	0.08862800	C	0.57368100	3.55969200	-0.71470000
C	-0.91807400	3.60323200	1.00444500	H	-0.49846800	3.56536800	-0.59291000
C	-2.32708400	3.33457300	-0.93618700	C	3.32890500	3.63790000	-1.09700700
C	-1.03691600	4.98494700	0.90148300	H	4.39371600	3.66625500	-1.27253600
H	-0.31447300	3.17735700	1.79798200	P	-1.76472200	0.86180100	0.35599500
C	-2.43993800	4.72208300	-1.04091100	C	-2.31480700	0.13684000	1.97172200
H	-2.83413200	2.70218400	-1.65420100	C	-1.49563500	-0.76000800	2.66779100
C	-1.79852000	5.54911800	-0.12296300	C	-3.55258500	0.49508400	2.52550900
H	-0.52975300	5.62229400	1.61705400	C	-1.91286900	-1.28955100	3.88891900
H	-3.03345200	5.15187200	-1.84019900	H	-0.55018400	-1.06257400	2.24003000
H	-1.88876100	6.62657300	-0.20385200	C	-3.96872100	-0.04290000	3.74086600
C	-2.65961900	0.27319900	-0.83154700	H	-4.18986800	1.21047000	2.01977800
C	-4.08312100	0.26264700	-0.62145700	C	-3.14792900	-0.93660900	4.42728500
C	-2.42420400	-0.21765800	-2.16195200	H	-1.26745300	-1.98254900	4.41733100
C	-4.70365800	-0.21919900	-1.80774300	H	-4.92939100	0.24386700	4.15421700
H	-4.59134800	0.54730800	0.28603600	H	-3.46839600	-1.35056800	5.37700400
C	-3.68120400	-0.51685700	-2.75572600	C	-2.43691000	2.57881700	0.51085600
H	-1.45231400	-0.36600000	-2.60931100	C	-2.04699300	3.35845900	1.60935200
H	-5.76392800	-0.36760200	-1.94918000	C	-3.28703200	3.13650200	-0.44900100
H	-3.82910300	-0.93462700	-3.74023800	C	-2.50543800	4.66427100	1.74705700
Fe	-3.39809900	-1.64668800	-1.02417600	H	-1.37897000	2.94581400	2.35711900
C	-2.04463500	-3.06120800	-0.39600600	C	-3.74126000	4.44935100	-0.31145500
C	-2.96838400	-2.76123200	0.65788000	H	-3.59772300	2.55077000	-1.30508000
C	-2.79419000	-3.58428600	-1.49389800	C	-3.35437700	5.21440500	0.78541700
H	-2.70886400	-2.32508000	1.60850300	H	-2.19572600	5.25501900	2.60182000
C	-4.27432500	-3.09127400	0.20466600	H	-4.40010200	4.86912400	-1.06347700
H	-2.37189500	-3.86770600	-2.44540200	H	-3.70948700	6.23328700	0.89204100
C	-4.16816300	-3.59107100	-1.12863700	C	-2.84412700	0.11933500	-0.91546000
H	-5.19123600	-2.95854100	0.75987100				

C	-4.21375600	-0.30388400	-0.79487900	C	-6.13020500	-0.41630500	-0.35052500
C	-2.48319700	-0.00217000	-2.30133800	H	-6.43278800	-1.42571900	-0.58121100
C	-4.68193600	-0.66764600	-2.08826100	C	-4.21778600	-3.18936400	-0.32782800
H	-4.78053300	-0.35806900	0.12106200	H	-5.25405800	-2.98951200	-0.55672300
C	-3.61495600	-0.48297800	-3.01588500	P	0.92573200	1.09219800	-0.02690200
H	-1.50556100	0.20329000	-2.71193100	C	0.50558400	2.41611900	-1.25268800
H	-5.66451700	-1.05213400	-2.31830400	C	-0.59837900	2.22764400	-2.09156100
H	-3.64468000	-0.70631100	-4.07180700	C	1.32235300	3.53907500	-1.45517600
Fe	-3.04746800	-1.84451800	-1.54106000	C	-0.90431700	3.15812100	-3.08515700
C	-1.37344800	-2.96707700	-1.11803200	H	-1.20535500	1.33713500	-1.98003300
C	-2.36677100	-3.16295700	-0.10389900	C	1.00997800	4.47303600	-2.43887500
C	-1.93114100	-3.40052300	-2.35957300	H	2.22089200	3.67187100	-0.86465000
H	-2.25487800	-2.90225700	0.93571800	C	-0.10777400	4.28747300	-3.25342000
C	-3.52572100	-3.70632200	-0.72161700	H	-1.75814100	2.99115800	-3.73229900
H	-1.42872500	-3.33757800	-3.31228700	H	1.64908200	5.33736600	-2.58143600
C	-3.26013400	-3.84502300	-2.11777200	H	-0.34321500	5.01062600	-4.02626000
H	-4.45634600	-3.94428200	-0.22762000	C	1.11089300	1.88408000	1.63714600
H	-3.95687000	-4.20151200	-2.86220600	C	1.24868500	0.99921100	2.71816500
C	3.03459700	-2.14359300	0.70594000	C	1.09702000	3.26089600	1.88600700
C	3.00083200	-3.23978500	-0.14884900	C	1.39394100	1.48648600	4.01458000
C	2.79067200	-2.28419900	2.06969900	H	1.23160600	-0.07045400	2.53921100
C	2.70966400	-4.49754400	0.37480800	C	1.22873400	3.74445800	3.18830600
H	3.15489300	-3.09803600	-1.20991100	H	0.97379000	3.96438000	1.07253600
C	2.49699900	-3.54429200	2.58403300	C	1.38364100	2.86043000	4.25355700
H	2.82583000	-1.41319700	2.71330500	H	1.50281700	0.79099400	4.83921200
C	2.45829500	-4.65130900	1.73712600	H	1.21174000	4.81406400	3.36667100
H	2.66420600	-5.35395300	-0.28764600	H	1.48824600	3.23862700	5.26428100
H	2.30042100	-3.66053100	3.64369900	C	-2.37313700	2.48459400	0.79575000
H	2.22782900	-5.63197300	2.13788500	H	-2.94016600	2.91136800	1.62549800
C	5.91568800	-1.17667300	0.19497100	H	-1.39539500	2.19797400	1.16492300
C	5.93086200	1.56213400	-0.59026200	H	-2.26599600	3.22937000	0.00542900
C	7.11024800	-0.50185700	-0.03814700	C	2.68594000	0.84683200	-0.51414700
H	8.05079300	-1.02607700	0.08140900	C	3.12092200	0.41799100	-1.81425300
C	7.11335700	0.84539200	-0.42316900	C	3.84729200	1.32706300	0.18398700
H	8.05822400	1.34715200	-0.59522900	C	4.52129400	0.64976200	-1.91461100
H	5.89734200	-2.21578500	0.49711800	H	2.49279900	-0.02871200	-2.57068300
H	5.96785700	2.60040100	-0.88066600	C	4.97107300	1.20498100	-0.68091000
C	-0.09223300	-2.19940800	-0.98504700	H	3.86036900	1.70612700	1.19389000
O	-0.00174400	-1.54352800	0.13689600	H	5.14029900	0.40374400	-2.76451600
O	0.71447600	-2.18586800	-1.91165100	H	5.99004400	1.46138300	-0.43176400
3^{Me}				Fe	4.10638600	-0.66537600	-0.36118800
Pt	-0.74448100	-0.78190900	0.17776200	C	3.16925600	-2.45908000	-0.04941400
N	-3.59431100	-0.77402000	-0.14688400	C	4.22852600	-2.63763400	-0.99034200
N	-3.06651200	1.30019400	0.31364400	C	3.75010600	-1.99834200	1.17789300
C	-4.79588700	-0.06850600	-0.13785800	H	4.09168300	-2.93816100	-2.01739400
C	-4.45070300	1.26226000	0.15170200	C	5.44820500	-2.27238600	-0.35690900
C	-1.93857400	-2.41974400	0.13210700	H	3.19899000	-1.75217800	2.07062700
C	-2.53072200	0.06496500	0.10784900	C	5.15307000	-1.88371200	0.98498800
C	-3.29263900	-2.16986900	-0.13412700	H	6.42556500	-2.26501100	-0.81662400
C	-6.73242500	1.91782900	0.02896200	H	5.86958700	-1.53709300	1.71518000
H	-7.50272200	2.67735600	0.08688100	C	1.71700400	-2.42210800	-0.41184400
C	-7.08554400	0.59431900	-0.26175800	O	0.98781300	-1.91153500	0.54194400
H	-8.12750100	0.34572000	-0.42465800	O	1.33727000	-2.76665400	-1.52388600
C	-3.78195700	-4.51215300	-0.22275700	3^{Ph}			
H	-4.49061000	-5.31912800	-0.36980000	C	-5.76118200	-1.53034400	-0.85890500
C	-2.44912300	-4.78816800	0.06479000	C	-4.60632600	-1.24858200	-1.63815300
H	-2.11487300	-5.81672400	0.14650400	C	-3.52247500	-2.02161000	-1.11571400
C	-1.53191100	-3.74681900	0.23606900	C	-4.02045800	-2.79275800	-0.01835800
H	-0.49292400	-3.96943500	0.43598200	C	-5.40247800	-2.49039500	0.13537300
C	-5.40203400	2.27244600	0.24043800	Fe	-4.23062000	-0.78290300	0.35989500
H	-5.12353600	3.29559700	0.45957100	C	-4.91227900	0.83786400	1.46770200

C	-3.86593000	1.25307000	0.59594300	H	7.67119400	1.44907100	0.04340700
C	-2.68223100	0.50460300	0.91942200	H	7.96468900	-0.95057800	0.54509700
C	-3.02700900	-0.38632700	1.99051200	H	3.64575700	-6.06431200	0.33605900
C	-4.39248400	-0.17020800	2.33260500	H	1.26579000	-6.25281700	-0.34025900
P	-0.95152800	0.88229500	0.38883200	H	-0.10116700	-4.20501400	-0.66258300
C	-1.25912900	2.25701900	-0.81890800	H	5.40166400	2.38910400	-0.35103200
C	-1.59304000	1.89053800	-2.13125300	H	6.03993000	-2.47250700	0.65591500
C	-1.94137600	2.86613800	-3.06379200	H	4.67279100	-3.85343300	0.64469200
C	-1.94748900	4.21416900	-2.70853600	H	1.46048500	0.60715100	2.04241300
C	-1.58737900	4.58444700	-1.41508400	H	-2.19676000	2.83724300	2.27533500
C	-1.24287400	3.61324100	-0.47538400	H	2.20265000	1.60099700	4.17416800
C	-2.08794700	-1.79422500	-1.45870900	H	-1.45219700	3.84325300	4.38846200
O	-1.77310900	-1.24436400	-2.51299800	H	0.75501400	3.23804400	5.35492600
Pt	0.51922900	-1.09266200	-0.23850700	H	-1.59089800	0.84526100	-2.42433800
O	-1.28223600	-2.13974800	-0.49938200	H	-0.96167100	3.92430400	0.52165200
C	1.50495400	-2.86058700	-0.23113000	H	-2.20903700	2.56538600	-4.07088900
C	2.86091400	-2.78541000	0.12019100	H	-1.57497800	5.63123300	-1.13091200
C	3.63822200	-3.91696800	0.34239100	H	-2.22472200	4.97015400	-3.43528400
C	3.05132200	-5.17284300	0.17216100	H	-2.36029600	-1.10169800	2.44741900
C	1.71514500	-5.27514400	-0.20256100	H	-3.94323800	1.99821200	-0.18001400
C	0.94425300	-4.12457700	-0.39526700	H	-4.94560000	-0.70561000	3.08994800
N	3.32736700	-1.43861800	0.19012200	H	-5.92802200	1.20423600	1.45465900
C	4.61073800	-0.89444700	0.22391500	H	-3.42758300	-3.44880500	0.59855000
C	4.45308400	0.47364300	-0.04342300	H	-4.52748200	-0.54682800	-2.45342800
N	3.07816700	0.70071800	-0.22171900	H	-6.06051400	-2.89415500	0.89062400
C	2.38368100	-0.46730700	-0.06850300	H	-6.73562200	-1.08094600	-0.98099900
C	5.53720000	1.34045100	-0.12271200	C	2.12764200	1.98524100	-2.06855300
C	6.80302200	0.80314400	0.09546000	C	1.81042200	3.21443200	-2.64016400
C	6.96863800	-0.55825600	0.37779400	C	1.96931500	4.38995900	-1.90976100
C	5.88212400	-1.42694800	0.44363400	C	2.42477000	4.33751100	-0.59351400
C	2.59775800	1.94299300	-0.75725100	C	2.73772200	3.11231100	-0.01064600
C	-0.39119800	1.69161700	1.96696200	H	2.02259300	1.06534200	-2.63058100
C	0.83735500	1.34071800	2.53478800	H	1.44024400	3.25036600	-3.65732900
C	1.25065300	1.89587000	3.74641000	H	1.72761700	5.34450800	-2.36207300
C	0.43737000	2.80886200	4.41113100	H	2.53422800	5.24875700	-0.01686200
C	-0.80089700	3.15058800	3.86691300	H	3.09080300	3.05990200	1.01179900
C	-1.21586600	2.59035600	2.66221900				