Electronic Supplementary Information

Synthesis, Characterization and Reactivity of Carbohydrate Platinum(IV)

Complexes with Thioglycoside Ligands

Cornelia Vetter, Papapida Pornsuriyasak, Jürgen Schmidt, Nigam P. Rath, Tobias Rüffer, Alexei V. Demchenko, Dirk Steinborn

Energies and Cartesian coordinates of calculated molecules

(Coordinates are given for the structures in the gas phase without considering the solvent.)

[PtMe₃(OAc-κ²*O*,*O*')(Me₂CO)]

File: PtMe3OAc_03.log/PtMe3OAc_03_mitsolvent.log	
SCF energy (gas phase, without solvent)	-660.950280154 Ha
Sum of electronic and thermal free energies (gas phase, without solvent)	-660.751904 Ha
Total free energy in acetone at 298 K	-660.745606 Ha

С	0.87973400	-1.94268500	-1.33877800
Н	1.33464900	-1.48460700	-2.22037800
Н	-0.08501600	-2.37980700	-1.60471300
Н	1.53896900	-2.71420700	-0.93950900
С	2.51755900	-0.39341800	0.46646100
Н	2.62112500	0.21182100	1.36914000
Н	3.04453800	0.07741600	-0.36528700
Н	2.90767900	-1.39610600	0.63833500
С	0.20458600	-1.88680800	1.38375800
Н	-0.69581700	-2.44476900	1.11387900
Н	0.05680500	-1.38362000	2.34397700
Н	1.03870400	-2.58435700	1.46967300
С	-2.74460900	-0.09068700	-0.07102200
С	-2.74612600	0.52401000	1.30246700
Н	-2.78145400	-0.28990300	2.03641800
Н	-3.62765700	1.14789800	1.46053400
Н	-1.82914000	1.09143800	1.46754400
С	-4.07110600	-0.27992400	-0.76026600
Н	-4.50081600	0.70183900	-0.98648800
Н	-4.77532200	-0.78657100	-0.09334400
Н	-3.94713900	-0.84515000	-1.68214400
С	0.54160700	2.23681100	-0.12710100
С	0.61051100	3.74334500	-0.19182700
Н	0.57462600	4.08667500	-1.22483000
Н	1.55280100	4.07115700	0.25637200
Н	-0.20140500	4.18402600	0.38853100
0	-1.71725200	-0.45198700	-0.63296300
0	0.24480500	1.66960200	0.97201300
0	0.80132100	1.54699300	-1.15562000

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Pt 0.53833300 -0.42107600 -0.01124800

[PtMe₃(OAc-кO)(Me₂CO)₂] (conformer 1)

File: PtMe3OAc_04.log/PtMe3OAc_04_ms_102_13_07.log-854.167955256 HaSCF energy (gas pahse, without solvent)-854.167955256 HaSum of electronic and thermal free energies (gas phase, without solvent)-853.893239 HaTotal free energy in acetone at 298 K-853.879722 Ha

С	-2.10262900	-0.71451900	-1.63418700
Η	-1.70719200	-1.51575800	-2.26387100
Η	-2.10473100	0.22241700	-2.19785200
Н	-3.12607300	-0.96231900	-1.34554600
С	-1.28126400	-2.38257400	0.58170400
Η	-1.08839100	-2.43216300	1.65325100
Η	-0.59338900	-3.03343600	0.04026100
Н	-2.31358200	-2.65022100	0.35856000
С	-2.43681600	0.18564400	1.09677600
Η	-2.75722300	1.15234800	0.70158800
Н	-2.08222200	0.28570400	2.12388800
Η	-3.27263300	-0.51292200	1.05802000
С	-0.14819800	2.78939900	-0.29492800
С	0.18270000	2.93634700	1.15981900
Н	-0.33347000	2.18958200	1.75994500
Н	-0.01681400	3.94710300	1.51957700
Н	1.25630800	2.73222100	1.25328100
С	-0.03526000	4.02107700	-1.15929300
Н	0.93202200	4.50656900	-0.99878400
Η	-0.80459700	4.74191600	-0.86282000
Н	-0.16098600	3.76628200	-2.21015900
С	1.67773000	0.01597400	1.76917400
С	2.38770700	-0.24299100	3.09635200
Н	3.41231800	0.12629700	3.06201500
Η	2.39040500	-1.31598900	3.30509100
Η	1.84399500	0.24009700	3.91182600
С	2.03325900	-0.96001300	-1.56620000
С	2.13976500	0.36395800	-2.26728000
Н	2.54768700	0.21153400	-3.27200700
Н	2.83729500	0.99319100	-1.70941000
Н	1.17118100	0.85351400	-2.32454400
С	3.29988100	-1.76253700	-1.41914500
Н	3.88517000	-1.27907300	-0.62989400
Η	3.89689100	-1.75424000	-2.33419800
Η	3.06966600	-2.78352800	-1.11857800
0	-0.47112000	1.72398600	-0.80721800
0	0.43427100	-0.31769100	1.77143300
0	0.98208000	-1.40634600	-1.12311800
Pt	-0.86086900	-0.47886100	-0.01211000
0	2.30037900	0.51548400	0.81992200

[PtMe₃(OAc-κO)(Me₂CO)₂] (conformer 2)

File: PtMe3OAc_05_neustart03.log/PtMe3OAc_06_step51.log

SCF energy (gas phase, without solvent) -854.166835523 Ha Sum of electronic and thermal free energies (gas phase, without solvent) -853.890961 Ha Total free energy in acetone at 298 K

С	-0.96061200	-2.31225500	-1.15382400
Н	-0.14345100	-2.64282000	-1.79890200
Н	-1.75417200	-1.87831200	-1.76876300
Н	-1.35731300	-3.16842500	-0.60462700
С	1.04345900	-2.17611900	0.91997700
Н	1.23221500	-1.86714300	1.94816000
Н	1.95867900	-2.11551300	0.33066300
Н	0.63845200	-3.18777200	0.89491200
С	-1.63511600	-1.35461400	1.49439100
Н	-2.63206600	-1.18203400	1.08068300
Н	-1.46293700	-0.71761400	2.36293800
Н	-1.54542400	-2.40364800	1.77615700
С	-2.49762900	1.57187600	-0.55184900
С	-2.46971800	2.05276100	0.87292000
Н	-1.53289200	1.77280000	1.35659000
Н	-3.30279500	1.58098200	1.40771400
Н	-2.63308000	3.13238300	0.92042300
С	-3.46166100	2.24248900	-1.49961500
Н	-3.12831700	3.26994700	-1.68179200
Н	-4.45669400	2.30814300	-1.05021500
Н	-3.50676400	1.70347100	-2.44443500
С	1.59505300	1.24775700	1.60791400
С	1.77267200	2.10132000	2.86276000
Н	2.75744900	2.56715900	2.87051000
Н	1.66397200	1.46912400	3.74825400
Н	0.99523800	2.86743500	2.91587700
С	2.03556300	0.60259500	-1.73158200
С	1.43171100	1.97949100	-1.69866300
Н	1.18261900	2.25964900	-2.73001300
Н	2.14983100	2.70264800	-1.31253100
Н	0.52802800	1.98955800	-1.09604100
С	3.47466000	0.49621100	-2.15286100
Н	4.06970700	0.79469300	-1.28368100
Н	3.70781900	1.17949500	-2.97356600
Н	3.72027200	-0.52990800	-2.42208100
0	-1.78101900	0.66719600	-0.96248600
0	0.39447000	0.78437300	1.46022600
0	1.39381800	-0.41599500	-1.49491800
Pt	-0.25099300	-0.83796500	0.08856000
0	2.55007700	1.05790800	0.85076700

Acetone

File: PtMe3OAc_aceton02.log/PtMe3OAc_aceton02_acetone.log SCF energy (gas phase, without solvent) -193.213024971 Ha Sum of electronic and thermal free energies (gas phase, without solvent) -193.158013 Ha Total free energy in acetone at 298 K -193.157973 Ha

3

-853.880388 Ha

С	-0.00000100	0.18639700	-0.00002000
С	-1.29145200	-0.61343800	0.00159900
Н	-1.30156800	-1.33473400	0.82445900
Н	-1.37661900	-1.18776300	-0.92685100
Н	-2.14133600	0.06190700	0.08895000
0	0.00000300	1.39551100	0.00000400
С	1.29145000	-0.61344400	-0.00160300
Η	1.37675700	-1.18742700	0.92705000
Н	1.30144700	-1.33503900	-0.82419600
Н	2.14131500	0.06188100	-0.08930100

Synthesis of *fac*-[PtMe₃I(4,4'-^tBu₂bpy)]

fac-[(PtMe₃I)₄] (200.0 mg, 0.14 mmol) was dissolved in benzene (5 ml) and a solution of 4,4'di-*tert*-butyl-2,2'-bipyridine (150.2 mg, 0.56 mmol) in benzene (2 ml) was added. The clear, yellow solution was stirred overnight. The reaction mixture was concentrated in *vacuo* and the yellow solid was washed with hexane (3 × 2 ml). (276 mg, 80%). Found: C 39.67, H 5.16, N 4.10. C₂₁H₃₃N₂IPt requires C 39.69, H 5.19, N 4.41%; v_{max}(KBr)/cm⁻¹ 2962 s, 2892 s, 2812 w, 1611 s, 1547 w, 1480 w, 1408 s, 1364 w, 1249 w, 1220 w, 1021 w, 890 w, 846 w, 604 w, 551 w; $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.86 (2H, m, *H*6/*H*6'), 8.10 (2H, m, *H*3/*H*3'), 7.57 (2H, m, *H*5/*H*5'), 1.51 (6H, s+d, ²*J*_{Pt,H} = 70.1, N_{*trans*}-PtC*H*₃), 1.44 (18H, s, C(C*H*₃)₃), 0.52 (3H, s+d, ²*J*_{Pt,H} = 73.5, I_{*trans*}-PtC*H*₃); $\delta_{\rm C}$ (125 MHz, CDCl₃) 163.1 (C4/C4'), 154.6 (C2/C2'), 146.9 (C6/C6'), 124.0 (C3/C3'), 120.0 (C5/C5'), 35.4 (C(CH₃)₃), 30.4 (C(CH₃)₃), 7.8 (s+d, ¹*J*_{Pt,C} = 682.8, N_{*trans*}-PtCH₃), -6.5 (s+d, ¹*J*_{Pt,C} = 665.6, I_{*trans*}-Pt CH₃); $\delta_{\rm Pt}$ (107 MHz, CDCl₃) –2841.

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fac-[PtMe₃(bpy)(ch-SEt)][BF₄] (8, ch-SEt = 4a). v_{max} (KBr)/cm⁻¹ 3127 w, 2964 w, 2906 m, 2106 w, 1759 s, 1603 m, 1495 w, 1477 w, 1449 m, 1375 m, 1319 w, 1235 s, 1211 s, 1090 s, 1052 s, 904 w, 771 s, 603 w, 520 w; $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.81 (1H, m, br, *H6/H6'*), 8.72 (2H, d, br, *H3/H3'*), 8.32 (2H, m, *H4/H4'*), 7.86 (2H, m, br, *H5/H5'*), 4.95 (1H, dd, br, *H2*_{ch}), 4.61 (2H, m, br, *H1*_{ch}, *H4*_{ch}), 4.33 (1H, d, br, *H3*_{ch}), 3.92 (2H, m, br, *H6*_{ach}, *H6*_{bch}), 3.41 (1H, m, br, *H5*_{ch}), 2.57 (1H, m, br, *CH*₂CH₃), 2.35 (1H, m, br, *CH*₂CH₃), 2.10 (3H, s, C(O)*CH*₃), 1.99 (3H, s, C(O)*CH*₃), 1.93 (3H, s, C(O)*CH*₃), 1.89 (3H, s, C(O)*CH*₃), 1.09 (6H, s+d, br, ²*J*_{Pt,H} = 67.8, N_{trans}-PtCH₃), 1.03 (3H, t, br, CH₂CH₃), 0.66 (3H, s+d, br, ²*J*_{Pt,H} = 72.0, ch_{trans}-PtCH₃); $\delta_{\rm C}$ (125 MHz, CDCl₃) 169.4 (2 × *C*(O)CH₃), 169.1 (2 × *C*(O)CH₃), 154.9 (*C*2, *C*2'), 146.9 (*C*6), 146.7 (*C*6'), 141.5 (*C*4, *C*4'), 128.2 (*C*5), 128.0 (*C*5'), 125.9 (*C*3, *C*3'), 83.4

 $(C1_{ch})$, 79.6 $(C3_{ch})$, 75.8 $(C5_{ch})$, 73.1 $(C2_{ch})$, 69.0 $(C4_{ch})$, 61.2 $(C6_{ch})$, 23.9 (CH_2CH_3) , 14.0 (CH_2CH_3) , 5.8 $(s+d, {}^{1}J_{Pt,C} = 662.0, ch_{trans}-PtCH_3)$, -5.0 $(s+d, {}^{1}J_{Pt,C} = 657.0, N_{trans}-PtCH_3)$, -5.1 $(s+d, {}^{1}J_{Pt,C} = 658.3, N_{trans}-PtCH_3)$; δ_{Pt} (107 MHz, CDCl₃) -2772.

fac-[PtMe₃(bpy)(ch-SEt)][BF₄] (9, *ch-SEt* = 4b). $v_{max}(KBr)/cm^{-1}$ 3433 m, 3253 w, 3163 w, 3083 w, 2962 w, 2903 m, 1829 w, 1751 s, 1492 w, 1475 m, 1448 m, 1370 m, 1315 m, 1250 s, 1226 s, 1084 s, 1055 s, 771 m; δ_{H} (400 MHz, CDCl₃) 8.78 (2H, m, br, *H6/H6'*), 8.73 (2H, m, br, *H3/H3'*), 8.33 (2H, m, *H4/H/4'*), 7.87 (2H, m, *H5/H5'*), 5.28 (1H, dd, br, *H4_{ch}*), 5.08 (1H, dd, br, *H2_{ch}*), 4.88 (1H, dd, br, *H3_{ch}*), 4.52 (1H, d, br, *H1_{ch}*), 4.07 (2H, m, br, *H6a_{ch}*, *H6b_{ch}*), 3.95 (1H, m, br, *H5_{ch}*), 2.73 (1H, m, br, *CH*₂CH₃), 2.57 (1H, m, br, *CH*₂CH₃), 2.03 (3H, s, C(O)*CH*₃), 2.01 (3H, s, C(O)*CH*₃), 2.00 (3H, s, C(O)*CH*₃), 1.99 (3H, s, C(O)*CH*₃), 1.11 (3H, s+d, ²*J*_{Pt,H} = 67.8, N_{trans}-Pt*CH*₃), 1.09 (3H, s+d, ²*J*_{Pt,H} = 69.3, N_{trans}-Pt*CH*₃), 1.01 (3H, t, br, CH₂CH₃), 0.65 (3H, s+d, ²*J*_{Pt,H} = 71.6, ch_{trans}-Pt*CH*₃); δ_{C} (125 MHz, CDCl₃) 170.3 (2 × *C*(O)*CH*₃), 169.6 (*C*(O)*CH*₃), 169.3 (*C*(O)*CH*₃), 154.6 (*C*2/*C2'*), 146.6 (*C*6/*C*6'), 141.7 (*C*4), 141.6 (*C*4'), 128.5 (*C*5/*C*5'), 126.0 (*C*3), 125.9 (*C*3'), 84.0 (*C*1_{ch}), 74.9 (*C*5_{ch}), 71.1 (*C*3_{ch}), 66.9 (*C*2_{ch}), 66.4 (*C*4_{ch}), 60.8 (*C*6_{ch}), 23.4 (*C*4₂*CH*₃), -5.4 (s+d, ¹*J*_{Pt,C} = 654.5, N_{trans}-Pt*CH*₃); δ_{Pt} (107 MHz, CDCl₃) –2529.

fac-[PtMe₃(bpy)(ch-SEt)][BF₄] (**10**, *ch-SEt* = **4c**). v_{max} (KBr)/cm⁻¹ 2963 w, 1731 s, 1644 m, 1601 m, 1451 m, 1384 m, 1315 w, 1261 s, 1178 m, 1092 s, 1027 m, 1759 s, 1603 m, 1495 w, 1477 w, 1449 m, 1375 m, 1319 w, 1235 s, 1211 s, 1090 s, 1052 s, 904 w, 802 w, 710 w, 468 w; δ_{H} (400 MHz, CDCl₃) 8.92 (2H, m, *H6/H6'*), 8.67 (2H, d, *H3/H3'*), 8.32 (2H, m, *H4/H4'*), 7.97–7.89 (6H, m, C(O)OC₆*H*₅), 7.87 (2H, m, *H5/H5'*), 7.42 (2H, d, C(O)OC₆*H*₅), 7.52–7.13 (12H, m, C(O)OC₆*H*₅), 6.04 (1H, dd, *H*_{3ch}), 5.71 (1H, dd, *H*_{4ch}), 5.55 (1H, dd, *H*_{2ch}), 5.17 (1H, d, ³*J*_{H,H} = 10.4, *H*_{1ch}), 4.59 (1H, m, *H*6a_{ch}), 4.51 (1H, m, *H*6b_{ch}), 4.41 (1H, m, *H5*_{ch}), 2.73 (2H, m, *CH*₂CH₃), 1.19 (3H, t, CH₂CH₃), 1.16 (6H, s+d, ²*J*_{Pt,H} = 67.5, N_{*trans*}-PtC*H*₃), 0.71 (3H, s+d, ²*J*_{Pt,H} = 72.3, ch_{*trans*}-PtC*H*₃); δ_{C} (125 MHz, CD₃Cl₃) 167.4–166.6 (*C*(O)C₆H₅), 156.4 (C2/C2'), 148.1 (C6), 148.0 (C6'), 142.1 (C4/C4'), 134.7–134.3 (C(O)C₆H₅), 130.7–129.4 (C(O)C₆H₅, *C5/C5'*), 125.8 (*C*3/C3'), 84.7 (*C*1_{ch}), 76.9 (*C*5_{ch}), 75.8 (*C*3_{ch}), 72.2 (*C*2_{ch}), 71.1 (*C*4_{ch}), 64.4 (*C*6_{ch}), 24.2 (*C*H₂CH₃), 15.6 (CH₂CH₃), 5.4 (s+d, ¹*J*_{Pt,C} = 660.0, ch_{*trans*}-PtCH₃), –4.7 (s+d, ¹*J*_{Pt,C} = 662.8, N_{trans}-PtCH₃); δ_{Pt} (107 MHz, CDCl₃)–2447.

fac-[PtMe₃(bpy)(ch-SEt)][BF₄] (**11**, *ch-SEt* = **4d**). $v_{max}(KBr)/cm^{-1}$ 3028, 2028 w, 1448 m, 1068 s, 1029 s, 1000 m, 765 m, 735 m, 698 m, 485 w; δ_{H} (500 MHz, CDCl₃) 8.81 (2H, d, *H6/H6'*), 8.71 (2H, m, *H3/H3'*), 8.27 (2H, m, *H4/H4'*), 7.65 (1H, m, *H5*), 7.51 (1H, m, *H5'*), 7.36–7.08 (20H, m, CH₂C₆*H*₅), 4.85–4.48 (8H, m, CH₂C₆*H*₅), 4.38 (1H, d, ${}^{3}J_{H,H}$ = 10.4, *H*1_{ch}), 3.73–3.57 (4H, m, *H3_{ch}*, *H5_{ch}*, *H6a_{ch}*, *H6b_{ch}*), 3.41 (*H2_{ch}*), 3.31 (*H4_{ch}*), 2.57 (1H, m, *CH*₂CH₃), 2.34 (1H, m, *CH*₂CH₃), 1.16 (3H, s+d, ${}^{2}J_{Pt,H}$ = 66.9, N_{*trans*}-PtC*H*₃), 1.14 (3H, s+d, ${}^{2}J_{Pt,H}$ = 66.9, N_{*trans*}-PtC*H*₃), 0.64 (3H, s+d, ${}^{2}J_{Pt,H}$ = 71.0, ch_{*trans*}-PtC*H*₃); δ_{C} (125 MHz, CDCl₃) 154.7 (*C2*), 154.6 (*C2'*), 146.8 (*C6*), 146.7 (*C6'*), 141.4 (*C4*, *C4'*), 137.8 (CH₂C₆H₅), 137.7 (CH₂C₆H₅), 137.0 (CH₂C₆H₅), 128.5–127.6 (CH₂C₆H₅, *C5*, *C5'*), 126.0 (*C3*), 125.9 (*C3'*), 85.8 (*C3_{ch}*), 84.6 (br, C1_{ch}), 81.7 (*C2_{ch}*), 79.7 (*C4_{ch}*), 79.2 (*C5_{ch}*), 75.6 (*CH*₂C₆H₅), 75.0 (2 × *CH*₂C₆H₅), 73.4 (*CH*₂C₆H₅), 70.3 (*C6_{ch}*), 23.1 (*CH*₂CH₃), 14.8 (CH₂CH₃), 5.1 (s+d, ${}^{1}J_{Pt,C}$ = 663.2, N_{*trans*}-PtCH₃), -5.2 (s+d, ${}^{1}J_{Pt,C}$ = 662.0, N_{*trans*-PtCH₃); δ_{Pt} (107 MHz, CDCl₃) –2446.}

fac-[PtMe₃(bpy)(ch-SEt)][BF₄] (**12**, *ch-SEt* = **4e**). $v_{max}(KBr)/cm^{-1}$ 2934 w, 2902 w, 2362 w, 1728 w, 1601 w, 1496 w, 1474 w, 1447 m, 1360 w, 1314 w, 1264 w, 1077 s, 1028 s, 770 m, 700 m; $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.83 (2H, m, br, *H6/H6'*), 8.64 (2H, m, br, *H3/H3'*), 8.57 (1H, d, br, *H6*_{pico}), 8.27 (2H, m, br, *H4/H4'*), 7.85 (1H, m, *H4*_{pico}), 7.70 (1H, t, *H5*), 7.67 (1H, t, *H5'*), 7.53 (1H, d, br, *H3*_{pico}), 7.39–7.13 (16H, m, CH₂C₆H₅), 4.94–4.34 (9H, m, *H1*_{ch}, CH₂C₆H₅, CH₂NC₅H₅), 3.84 (2H, m, br, *H6*_{ach}, *H6*_{bch}), 3.67 (2H, m, *H3*_{ch}, *H4*_{ch}), 3.52 (1H, m, br, *H5*_{ch}), 3.43 (1H, dd, *H2*_{ch}), 2.68 (1H, m, br, CH₂CH₃), 2.38 (1H, m, br, CH₂CH₃), 1.19 (3H, s+d, ²J_{Pt,H} = 67.4, N_{trans}-PtCH₃), 1.18 (3H, s+d, ²J_{Pt,H} = 67.4, N_{trans}-PtCH₃), 0.68 (3H, s+d, ²J_{Pt,H} = 71.1, ch_{trans}-PtCH₃); $\delta_{\rm C}$ (125 MHz, CD₂Cl₂) 154.9 (C2/C2'), 150.0 (br, C6_{pico}), 147.6 (C6), 147.4 (C6'), 141.3 (C4), 141.2 (C4'), 138.7–137.9 (CH₂C₆H₅, CH₂C₅H₅N), 70.4 (C6_{ch}), 82.1 (C2_{ch}), 79.7 (C5_{ch}), 78.2 (C4_{ch}), 75.8–73.9 (CH₂C₆H₅, CH₂C₅H₅N), 70.4 (C6_{ch}), 23.6 (CH₂CH₃), 15.0 (CH₂CH₃), 5.2 (s+d, ¹J_{Pt,C} = 648.4, ch_{trans}-PtCH₃), -4.6 (s+d, ¹J_{Pt,C} = 662.2, N_{trans}-PtCH₃), -4.7 (s+d, ¹J_{Pt,C} = 661.5, ch_{trans}-PtCH₃). $\delta_{\rm Pt}$ (107 MHz, CDCl₃) –2469.

 $fac-[PtMe_3(4,4'-{}^tBu_2bpy)(ch-SEt)][BF_4]$ (13, ch-SEt = 4a). $v_{max}(KBr)/cm^{-1}$ 3126 w, 2967 w, 2906 w, 1759 s, 1603 w, 1495 w, 1476 w, 1449 m, 1375 m, 1235 s, 1211 s, 1051 s, 1034 s, 904 w, 771 s, 603 w. $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.80 (1H, m, br, H6), 8.62 (1H, m, br, H6'), 8.49

(2H, br, *H3/H3'*), 7.87 (1H, m, br, *H5*), 7.79 (1H, m, br, *H5'*), 5.01 (1H, dd, br, *H2*_{ch}), 4.93 (1H, dd, br, *H4*_{ch}), 4.61 (1H, dd, br, *H3*_{ch}), 4.47 (1H, d, ${}^{3}J_{H,H} = 9.8$, *H1*_{ch}), 3.98 (1H, m, br, *H6*_{ach}), 3.93 (1H, m, br, *H6*_{bch}), 3.59 (1H, m, br, *H5*_{ch}), 2.60 (2H, m, br, *CH*₂CH₃), 1.95 (6H, s, br, C(O)*CH*₃), 1.85 (3H, s, br, C(O)*CH*₃), 1.80 (3H, s, br, C(O)*CH*₃), 1.46 (18H, s, br, 2 × (*CH*₃)₃C), 1.20 (3H, t, br, *CH*₂*CH*₃), 1.10 (3H, s+d, br, ${}^{2}J_{Pt,H} = 67.1$, N_{*trans*-Pt*CH*₃), 1.03 (3H, s+d, br, ${}^{2}J_{Pt,H} = 66.4$, N_{*trans*-Pt*CH*₃), 0.66 (3H, s+d, br, ${}^{2}J_{Pt,H} = 72.6$, ch_{*trans*-Pt*CH*₃); δ_{C} (125 MHz, CDCl₃) 170.1 (2 × *C*(O)CH₃), 169.4 (*C*(O)CH₃), 168.8 (*C*(O)CH₃), 155.0 (*C*2), 154.6 (*C*2'), 147.3 (*C*6), 146.5 (*C*6'), 125.3 (*C*5), 125.0 (*C*5'), 122.0 (*C*3), 121.9 (*C*3'), 83.5 (*C*1_{ch}), 80.5 (*C*3_{ch}), 76.0 (*C*5_{ch}), 73.4 (*C*2_{ch}), 69.0 (*C*4_{ch}), 61.4 (*C*6_{ch}), 35.9 ((*CH*₃)₃*C*), 30.9 ((*CH*₃)₃*C*), 24.6 (*CH*₂CH₃), 15.2 (*CH*₂CH₃), 5.8 (s+d, ${}^{1}J_{Pt,C} = 647.1$, ch_{*trans*-Pt*CH*₃), -5.2 (s+d, ${}^{1}J_{Pt,C} = 659.4$, N_{*trans*-Pt*CH*₃), -5.3 (s+d, ${}^{1}J_{Pt,C} = 664.6$, N_{*trans*-Pt*CH*₃); δ_{Pt} (107 MHz, CDCl₃) -2769.}}}}}}

fac-[PtMe₃(4,4'-^tBu₂bpy)(ch-SEt)][BF₄] (*14*, *ch-SEt* = *4c*). $v_{max}(KBr)/cm^{-1}$ 2970 w, 2911 w, 1733 s, 1615 m, 1493 w, 1452 m, 1413 m, 1316 m, 1269 s, 1179 m, 1091 s, 1069 s, 1026 s, 711 m; δ_{H} (500 MHz, CDCl₃) 8.77 (1H, m, br, *H*6), 8.62 (1H, m, br, *H*6'), 8.49 (2H, s, br, *H*3, *H*3'), 7.91–7.69 (9H, m, C(O)C₆*H*₅, *H*5), 7.61 (1H, d, br, *H*5'), 5.67 (1H, dd, br, *H*3_{ch}), 5.18 (1H, dd, br, *H*4_{ch}), 4.96 (1H, dd, br, *H*2_{ch}), 4.79 (1H, d, br, *H*1_{ch}), 4.35 (1H, dd, *H*6a_{ch}), 4.06 (1H, dd, *H*6b_{ch}), 3.97 (1H, m, *H*5_{ch}), 2.50 (1H, m, br, *CH*₂CH₃), 2.37 (1H, m, br, *CH*₂CH₃), 1.41 (18H, s, 2 × (C*H*₃)₃C), 1.04 (6H, s+d, ²*J*_{Pt,H} = 68.2, N_{trans}-PtC*H*₃), 1.02 (3H, t, br, CH₂CH₃), 0.59 (3H, s+d, br, ²*J*_{Pt,H} = 72.2, ch_{trans}-PtC*H*₃); δ_{C} (125 MHz, CDCl₃) 165.8 (2 × *C*(O)C₆H₅), 165.1 (2 × *C*(O)C₆H₅), 165.0 (C4), 164.8 (C4'), 154.8 (C2/C2'), 147.2 (br, C6), 146.4 (C6'), 133.5 (C(O)C₆H₅), 133.2 (C(O)C₆H₅), 129.8–128.2 (C(O)C₆H₅), 125.4 (C5), 125.1 (C5'), 122.0 (C3/C3'), 83.9 (br, C1_{ch}), 76.2 (C5_{ch}), 73.7 (br, C3_{ch}), 69.7 (br, C2_{ch}), 68.2 (br, C4_{ch}), 61.7 (br, C6), 35.9 ((CH₃)₃C), 30.2 ((CH₃)₃C), 24.3 (br, CH₂CH₃), 14.0 (CH₂CH₃), -5.2 (s+d, ¹*J*_{Pt,C} = 662.0, N_{trans}-PtCH₃); δ_{Pt} (107 MHz, CDCl₃) –2435.

fac-[PtMe₃(4,4'-^tBu₂bpy)(ch-STaz)][BF₄] (15, ch-STaz = 5c). $v_{max}(KBr)/cm^{-1}$ 3068 w, 2960 s, 2900 s, 2818 w, 1736 s, 1614 s, 1525 m, 1488 m, 1452 s, 1412 s, 1368 w, 1263 s, 1178 s, 1066 s, 895 m, 848 m, 802 w, 708 s, 606 w; δ_{H} (500 MHz, CDCl₃) 8.68 (2H, d, br, *H6/H6'*), 8.23 (2H, d, br, *H3/H3'*), 8.03–7.71 (8H, m, C(O)C₆H₅), 7.67 (2H, d, br, *H5/H5'*), 7.56–7.15 (12H, m, C(O)C₆H₅), 5.99 (2H, m, *H3_{ch}*, *H4_{ch}*), 5.78 (1H, d, ³*J*_{H,H} = 7.7, *H*1_{ch}), 5.64 (m, 1H, *H2_{ch}*), 4.81 (1H, m, *H*5_{ch}), 4.54 (1H, m, *H*6a_{ch}), 4.33 (1H, m, *H*6b_{ch}), 3.87 (2H, m, br, NCH₂), 3.21 (2H, m, br, SCH₂), 1.41 (18H, s, 2 × (CH₃)₃C), 1.13 (6H, s+d, ²*J*_{Pt,H} = 68.1, N_{trans}-

PtCH₃), 0.53 (3H, s+d, ${}^{2}J_{Pt,H} = 71.4$, ch_{trans}-PtCH₃); δ_{C} (125 MHz, CDCl₃) 166.1 (*C*(O)C₆H₅), 165.6 (*C*(O)C₆H₅), 164.7 (*C*(O)C₆H₅), 154.6 (*C*_{tert}.STaz), 146.7 (*C*(*O*/C6'), 133.6–131.2 (C(O)C₆H₅), 129.9–128.2 (C(O)C₆H₅), 124.8 (C3/C3'), 121.1 (C5/C5'), 91.1 (C1_{ch}), 69.5 (*C*2_{ch}), 69.2 (*C*3_{ch}), 68.0 (*C*4_{ch}), 66.8 (*C*5_{ch}), 62.4 (*C*6_{ch}), 52.7 (NCH₂), 33.0 (SCH₂), 30.3 (*C*H₃)₃C), -3.3 (s+d, ${}^{1}J_{Pt,C} = 678.2$, ch_{trans}-PtCH₃), -5.4 (s+d, ${}^{1}J_{Pt,C} = 675.7$, N_{trans}-PtCH₃); δ_{Pt} (107 MHz, CDCl₃): –2716.

fac-[PtMe₃(4,4'-^tBu₂bpy)(ch-STaz)][BF₄] (16, ch-STaz = 5g). v_{max} (KBr)/cm⁻¹ 2966 m, 2899 m, 1730 s, 1614 m, 1521 w, 1489 w, 1452 m, 1412 m, 1368 w, 1315 m, 1281 s, 1262 s, 1178 m, 1089 s, 1069 s, 1025 s, 849 w, 710 s; δ_{H} (400 MHz, CDCl₃) 8.78 (2H, m, *H6/H6'*), 8.22 (2H d, , *H3/H3'*), 7.97–7.73 (9H, m, C(O)C₆*H*₅, *H*4), 7.69 (1H, m, *H4'*), 7.54 (9H, m, C(O)C₆*H*₅), 5.92 (1H, dd, *H3*_{ch}), 5.41 (1H, dd, *H4*_{ch}), 5.37 (1H, dd, *H2*_{ch}), 5.21 (1H, d, ³*J*_{H,H} = 9.8, *H1*_{ch}), 4.12 (1H, m, NC*H*), 3.80 (1H, m, *H5*_{ch}), 3.75 (1H, m, *H6*_{ach}), 3.59 (1H, m, *H6*_{bch}), 3.26 (2H, m, NC*H*, SC*H*), 3.10 (1H, m, SC*H*), 1.45 (18H, s, br, 2 × (C*H*₃)₃C), 1.02 (3H, s+d, ²*J*_{Pt,H} = 66.9, N_{trans}-PtC*H*₃), 0.83 (3H, s+d, ²*J*_{Pt,H} = 67.6, N_{trans}-PtC*H*₃), 0.32 (3H, s+d, ²*J*_{Pt,H} = 72.5, ch_{trans}-PtC*H*₃); δ_{C} (125 MHz, CDCl₃) 166.0–165.2 (3 × C(O)C₆H₅), 155.0 (C2), 154.4 (C2'), 147.7 (C6), 147.1 (C6'), 134.0–133.4 (C(O)C₆H₅, C4/C4'), 129.9–128.3 (C(O)C₆H₅), 125.3 (C5'), 121.1 (C3/C3'), 84.0 (C1_{ch}), 79.2 (C5_{ch}), 73.1 (C3_{ch}), 70.4 (C2_{ch}), 68.7 (C4_{ch}), 64.6 (NCH₂), 61.0 (C6_{ch}), 35.8 (SCH₂), 35.7 (C(CH₃)₃), 30.3 (C(CH₃)₃), 30.2 (C(CH₃)₃), -3.2 (s+d, ¹*J*_{Pt,C} = 667.0, N_{trans}-PtCH₃), -4.7 (s+d, ¹*J*_{Pt,C} = 684.4, N_{trans}-PtCH₃), -6.1 (s+d, ¹*J*_{Pt,C} = 676.6, ch_{trans}-PtCH₃). δ_{Pt} (107 MHz, CDCl₃) –2452.

fac-[PtMe₃(bpy)(ch-STaz)][BF₄] (**17**, *ch-STaz* = **5a**). v_{max} (KBr)/cm⁻¹ 3488 w, 3445 w, 2966 w, 2893 w, 1754 s, 1602 w, 1447 m, 1375 m, 1227 s, 1091 s, 1058 s, 914 w, 803 m, 767 m; δ_{H} (400 MHz, CDCl₃) 8.94 (m, 1H, *H*6), 8.89 (1H, m, *H*6'), 8.60 (2H, m, *H3/H3'*), 8.26 (2H, m, H4/H4'), 7.83 (1H, m, H5), 7.78 (m, 1H, H5'), 5.19 (1H, dd, H3_{ch}), 5.00–4.88 (3H, m, H1_{ch}, H2_{ch}, H4_{ch}), 4.15 (1H, m, H6a_{ch}), 4.07 (1H, m, NC*H*), 4.01 (1H, m, H6b_{ch}), 3.72 (1H, m, H5_{ch}), 3.36–3.08 (3H, m, NC*H*, SC*H*₂), 2.05 (3H, s, C(O)CH₃), 1.96 (9H, s, C(O)CH₃), 1.17 (3H, s+d, ²*J*_{Pt,H} = 67.2, N_{trans}-PtC*H*₃), 1.13 (3H, s+d, ²*J*_{Pt,H} = 68.5 Hz, N_{trans}-PtC*H*₃), 0.45 (3H, s+d, ²*J*_{Pt,H} = 72.2, ch_{trans}-PtC*H*₃); δ_{C} (100 MHz, CDCl₃) 177.2 (*C*(O)CH₃), 170.0 (*C*(O)CH₃), 169.3 (*C*(O)CH₃), 169.0 (*C*(O)CH₃), 154.7 (C2), 154.5 (C2'), 147.6 (C6), 147.2 (C6'), 140.8 (C4/C4'), 127.9 (C5), 127.4 (C5'), 125.1 (C3), 125.0 (C3'), 83.8 (C1_{ch}), 76.1 (C5_{ch}), 73.0 (C3_{ch}), 69.2 (*C*4_{ch} or *C*2_{ch}), 67.7 (*C*4_{ch} or *C*2_{ch}), 64.5 (N*C*H₂), 61.6 (C6, C4_{ch} or C2_{ch}), 32.5 (SCH₂), 20.7 (C(O)CH₃), 20.5 (C(O)CH₃), -3.2 (s+d, ¹*J*_{Pt,C} = 677.0, N_{trans}-PtCH₃), -4.2 (s+d,

 ${}^{1}J_{Pt,C} = 677.8$, N_{trans}-PtCH₃), -5.5 (s+d, ${}^{1}J_{Pt,C} = 673.1$, ch_{trans}-PtCH₃). δ_{Pt} (107 MHz, CDCl₃) -2730.

fac-[PtMe₃(bpy)(ch-STaz)][BF₄] (**18**, *ch-STaz* = **5b**). $v_{max}(KBr)/cm^{-1}$ 2958 w, 2900 w, 1729 s, 1600 m, 1525 w, 1450 m, 1315 m, 1268 s, 1178 w, 1083 s, 1070 s, 1027 s, 767 w, 711 s; δ_{H} (400 MHz, CDCl₃) 8.85 (2H, m, *H6/H6'*), 8.49 (2H, m, *H3/H3'*), 8.15 (2H, m, *H4/H4'*), 7.94–7.74 (8H, m, C(O)C₆*H*₅), 7.57 (2H, m, *H5/H5'*), 7.53–7.21 (12H, m, C(O)C₆*H*₅), 5.92 (1H, dd, *H3*_{ch}), 5.59 (1H, dd, *H4*_{ch}), 5.24 (1H, dd, *H2*_{ch}), 5.24 (1H, d, ²*J*_{H,H} = 10.0, *H1*_{ch}), 4.53 (1H, m, *H6a*_{ch}), 4.43 (1H, m, *H6b*_{ch}), 4.23 (1H, m, *H5*_{ch}), 3.95 (1H, m, NC*H*), 3.38 (1H, m, NC*H*), 2.90 (2H, m, SC*H*₂), 1.08 (3H, s+d, ²*J*_{Pt,H} = 67.2, N_{*trans*}-PtC*H*₃), 0.93 (3H, s+d, ²*J*_{Pt,H} = 67.2, N_{*trans*}-PtC*H*₃), 0.38 (3H, s+d, ²*J*_{Pt,H} = 72.2, ch_{*trans*}-PtC*H*₃), 0.93 (3H, s+d, ²*J*_{Pt,H} = 67.2, N_{*trans*}-PtC*H*₃), 165.3 (2 × *C*(O)C₆H₅), 165.1 (*C*(O)C₆H₅), 154.7 (*C*2), 154.6 (*C*2'), 147.6 (*C*6), 147.1 (*C*6'), 140.8 (*C*4), 140.7 (*C*4'), 134.0–128.0 (C(O)C₆H₅, *C*5), 125.0 (C5), 83.8 (*C*1_{ch}), 76.6 (*C*5_{ch}), 73.3 (*C*3_{ch}), 70.0 (*C*2_{ch}), 68.8 (*C*4_{ch}), 64.6 (NCH₂), 62.7 (*C*6_{ch}), 32.0 (SCH₂), -3.6 (s+d, ¹*J*_{Pt,C} = 676.2, N_{*trans*}-PtCH₃); δ_{Pt} (107 MHz, CDCl₃): –2683.

fac-[PtMe₃(bpy)(ch-STaz)][BF₄] (**19**, *ch-STaz* = **5c**). v_{max} (KBr)/cm⁻¹ 2960 w, 2900 w, 2356 w, 1727 s, 1600 m, 1525 w, 1451 m, 1315 m, 1263 s, 1178 w, 1092 s, 1067 s, 1025 s, 802 m, 767 w, 708 s, 505 w; $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.86 (2H, m, *H6/H6'*), 8.57 (2H, m, *H3/H3'*), 8.19 (2H, m, *H4/H4'*), 8.07–7.18 (22H, m, C(O)C₆H₅, *H5/H5'*), 5.97 (1H, dd, *H4*_{ch}), 5.69 (2H, m, *H2*_{ch}, *H3*_{ch}), 5.27 (1H, d, ³*J*_{H,H} = 9.5, *H1*_{ch}), 4.53 (1H, m, *H6*a_{ch}), 4.42 (3H, m, *H5*_{ch}, *H6*b_{ch}, NCH), 3.94 (1H, m, NCH), 2.92 (1H, m, SCH), 2.81 (1H, m, SCH), 1.08 (3H, s+d, ²*J*_{Pt,H} = 68.1, N_{trans}-PtCH₃), 0.93 (3H, s+d, ²*J*_{Pt,H} = 67.2, N_{trans}-PtCH₃), 0.39 (3H, s+d, ²*J*_{Pt,H} = 72.2, ch_{trans}-PtCH₃); $\delta_{\rm C}$ (125 MHz, CDCl₃) 165.9 (*C*(O)C₆H₅), 165.4 (*C*(O)C₆H₅), 165.1 (*C*(O)C₆H₅), 154.9 (C2), 154.7 (C2'), 147.4 (C6), 147.0 (C6'), 140.9 (C4), 140.2 (C4'), 133.9 (C(O)C₆H₅), 133.6 (C(O)C₆H₅), 133.5 (C(O)C₆H₅), 130.0–128.2 (C(O)C₆H₅, C5, C5'), 125.2 (C3), 124.9 (C3'), 84.2 (C1_{ch}), 75.8 (C5_{ch}), 71.9 (C3_{ch}), 67.8 (C4_{ch}), 67.7 (C2_{ch}), 64.4 (NCH₂), 62.3 (*C*6_{ch}), 31.9 (SCH₂), -3.6 (s+d, ¹*J*_{Pt,C} = 678.2, N_{trans}-PtCH₃), -4.2 (s+d, ¹*J*_{Pt,C} = 676.9, N_{trans}-PtCH₃), -5.7 (s+d, ¹*J*_{Pt,C} = 674.4, N_{trans}-PtCH₃); $\delta_{\rm Pt}$ (107 MHz, CDCl₃) -2710.

 $fac-[PtMe_3(bpy)(ch-STaz)][BF_4]$ (20, ch-STaz = 5d). $v_{max}(KBr)/cm^{-1}$ 2598 m, 1601 w, 1449 m, 1146 m, 1090 s, 1074 s, 1028 s, 745 m, 698 m, 520 m; δ_H (400 MHz, CDCl₃) 8.87 (1H, d, H6), 8.81 (1H, d, H6'), 8.57 (2H, d, H3/H3'), 8.15 (1H, m, H4), 8.10 (1H, m, H4'), 7.66 (1H, m)

m, *H*5), 7.56 (1H, m, *H*5'), 7.38–7.11 (20 H, m, CH₂C₆H₅), 4.86–4.41 (9H, m, CH₂C₆H₅, *H*1_{ch}), 3.86 (1H, m, NC*H*), 3.66 (4H, m, *H*3_{ch}, *H*5_{ch}, *H*6a_{ch}, *H*6b_{ch}), 3.44 (3H, m, *H*2_{ch}, *H*4_{ch}, NC*H*), 3.00 (2H, m, SC*H*₂), 1.23 (3H, s+d, ${}^{2}J_{Pt,H} = 68.1$, N_{*trans*}-PtC*H*₃), 1.21 (3H, s+d, ${}^{2}J_{Pt,H} =$ 67.2, N_{*trans*}-PtC*H*₃), 0.45 (3H, s+d, ${}^{2}J_{Pt,H} =$ 72.2, ch_{*trans*}-PtC*H*₃); δ_{C} (100 MHz, CDCl₃) 147.2 (C2), 147.0 (C2'), 141.0 (C6/C6'), 138.7–137.2 (CH₂C₆H₅), 128.7–127.6 (CH₂C₆H₅, C5/C5'), 125.2 (C3/C3'), 86.4 (C3_{ch}), 85.6 (C1_{ch}), 79.7 (C2_{ch}), 79.3 (C4_{ch}), 77.3 (C5_{ch}), 75.7 (CH₂C₆H₅), 75.0 (CH₂)C₆H₅), 73.3 (CH₂C₆H₅), 68.3 (C6_{ch}), 64.4 (NCH₂), 32.1 (SCH₂), -3.7 (s+d, ${}^{1}J_{Pt,C} =$ 679.4, N_{*trans*}-PtCH₃), -4.0 (s+d, 3H, ${}^{1}J_{Pt,C} =$ 679.3, N_{*trans*}-PtCH₃), -5.7 (s+d, ${}^{1}J_{Pt,C} =$ 674.3, ch_{*trans*}-PtCH₃); δ_{Pt} (107 MHz, CDCl₃): -2695.

fac-[PtMe₃(bpy)(ch-STaz)][BF₄] (21, *ch-STaz* = 5*e*). v_{max} (KBr)/cm⁻¹ 2948 m, 2895 s, 2816 m, 1601 m, 1569 w, 1473 m, 1446 s, 1312 w, 1230 w, 1186 m, 1154 s, 1098 s, 991 m, 961 m, 919 w, 767 s; $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.91 (2H, m, *H6/H6'*), 8.66 (2H, d, *H3/H3'*), 8.27 (2H, m, *H4/H4'*), 7.79 (2H, m, *H5/H5'*), 4.52 (1H, d, , ³*J*_{H,H} = 10.0, *H*1_{ch}), 3.88 (1H, m, NC*H*), 3.59–3.15 (19H, m, 4 × OC*H*₃, *H*2_{ch}, *H*3_{ch}, *H*4_{ch}, *H*5_{ch}, *H*6a_{ch}, *H*6b_{ch}, NC*H*), 2.95 (2H, m, SC*H*₂), 1.19 (3H, s+d, ²*J*_{Pt,H} = 68.1, N*trans*-PtC*H*₃), 1.18 (3H, s+d, ²*J*_{Pt,H} = 67.2, N*trans*-PtC*H*₃), 0.42 (3H, s+d, ²*J*_{Pt,H} = 72.2, ch_{trans}-PtC*H*₃); $\delta_{\rm C}$ (125 MHz, CDCl₃) 155.0 (*C*2, *C2'*), 147.1 (*C*6), 146.9 (*C*6'), 141.1 (*C*4, *C*4'), 127.5 (*C*5, *C*5'), 125.6 (*C*3/*C*3'), 88.0 (*C*3_{ch}), 85.4 (*C*1_{ch}), 81.7 (*C*2_{ch}), 78.9 (*C*4_{ch}), 78.6 (*C*5_{ch}), 70.6 (*C*6_{ch}), 64.3 (NCH₂), 60.9 (OCH₃), 60.7 (OCH₃), 60.4 (OCH₃), 59.2 (OCH₃), 32.1 (SCH₂), -4.0 (s+d, ¹*J*_{Pt,C} = 680.6, N*trans*-PtCH₃), -4.1 (s+d, ¹*J*_{Pt,C} = 680.7, N*trans*-PtCH₃), -5.5 (s+d, ¹*J*_{Pt,C} = 673.8, ch*trans*-PtCH₃); $\delta_{\rm Pt}$ (107 MHz, CDCl₃) -2704.

fac-[PtMe₃(bpy)(ch-STaz)][BF₄] (**22**, *ch-STaz* = **5***f*). v_{max} (KBr)/cm⁻¹ 2962 m, 2900 m, 2356 w, 3341 w, 1745 s, 1602 m, 1525 m, 1448 m, 1367 m, 1315 m, 1238 s, 1052 s, 912 w, 808 w, 771 m, 701 w; $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.84 (2H, m, *H6/H6′*), 8.58 (2H, d, *H3/H3′*), 8.18 (1H, m, *H4*), 8.13 (1H, m, *H4′*), 7.73 (1H, m, *H5*), 7.63 (1H, m, *H5′*), 7.36–7.20 (5H, m, CH₂C₆*H*₅), 5.17 (1H, dd, *H*_{3ch}), 4.90 (1H, dd, *H*_{4ch}), 4.85 (1H, d, ³*J*_{H,H} = 10.0, *H*_{1ch}), 4.59 (2H, dd, *CH*₂C₆*H*₅), 4.12 (1H, m, br, *H6*a_{ch}), 3.97 (1H, m, br, *H6*b_{ch}), 3.87 (1H, m, br, NC*H*), 3.03 (1H, m, br, *H5*_{ch}), 3.58 (1H, dd, *H*2_{ch}), 3.42 (1H, m, br, NC*H*), 3.10 (1H, m, br, SC*H*), 3.03 (1H, m, br, SC*H*), 1.19 (6H, s+d, ²*J*_{Pt,H} = 68.1, N_{*trans*}-PtC*H*₃), 0.42 (3H, s+d, ²*J*_{Pt,H} = 72.2, ch_{*trans*}-PtC*H*₃); $\delta_{\rm C}$ (125 MHz, CDCl₃) 170.3 (CH₃C(O)O), 169.7 (CH₃C(O)O), 169.5 (CH₃C(O)O), 154.8 (C2), 154.7 (C2′), 147.3 (C6), 147.1 (C6′), 141.0 (C4/C4′), 136.8 (CH₂C₆H₅), 128.6 (CH₂C₆H₅), 128.2 (C5/C5′), 127.6 (CH₂C₆H₅), 68.0 (C4_ch), 64.6 (NCH₂), 85.3 (C1_{ch}), 77.6 (C2_{ch}), 75.9 (C5_{ch}), 75.3 (C3_{ch}), 74.8 (CH₂)C₆H₅), 68.0 (C4_{ch}), 64.6 (NCH₂),

61.7 (C6_{ch}), 32.3 (SCH₂), 20.7 (C(O)CH₃), 20.6 (C(O)CH₃), 20.5 (C(O)CH₃), -3.7 (s+d, ${}^{1}J_{Pt,C}$ = 679.4, N_{trans}-PtCH₃), -4.1 (s+d, ${}^{1}J_{Pt,C}$ = 679.8, N_{trans}-PtCH₃), -5.6 (s+d, ${}^{1}J_{Pt,C}$ = 677.5, ch_{trans}-PtCH₃); δ_{Pt} (107 MHz, CDCl₃) -2444.

fac-[PtMe₃(bpy)(ch-STaz)][BF₄] (23, *ch-STaz* = 5g). v_{max} (KBr)/cm⁻¹ 2962 m, 2901 m, 1729 s, 1601 m, 1525 w, 1449 m, 1316 m, 1280 s, 1259 s, 1179 w, 1091 s, 1069 s, 1026 s, 804 w, 768 m, 711 s; $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.88 (1H, m, *H*6), 8.84 (1H, m, *H*6'), 8.50 (2H, m, *H3/H3'*), 8.15 (1H, m, *H4*), 7.97 (1H, m, *H4'*), 7.93–7.83 (4H, m, C(O)C₆*H*₅), 7.77 (1H, m, *H5*), 7.72 (2H, m, C(O)C₆*H*₅), 7.56 (1H, m, *H5'*), 7.46–7.18 (9H, m, C(O)C₆*H*₅), 5.89 (1H, dd, *H*_{3ch}), 5.44 (1H, dd, *H*2_{ch}), 5.41 (1H, dd, *H*4_{ch}), 5.21 (1H, d, ³J_{H,H} = 10.4, *H*1_{ch}), 4.00 (1H, m, br, NC*H*), 3.84 (1H, m, br, *H5*_{ch}), 3.75 (2H, m, br, *H*6a_{ch}, O*H*_{ch}), 3.62 (1H, m, br, *H*6b_{ch}), 3.42 (1H, m, br, NC*H*), 3.19 (1H, m, SC*H*), 3.06 (1H, m, SC*H*), 1.06 (3H, s+d, ²*J*_{Pt,H} = 67.2, N*trans*-PtC*H*₃), 0.93 (3H, s+d, ²*J*_{Pt,H} = 67.2, N*trans*-PtC*H*₃), 0.37 (3H, s+d, ²*J*_{Pt,H} = 72.2, ch*trans*-PtC*H*₃); $\delta_{\rm C}$ (125 MHz, CDCl₃) 154.8 (C2), 154.7 (C2'), 147.7 (C6), 147.1 (C6'), 140.9 (C4), 140.7 (C4'), 127.7 (C5), 127.5 (C5'), 125.0 (C3/C3'), 84.0 (C1_{ch}), 79.2 (C5_{ch}), 73.3 (C3_{ch}), 70.1 (C4_{ch}), 68.6 (C2_{ch}), 64.3 (NCH₂), 61.0 (C6_{ch}), 32.4 (SCH₂), -3.6 (s+d, ¹*J*_{Pt,C} = 679.4, N*trans*-PtCH₃), -4.2 (s+d, ¹*J*_{Pt,C} = 675.6, N*trans*-PtCH₃), -5.7 (s+d, ¹*J*_{Pt,C} = 678.5, ch*trans*-PtCH₃); $\delta_{\rm Pt}$ (107 MHz, CDCl₃) –2445.

*fac-[PtMe*₃(*OAc-κ*²*O*,*O'*)(*ch-SEt*)] (24, *ch-SEt* = 4a). v_{max} (KBr)/cm⁻¹ 2359 w, 2338 w, 1747 s, 1534 m, 1408 m, 1408 m, 1367 m, 1232 s, 1091 m, 1046 s; $\delta_{\rm H}$ (400 MHz, CDCl₃): 5.17 (1H, dd, *H*3_{ch}), 5.02 (2H, m, 1 × br, *H*2_{ch} *H*4_{ch}), 4.54 (1H, d, br, *H*1_{ch}), 4.18 (1H, m, *H*6a_{ch}), 4.11 (1H, m, *H*6b_{ch}), 3.70 (1H, m, br, *H*5_{ch}), 2.75 (2H, m, br, *CH*₂CH₃), 2.11 (3H, s, C(O)*CH*₃), 2.02 (3H, s, C(O)*CH*₃), 2.01 (3H, s, C(O)*CH*₃), 1.97 (3H, s, C(O)*CH*₃), 1.95 (3H, s, *CH*₃C(O)O), 1.24 (3H, t, CH₂CH₃), 1.08 (9H, s+d, br, ²*J*_{Pt,H} = 77.2, Pt*CH*₃); $\delta_{\rm C}$ (125 MHz, CDCl₃) 170.3 (*C*(O)*CH*₃), 169.9 (*C*(O)*CH*₃), 169.1 (2 × *C*(O)*CH*₃), 83.3 (br, *C*1), 76.0 (br, *C*3_{ch}), 73.9 (*C*5_{ch}), 69.8 (*C*2_{ch}), 68.3 (*C*4_{ch}), 62.1 (*C*6_{ch}); 24.4 (*CH*₃C(O)O), 24.0 (*CH*₂CH₃), 20.8 (2 × C(O)*CH*₃), 20.6 (2 × C(O)*CH*₃), 14.3 (*CH*₂*CH*₃), -11.2 (s+d, br, Pt(*CH*₃)₃); $\delta_{\rm Pt}$ (107 MHz, CDCl₃) –2175.

 $fac-[PtMe_3(OAc-\kappa^2 O, O')(ch-SEt)]$ (25, ch-SEt = 4b). $v_{max}(KBr)/cm^{-1}$ 2968 w, 2904 w, 1752 s, 1560 w, 1540 w, 1425 m, 1372 m, 1226 s, 1152 w, 1087 m, 1056 m, 918 w; δ_H (400 MHz, CDCl₃) 5.39 (1H, dd, $H4_{ch}$), 5.23 (1H, dd, br, $H2_{ch}$), 5.00 (1H, dd, $H3_{ch}$), 4.51 (1H, d, br, $H1_{ch}$), 4.08 (2H, m, $H6a_{ch}$, $H6b_{ch}$), 3.93 (1H, m, br, $H5_{ch}$), 2.75 (2H, m, br, CH_2CH_3), 2.10

(3H, s, C(O)CH₃), 2.02 (3H, s, C(O)CH₃), 1.99 (3H s, , C(O)CH₃), 1.93 (3H, s, C(O)CH₃), 1.83 (3H, s, CH₃C(O)O), 1.26 (3H, t, CH₂CH₃), 1.07 (9H, s+d, br, ${}^{2}J_{Pt,H} = 78.0$, PtCH₃); δ_{C} (125 MHz, CDCl₃) 170.3 (*C*(O)CH₃), 170.0 (*C*(O)CH₃), 169.9 (*C*(O)CH₃), 169.5 (*C*(O)CH₃), 83.8 (br, C1_{ch}), 74.7 (br, C5_{ch}), 71.8 (C3_{ch}), 67.2 (C2_{ch}, C4_{ch}), 61.4 (C6_{ch}), 25.0 (br, CH₃C(O)O), 24.0 (br, CH₂CH₃), 20.8 (C(O)CH₃), 20.6 (C(O)CH₃), 20.5 (C(O)CH₃), 14.5 (br, CH₂CH₃), -11.7 (s+d, br, Pt(CH₃)₃); δ_{Pt} (107 MHz, CDCl₃) -2174.

fac-[PtMe₃(OAc-\kappa^2 O, O')(ch-SEt)] (26, ch-SEt = 4c). v_{max} (KBr)/cm⁻¹ 3064 w, 2962 m, 2898 m, 1727 s, 1600 m, 1583 m, 1550 w, 1492 w, 1452 s, 1409 m, 1315 s, 1263 s, 1178 s, 1089 s, 1068 s, 1025 s, 975 m, 854 w, 802 w, 746 w, 707 s, 686 s, 617 w, 559 w, 493 w; $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.01–7.21 (C(O)C₆*H*₅), 5.91 (1H, dd, *H*3_{ch}), 5.67 (1H, dd, *H*4_{ch}), 5.60 (1H, dd, br, *H*2_{ch}), 4.95 (1H, d, br, *H*1_{ch}), 4.65 (1H, m, br, *H*6a_{ch}), 4.47 (1H, m, *H*6b_{ch}), 4.20 (1H, m, br, *H*5_{ch}), 2.83 (2H, m, br, *CH*₂CH₃), 1.94 (3H, s, *CH*₃C(O)O), 1.28 (3H, t, *CH*₂*CH*₃), 1.10 (9H, s+d, br, ²*J*_{Pt,H} = 77.2, PtC*H*₃); $\delta_{\rm C}$ (125 MHz, CDCl₃): 165.0–164.1 (*C*(O)C₆H₅), 132.5–127.3 (C(O)C₆H₅), 82.8 (br, *C*1_{ch}), 75.5 (br, *C*5_{ch}), 73.0 (*C*3_{ch}), 69.5 (*C*4_{ch}), 68.4 (br, *C*2_{ch}), 62.0 (br, *C*6_{ch}), 28.0 (br, *C*H₂CH₃), 24.2 (*C*H₃C(O)O), 13.6 (br, *C*H₂*C*H₃), -11.4 (s+d, br, Pt(*C*H₃)₃). $\delta_{\rm Pt}$ (107 MHz, CDCl₃) –2173.

*fac-[PtMe*₃(*OAc-κ*²*O*,*O'*)(*ch-SEt*)] (27, *ch-SEt* = 4d). v_{max} (KBr)/cm⁻¹ 3029 m, 1966 2, 2900 m, 2862 m, 1570 m, 1495 w, 1452 m, 1404 m, 1359 m, 1325 w, 1263 w, 1211 w, 1145 m, 1088 s, 1026 s, 737 s, 697 s; $\delta_{\rm H}$ (400 MHz, CDCl₃) 7.30–6.98 (20H, m, (CH₂C₆H₅), 4.85–4.42 (9H, m, (CH₂C₆H₅, *H*1_{ch}), 3.73–3.47 (4H, m, br, *H*3_{ch}, *H*5_{ch}, *H*6a_{ch}, *H*6b_{ch}), 3.41 (2H, m, br, *H*2_{ch}, *H*4_{ch}), 2.87 (1H, m, br, *CH*₂CH₃), 2.73 (1H, m, br, *CH*₂CH₃), 1.91 (3H, s, *CH*₃C(O)O), 1.27 (3H, t, CH₂CH₃), 0.96 (9H, s+d, br, ²*J*_{Pt,H} = 75.1, Pt(*C*H₃)₃); $\delta_{\rm C}$ (100 MHz, CDCl₃) 138.7 (CH₂C₆H₅), 138.3 (CH₂C₆H₅), 137.9 (2 × CH₂C₆H₅), 128.5–127.6 (CH₂C₆H₅), 86.6 (*C*3_{ch}), 83.3 (br, *C*1_{ch}), 81.8 (*C*2_{ch}), 79.3 (*C*4_{ch}), 77.7 (*C*5_{ch}), 75.8 (*C*H₂C₆H₅), 75.6 (*C*H₂C₆H₅), 75.1 (*C*H₂C₆H₅), 73.5 (*C*H₂C₆H₅), 70.4 (*C*6_{ch}), 24.8 (br, *C*H₂CH₃), 24.4 (*C*H₃C(O)O), 14.3 (br, CH₂CH₃), -11.3 (s+d, br, Pt(*C*H₃)₃); $\delta_{\rm Pt}$ (107 MHz, CDCl₃) –2149.

fac-[PtMe₃(OAc-\kappa^2 O, O')(ch-SEt)] (28, ch-SEt = 4e). ν_{max} (KBr)/cm⁻¹ 2959 m, 2894 m, 2356 w, 1602 w, 1568 m, 1494 w, 1452 m, 1402 m, 1358 w, 1262 w, 1232 w, 1132 m, 1084 s, 1067 s, 1027 s, 751 m, 736 m, 697 m; $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.54 (1H, m, br, $H6_{\rm pico}$), 7.80 (1H, m, br, $H3_{\rm pico}$), 7.70 (1H, d, br, $H3_{\rm pico}$), 7.37–7.25 (16H, m, (CH₂C₆H₅), $H5_{\rm pico}$), 5.06–4.61 (CH₂C₆H₅, CH₂C₅H₅N), 4.48 (1H, d, br, ${}^{3}J_{\rm H,\rm H}$ = 9.5, $H1_{\rm ch}$), 3.97 (1H, m, br, $H6a_{\rm ch}$), 3.85 (1H,

m, $H6b_{ch}$), 3.70 (1H, dd, $H3_{ch}$), 3.61 (1H, dd, $H4_{ch}$), 3.53 (1H, m, br, $H5_{ch}$), 3.45 (1H, dd, $H2_{ch}$), 2.74 (2H, m, br, CH_2CH_3), 1.79 (3H, s, $CH_3C(O)O$), 1.30 (3H, t, CH_2CH_3), 1.15 (9H, s+d, ${}^2J_{Pt,H} = 76.4$, Pt(CH_3)₃); δ_C (125 MHz, CDCl₃) 159.5 ($C2_{pico}$), 149.4 ($C6_{pico}$), 138.4–137.8 ($C4_{pico}$, $CH_2C_6H_5$), 128.4–127.7 ($CH_2C_6H_5$), 123.9 ($C5_{pico}$), 123.3 ($C3_{pico}$), 86.6 ($C3_{ch}$), 85.1 ($C1_{ch}$), 81.7 ($C2_{ch}$), 78.8 ($C4_{ch}$), 77.9 ($C5_{ch}$), 75.8 ($CH_2C_6H_5$), 75.5 ($CH_2C_6H_5$), 75.1 ($CH_2C_6H_5$), 70.6 ($C6_{ch}$), 25.0 ($CH_3C(O)O$), 24.8 (CH_2CH_3), 15.1 (CH_2CH_3), –10.3 (s+d, br, Pt(CH_3)₃); δ_{Pt} (107 MHz, CDCl₃) –2444.

*fac-[PtMe*₃(*OAc-κ*²*O*,*O'*)(*ch-STaz*)] (**29**, *ch-STaz* = **5***a*). v_{max} (KBr)/cm⁻¹ 2959 w, 2899 w, 1753 s, 1534 m, 1410 m, 1369 m, 1226 s, 1036 s, 981 w, 912 w; $\delta_{\rm H}$ (400 MHz, CDCl₃) 5.20 (1H, dd, H_{3ch}), 5.09 (2H, m, H_{2ch} , H_{4ch}), 4.96 (1H, d, br, ${}^{3}J_{\rm H,H}$ = 10.0, H_{1ch}), 4.39 (1H, m, br, NC*H*), 4.21 (1H, m, *H*6a_{ch}), 4.14 (2H, m, br, NC*H*, *H*6b_{ch}), 3.76 (1H, m, *H*5_{ch}), 3.30 (2H, m, SC*H*₂), 2.02 (3H, s, C(O)C*H*₃), 2.00 (3H, s, C(O)C*H*₃), 1.97 (3H, s, C(O)C*H*₃), 1.94 (3H, s, C(O)C*H*₃), 1.83 (3H, s, C*H*₃C(O)O), 1.00 (9H, s+d, br, ${}^{2}J_{Pt,H}$ = 77.8, Pt(C*H*₃)₃); $\delta_{\rm C}$ (125 MHz, CDCl₃) 170.4 (*C*(O)CH₃), 170.0 (*C*(O)CH₃), 169.0 (*C*(O)CH₃), 83.5 (*C*1_{ch}), 76.1 (*C*5_{ch}), 73.5 (*C*3_{ch}), 69.2 (*C*2_{ch}), 67.7 (*C*4_{ch}), 63.6 (NCH₂), 61.7 (*C*6_{ch}), 31.7 (SC*H*₂), 25.0 (*C*H₃C(O)O), - 11.7 (s+d, br, Pt(*C*H₃)₃); $\delta_{\rm Pt}$ (107 MHz, CDCl₃) –1910.

*fac-[PtMe*₃(*OAc-κ*²*O*,*O'*)(*ch-STaz*)] (**30**, *ch-STaz* = **5b**). v_{max} (KBr)/cm⁻¹ 2962 w, 2895 w, 2356 w, 2336 w, 1735 s, 1601 w, 1537 m, 1452 m, 1412 w, 1316 w, 1264 s, 1178 w, 1088 s, 1069 s, 1025 s, 801 w, 707 s, 684 w; $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.04–7.22 (20H, m, C(O)C₆*H*₅), 5.97 (1H, dd, *H*3_{ch}), 5.70 (2H, m, *H*2_{ch}, *H*4_{ch}), 5.35 (1H, d, br, ³*J*_{H,H} = 10.0, *H*1_{ch}), 4.67 (1H, m, br, *H*6a_{ch}), 4.51 (1H, m, br, *H*6b_{ch}), 4.33 (2H, m, br, NC*H*₂), 4.14 (1H, m, br, *H*5_{ch}), 3.11 (2H, m, br, SC*H*₂), 1.81 (3H, s, C*H*₃C(O)O), 0.91 (9H, s+d, br, ²*J*_{Pt,H} = 77.2, Pt(C*H*₃)₃); $\delta_{\rm C}$ (100 MHz, CDCl₃): 165.8 (*C*(O)C₆H₅), 165.5 (*C*(O)C₆H₅), 164.9 (*C*(O)C₆H₅), 164.7 (*C*(O)C₆H₅), 133.4–128.2 (C(O)C₆H₅), 84.0 (C1_{ch}), 76.7 (C5_{ch}), 73.9 (C3_{ch}), 70.3 (C2_{ch}), 69.2 (C4_{ch}), 63.6 (NCH₂), 63.0 (C6_{ch}), 32.3 (SCH₂), 24.8 (CH₃C(O)O), -11.1 (s+d, br, Pt(CH₃)₃); $\delta_{\rm Pt}$ (107 MHz, CDCl₃) –1921.

fac-[PtMe₃(OAc-\kappa^2 O, O')(ch-STaz)] (**31**, *ch-STaz* = **5c**). v_{max} (KBr)/cm⁻¹ 3743 w, 3432 w, 3399 w, 2962 w, 2898 w, 2289 w, 1727 s, 1596 w, 1535 w, 1448 m, 1402 m, 1267 s, 1176 w, 1093 s, 1070 s, 1029 m, 709 s, 594 w; δ_{H} (500 MHz, CDCl₃) 8.03–7.16 (20H, m, C(O)C₆H₅), 6.00 (1H, dd, H4_{ch}), 5.86 (1H, dd, H2_{ch}), 5.62 (1H, dd, m, H3_{ch}), 5.31 (1H, d, ³J_{H,H} = 10.0, H1_{ch}), 4.59 (1H, m, H6a_{ch}), 4.43 (2H, m, H6b_{ch}, H5_{ch}), 4.34 (1H, m, br, NCH), 4.09 (1H, m,

br, NC*H*), 3.09 (2H, m, br, SC*H*₂), 1.85 (3H, s, C*H*₃C(O)O), 0.87 (9H, s+d, br, ${}^{2}J_{Pt,H} = 73.0$, Pt(C*H*₃)₃); δ_{C} (125 MHz, CDCl₃) 166.0 (*C*(O)C₆H₅), 165.5 (*C*(O)C₆H₅), 165.4 (*C*(O)C₆H₅), 164.9 (*C*(O)C₆H₅), 133.8 (C(O)C₆H₅), 133.5 (C(O)C₆H₅), 133.4 (C(O)C₆H₅), 130.0–128.3 (C(O)C₆H₅), 84.6 (C1_{ch}), 76.9 (C5_{ch}), 75.7 (C5_{ch}), 72.5 (C3_{ch}), 68.2 (C2_{ch}), 67.7 (C4_{ch}), 63.6 (NCH₂), 62.4 (C6_{ch}), 32.2 (SCH₂), 24.6 (CH₃C(O)O), -11.3 (s+d, br, Pt(CH₃)₃). δ_{Pt} (107 MHz, CDCl₃) –1918.

*fac-[PtMe*₃(*OAc-κ*²*O*,*O'*)(*ch-STaz*)] (**32**, *ch-STaz* = **5d**). v_{max} (KBr)/cm⁻¹ 2962 m, 2900 m ,1550 s, 1455 s, 1418 s, 1363 m, 1326 m, 1239 w, 1089 s, 911 w, 805 w, 737 m, 698; δ_{H} (500 MHz, CDCl₃) 7.38–7.17 (20H, m, CH₂)C₆*H*₅), 4.96–4.55 (9H, m, CH₂C₆H₅, *H*1_{ch}), 4.46 (1H, m, br, NC*H*), 4.20 (1H, m, br, NC*H*), 3.75 (4H, m, *H*3_{ch}, *H*5_{ch}, *H*6a_{ch}, *H*6b_{ch}), 3.59 (2H, m, *H*2_{ch}, *H*4_{ch}), 3.25 (2H, m, SC*H*₂), 1.91 (3H, s, CH₃C(O)O), 1.17 (9H, s+d, br, ²*J*_{Pt,H} = 74.4, Pt(C*H*₃)₃); δ_{C} (125 MHz, CDCl₃) 138.1–137.2 (CH₂C₆H₅), 128.4–127.6 CH₂C₆H₅), 86.6 (C3_{ch}), 85.9 (C1_{ch}), 80.6 (C2_{ch}), 79.4 (C4_{ch}), 77.4 (C5_{ch}), 75.8 CH₂C₆H₅), 75.1 (CH₂C₆H₅), 73.4 (CH₂C₆H₅), 68.5 (C6_{ch}), 63.6 (NCH₂), 32.4 (SCH₂), 25.4 (CH₃C(O)O), -11.3 (s+d, br, Pt(CH₃)₃); δ_{Pt} (107 MHz, CDCl₃) –1907.

*fac-[PtMe*₃(*OAc-κ*²*O,O'*)(*ch-STaz*)] (**33**, *ch-STaz* = **5e**). (30 mg, 35%); v_{max} (KBr)/cm⁻¹ 2954 m, 2898 s, 2831 m, 1531 s, 1409 m, 1263 w, 1151 m, 1093 s, 1037 s, 985 w, 806 w; $\delta_{\rm H}$ (400 MHz, CDCl₃) 4.69 (1H, d, ${}^{3}J_{\rm H,H}$ = 10.0, *H*1_{ch}), 4.43 (1H, m, br, NC*H*), 4.12 (1H, m, NC*H*), 3.66–3.19 (17H, m, 4 × OC*H*₃, *H*5_{ch}, *H*6a_{ch}, *H*6b_{ch}, SC*H*₂), 3.16 (2H, m, *H*3_{ch}, *H*4_{ch}), 3.05 (1H, m, *H*2), 1.87 (3H, s, C*H*₃C(O)O), 1.07 (9H, s+d, br, ${}^{2}J_{\rm Pt,H}$ = 75.6, Pt(C*H*₃)₃); $\delta_{\rm gc}$ (125 MHz, CDCl₃) 88.4 (C3_{ch}), 85.6 (C1_{ch}), 82.3 (C2_{ch}), 78.9 (C4_{ch}), 78.8 (C5_{ch}), 70.9 (C6_{ch}), 63.5 (NCH₂), 61.0 (2 × OCH₃), 60.5 (OCH₃), 59.3 (OCH₃), 32.4 (SCH₂), 24.5 (CH₃C(O)O), -11.4 (s+d, br, Pt(CH₃)₃); $\delta_{\rm Pt}$ (107 MHz, CDCl₃) –1904.

*fac-[PtMe*₃(*OAc-κ*²*O*,*O'*)(*ch-STaz*)] (*34*, *ch-STaz* = *5f*). v_{max} (KBr)/cm⁻¹ 2963 w, 2909 w, 1749 s, 1560 w, 1540 w, 1420 m, 1375 m, 1262 s, 1237 s, 1093 s, 1052 s, 802 m; $\delta_{\rm H}$ (400 MHz, CDCl₃): 7.24 (5H, m, CH₂C₆*H*₅), 5.19 (1H, dd, *H*3), 4.98 (2H, m, *H*1_{ch}, *H*4_{ch}), 4.64 (2H, dd, *CH*₂C₆H₅), 4.46 (1H, m, br, NC*H*), 4.15 (3H, m, br, *H*6a_{ch}, *H*6b_{ch}, NC*H*), 3.76 (1H, m, *H*5_{ch}), 3.61 (1H, dd, *H*2_{ch}), 3.30 (2H, m, br, SC*H*₂), 2.03 (3H, s, C(O)C*H*₃), 1.96 (3H, s, C(O)C*H*₃), 1.87 (3H, s, *CH*₃C(O)O), 1.86 (3H, s, C(O)C*H*₃), 1.08 (9H, s+d, br, ²*J*_{Pt,H} = 76.4, PtC*H*₃); $\delta_{\rm C}$ (125 MHz, CDCl₃) 170.4 (*C*(O)CH₃), 169.3 (*C*(O)CH₃), 169.5 (*C*(O)CH₃), 136.8 (CH₂C₆H₅), 128.8–128.2 (CH₂C₆H₅), 85.5 (*C*1_{ch}), 78.1 (*C*2_{ch}), 75.8 (*C*5_{ch}), 75.5 (*C*H₂C₆H₅),

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75.4 (C3_{ch}), 68.1 (C4_{ch}), 63.7 (br, NCH₂), 61.8 (C6_{ch}), 32.6 (br, SCH₂), 24.9 (CH₃C(O)O), 20.7 (C(O)CH₃), 20.6 (C(O)CH₃), 20.5 (C(O)CH₃), -11.3 (s+d, br, Pt(CH₃)₃); δ_{Pt} (107 MHz, CDCl₃) -1911.

fac-[PtMe₃(OAc-\kappa^2 O, O')(ch-STaz)] (**35**, *ch-STaz* = **5***g*). v_{max} (KBr)/cm⁻¹ 2956 w, 2897 w, 1729 s, 1600 w, 1579 w, 1531 w, 1450 m, 1315 m, 1278 s, 1258 s, 1177 w, 1087 s, 1067 s, 1025 m, 966 w, 708 s; $\delta_{\rm H}$ (400 MHz, CDCl₃) 7.92–7.21 (15H, m, C(O)C₆H₅), 5.97 (1H, dd, *H*3_{ch}), 5.61 (1H, dd, br, *H*2_{ch}), 5.52 (1H, dd, *H*4_{ch}), 4.74 (1H, d, br, *H*1_{ch}), 4.26 (1H, m, br, NC*H*), 4.15 (1H, m, br, NC*H*), 3.94 (1H, m, br, *H*5_{ch}), 3.85 (1H, m, br, *H*6a_{ch}), 3.73 (1H, m, br, *H*6b_{ch}), 3.32 (2H, m, br, SC*H*₂), 1.82 (C*H*₃C(O)O), 0.91 (9H, s+d, br, ²*J*_{Pt,H} = 76.4, PtC*H*₃); $\delta_{\rm C}$ (125 MHz, CDCl₃): 133.6–133.3 (C(O)C₆H₅), 129.8–128.5 (C(O)C₆H₅), 85.2 (br, C1_{ch}), 79.3 (C5_{ch}), 73.8 (C3_{ch}), 70.3 (C2_{ch}), 69.2 (br, C4_{ch}), 64.1 (br, NCH₂), 35.2 (br, SCH₂), 25.0 (br, CH₃C(O)O), -11.5 (s+d, br, Pt(CH₃)₃); $\delta_{\rm Pt}$ (107 MHz, CDCl₃) –1916.

fac-[PtMe₃(ch-SEt)][BF₄] (**36**, *ch-SEt* = **4a**). v_{max} (KBr)/cm⁻¹ 2962 w, 2899 w, 1752 s, 1602 w, 1473 w, 1446 m, 1374 m, 1227 s, 1034 s, 912 w, 769 m; $\delta_{\rm H}$ (400 MHz, CDCl₃) 5.25 (1H, dd, $H_{\rm 3ch}$), 5.12 (1H, dd, $H_{\rm 2ch}$), 5.10 (1H, dd, $H_{\rm 4ch}$), 4.85 (1H, d, br, $H_{\rm 1ch}$), 4.31 (1H, m, br, $H_{\rm 6ach}$), 4.16 (1H, m, br, $H_{\rm 6bch}$), 4.01 (1H, m, br, $H_{\rm 5ch}$), 3.04 (2H, m, br, CH_2CH_3), 2.08 (3H, s, C(O)CH₃), 2.07 (3H, s, C(O)CH₃) 2.02 (3H, s, C(O)CH₃), 1.98 (3H, s, (C(O)CH₃), 1.36 (3H, t, CH₂CH₃), 1.28 (9H, s+d, br, ² $J_{\rm Pt,H}$ = 73.9, PtCH₃); $\delta_{\rm C}$ (125 MHz, CDCl₃) 171.7 (br, $C(O)CH_3$), 169.9 ($C(O)CH_3$), 169.7 ($C(O)CH_3$), 81.6 (br, C1), 76.5 (C5), 73.4 (C3), 69.4 (C2), 67.5 (C4), 61.9 (C6), 25.4 (CH_2CH_3), 20.7 (C(O)CH₃), 20.6 (C(O)CH₃), 20.5 (2 × C(O)CH₃), 14.9 (CH₂CH₃), -11.2 (s+d, br, Pt(CH₃)₃). $\delta_{\rm Pt}$ (107 MHz, CDCl₃): -2673.

fac-[PtMe₃(ch-SEt)][BF₄] (**37**, *ch-SEt* = **4c**). v_{max} (KBr)/cm⁻¹ 2971 w, 2904 w, 1751 s, 1600 w, 1430 w, 1373 m, 1226 s, 1079 s, 1056 s, 916 w; δ_{H} (500 MHz, CDCl₃) 8.02–7.71 (8H,m, C(O)C₆H₅), 7.51–7.18(12H, m, C(O)C₆H₅), 5.69 (1H, dd, br, $H3_{ch}$), 5.56 (1H, dd, br, $H4_{ch}$), 5.28 (1H, d, br, $H1_{ch}$), 4.95 (2H, m, br, $H6a_{ch}$, $H6b_{ch}$), 4.32 (1H, m, br, $H5_{ch}$), 2.92 (2H, m, CH_2CH_3), 1.26 (9H, s+d, br, ${}^2J_{Pt,H}$ = 74.0, Pt(CH_3)₃), 1.18 (t, br, 3H, CH_2CH_3); δ_C (100 MHz, CDCl₃) 166.7 (br, $C(O)C_6H_5$), 166.1 (br, $C(O)C_6H_5$), 165.4 ($C(O)C_6H_5$), 165.1 ($C(O)C_6H_5$), 134.0 ($C(O)C_6H_5$), 133.6 (2 × C(O)C_6H_5), 133.3 ($C(O)C_6H_5$), 130.1–128.1 ($C(O)C_6H_5$), 80.8 (br, $C1_{ch}$), 77.2 ($C5_{ch}$), 73.6 ($C3_{ch}$), 70.3 (br, $C2_{ch}$), 68.1 (br, $C4_{ch}$), 62.0 ($C6_{ch}$), 21.2 (br, CH_2CH_3), 14.0 (br, CH_2CH_3), -11.7 (s+d, br, Pt(CH_3)₃); δ_{Pt} (107 MHz, CDCl₃) –2442.

*fac-[PtMe*₃(*ch-SEt*)][*BF*₄] (**38**, *ch-SEt* = **4d**). v_{max} (KBr)/cm⁻¹ 3027.w, 2975 w, 2902 w, 2522, w, 2027 w, 1495 w, 1453 m, 1071 s, 1000 m, 736 w, 697 m, 533 w; $\delta_{\rm H}$ (400 MHz, CDCl₃): 7.36–7.12 (20H, m, (CH₂C₆H₅), 4.87–4.44 (9H, m, br, *H*1_{ch}, *CH*₂C₆H₅), 3.73 (2H, m, br, *H*3_{ch}, *H*5_{ch}), 3.62 (4H, m, br, *H*2_{ch}, *H*4_{ch}, *H*6a_{ch}, *H*6b_{ch}), 3.07 (1H, m, br, *CH*₂CH₃), 2.93 (1H, m, br, *CH*₂CH₃), 1.34 (3H, t, br, CH₂CH₃), 1.18 (9H, s+d, br, ²*J*_{Pt,H} = 75.9, Pt(*CH*₃)₃); $\delta_{\rm C}$ (125 MHz, CDCl₃) 138.0–127.6 (CH₂C₆H₅), 86.3 (C3), 83.7 (br, C1), 81.7(br, C2), 80.0 (C4), 79.4 (br, C4), 78.7 (C5), 75.6 (*C*H₂C₆H₅), 75.3 (*C*H₂C₆H₅), 75.0 (*C*H₂C₆H₅), 73.4 (*C*H₂C₆H₅), 67.6 (br, C6), 25.5 (*C*H₂CH₃), 14.3 (CH₂CH₃), -11.3 (s+d, br, Pt(*C*H₃)₃); $\delta_{\rm Pt}$ (107 MHz, CDCl₃) –2610.

fac-[PtMe₃(ch-SEt)][BF₄] (**39**, *ch-SEt* = **4e**). v_{max} (KBr)/cm⁻¹ 2902 w, 1610 w, 1497 w, 1454 m, 1360 w, 1286 w, 1245 w, 1070 s, 1028 s, 754 m, 699 m; δ_{H} (400 MHz, (CD₃)₂CO) 8.80 (1H, d, br, *H*6), 8.22 (1H, tr, *H*4), 7.82 (1H, d, *H*3), 7.75 (1H, m, *H*5), 7.36–7.29 (19H, m, CH₂C₆*H*₅, CH₂C₅H₅N), 4.96–4.69 (8H, m, *CH*₂C₆H₅, *CH*₂C₅H₅N), 4.63 (1H, d, ³*J*_{H,H} = 10.7, *H*1_{ch}), 3.96 (2H, m, *H*6a_{ch}, *H*6b_{ch}), 3.77 (2H, m, *H*3_{ch}, *H*5_{ch}), 3.50 (1H, dd, *H*2_{ch}), 3.42 (1H, dd, *H*4_{ch}), 2.75 (2H, m, *CH*₂CH₃), 1.23 (3H, tr, br, CH₂CH₃), 1.12 (6H, s+d, br, ²*J*_{Pt,H} = 72.8, ch_{trans}-PtCH₃), 1.06 (3H, s+d, ²*J*_{Pt,H} = 69.8, N_{trans}-PtCH₃); δ_{C} (125 MHz, (CD₃)₂CO) 143.6 (C6), 140.1 (C4), 139.0–138.2 (CH₂C₆H₅, CH₂C₅ H₅N), 128.3–127.3 (CH₂C₆H₅, CH₂C₅H₅N), 125.0 (C5), 124.0 (C3), 86.3 (C3_{ch}), 84.5 (C1_{ch}), 81.6 (C2_{ch}), 78.4 (C5_{ch}), 77.6 (C4_{ch}), 75.1–74.4 (*C*H₂C₆H₅, *C*H₂C₅H₅N), 70.4 (C6_{ch}), 24.3 (*C*H₂CH₃), 14.7 (CH₂CH₃), -5.4 (s+d, br, Pt(CH₃)₃), -8.6 (s+d, br, Pt(CH₃)₃); δ_{Pt} (107 MHz, (CD₃)₂CO) –2068.

fac-[PtMe₃(ch-SEt)][BF₄] (**40**, *ch-SEt* = **4f**). v_{max} (KBr)/cm⁻¹ 2970 w, 2907 m, 2519 w, 2020 w, 1726 w, 1599 m, 1577 m, 1467 s, 1350 m, 1332 m, 1286 m, 1252 m, 1140 s, 1073 s, 1028 s, 780 m, 740 m, 699 m; δ_{H} (400 MHz, (CD₃)₂CO) 9.12 (1H, d, *H*6'), 9.03 (1H, d, *H*5), 8.66 (1H, d, *H*3'), 8.52 (2H, m, *H*4, *H*4'), 8.04 (1H, t, *H*5'), 7.80 (1H, d, *H*3), 7.42–7.13 (15H, m, CH₂C₆*H*₅), 4.96–4.61 (6H, m, *CH*₂C₆*H*₅), 4.46 (1H, d, ³*J*_{H,H} = 10.2, *H*1_{ch}), 4.12 (3H, m, *H*2_{ch}, *H*6a_{ch}, *H*6b_{ch}), 3.77 (2H, m, *H*5_{ch}, *H*4_{ch}), 3.31 (1H, m, br, *CH*₂CH₃), 3.02 (1H, m, *CH*₂CH₃), 1.26 (3H, s+d, ²*J*_{Pt,H} = 69.3. PtCH₃), 0.89 (3H, s+d, ²*J*_{Pt,H} = 72.9, PtCH₃); δ_{C} (125 MHz, (CD₃)₂CO): 167.2, 156.6, 154.0, 147.8, 145.1, 142.2, 139.2 (CH₂C₆H₅), 138.8 (CH₂C₆H₅), 138.4 (CH₂C₆H₅), 129.2–128.1 (CH₂C₆H₅), 126.6, 118.8, 113.3, 85.9, 80.8, 78.3, 78.2, 75.2–74.0 (*C*H₂C₆H₅), 71.5 (*C*6), 25.9 (*C*H₂CH₃), 14.8 (CH₂CH₃), 4.5 (s+d, ¹*J*_{Pt,C} = 664.0, PtCH₃), -1.3 (s+d, ¹*J*_{Pt,C} = 690.17, PtCH₃), -3.8 (s+d, ¹*J*_{Pt,C} = 641.9, PtCH₃). δ_{Pt} (107 MHz, (CD₃)₂CO) – 2679.

fac-[PtMe₃(ch-STaz)][BF₄] (**41**, *ch-STaz* = **5h**). v_{max} (KBr)/cm⁻¹ 2912 w, 1599 m, 1577 m, 1522 w, 1496 w, 1466 w, 1283 w, 1071 s, 1028 s, 779 m, 741 m, 699 m cm⁻¹; $\delta_{\rm H}$ (400 MHz, (CD₃)₂CO) 9.16 (1H, d, *H*6'), 8.36 (2H, m, *H*4', *H*3'), 8.11 (1H, t, *H*4), 7.97 (t, 1H, *H*5'), 7.73 (1H, d, *H*3), 7.48 (1H, d, *H*5), 7.43–7.02 (15H, m, CH₂C₆*H*₅), 5.21 (1H, d, ³*J*_{H,H} = 9.96, *H*1_{ch}), 4.98–4.51 (8H, m, C*H*₂C₆H₅, *H*6a _{ch}, *H*6b _{ch}), 4.36 (2H, m, NC*H*₂), 3.93 (2H, m, *H*3_{ch}, *H*5_{ch}), 3.68 (1H, dd, *H*4_{ch}), 3.40 (1H, dd, *H*2_{ch}), 3.27 (1H, m, SC*H*), 2.99 (1H, m, br, SC*H*), 1.75 (3H, s+d, ²*J*_{Pt,H} = 70.5, PtC*H*₃), 1.31 (3H, s+d, ²*J*_{Pt,H} = 71.4, PtC*H*₃), 0.81 (3H, s+d, ²*J*_{Pt,H} = 73.0, PtC*H*₃); $\delta_{\rm C}$ (201 MHz, (CD₃)₂CO): 147.6 (C6'), 144.3 (C4), 141.5 (C4'), 139.2 (CH₂C₆H₅), 139.1 (CH₂C₆H₅), 138.8 (CH₂C₆H₅), 129.2–128.1 (C5', CH₂C₆H₅), 125.9 (C3'), 118.5 (C3), 111.5 (C5), 89.1 (C1_{ch}), 86.6 (C3_{ch}), 83.9 (C2_{ch}), 79.0 (C5_{ch}), 78.3 (C4_{ch}), 75.8 (CH₂C₆H₅), 75.7 (CH₂C₆H₅), 75.5 (CH₂C₆H₅), 65.7 (C6_{ch}), 65.1 (NCH₂), 33.9 (SCH₂), 0.2 (s+d, ¹*J*_{Pt,C} = 726.4, PtCH₃), -4.9 (s+d, ¹*J*_{Pt,C} = 639.9, PtCH₃), -8.1 (s+d, ¹*J*_{Pt,C} = 688.2, PtCH₃); $\delta_{\rm Pt}$ (107 MHz, CD₃)₂CO) –2377.

fac-[PtMe₃(ch-SPT)][BF₄] (**42**, *ch-SPT* = **6a**). v_{max} (KBr)/cm⁻¹ 3116 w, 3068 w, 2970 w, 2906 w, 2349 w, 1735 s, 1602 m, 1584 w, 1492 w, 1467 m, 1452 m, 1385 w, 1317 m, 1272 s, 1180 m, 1088 s, 1069 s, 1025 s, 855 w, 803 w, 771 w, 710 s, 686 m cm⁻¹; δ_{H} (400 MHz, (CD₃)₂CO) 9.00 (1H, s, H_{Taz}), 8.94 (1H, d, br, *H*6), 8.52 (1H, d, *H*3), 8.33 (1H, t, *H*4), 7.85 (1H, t, *H*5), 5.62 (1H, d, ³ $J_{H,H}$ = 10.4, H_{1ch}), 5.49 (1H, dd, H_{3ch}), 5.30 (1H, dd, br, H_{2ch}), 5.21 (1H, dd, H_{4ch}), 4.30 (3H, m, H_{5ch} , H_{6ach} , H_{6bch}), 2.08 (3H, s, C(O)CH₃), 2.06 (3H, s, C(O)CH₃), 2.03 (3H, s, C(O)CH₃), 1.98 (3H, s, C(O)CH₃), 1.47 (9H, s+d, br, PtCH₃); δ_{C} (125 MHz, (CD₃)₂CO) 169.8 (*C*(O)CH₃), 169.3 (*C*(O)CH₃), 169.2 (*C*(O)CH₃), 169.1 (*C*(O)CH₃), 151.0 (*C*6), 140.7 (*C*4), 126.5 (br, *C*5), 124.7 (br, C_{Taz}), 123.6 (br, *C*3), 83.8 (br, *C*1_{ch}), 76.1 (*C*5_{ch}), 72.7 (*C*3_{ch}), 69.3 (br, *C*2_{ch}), 67.9 (*C*4_{ch}), 61.7 (*C*6_{ch}), 19.9 (C(O)CH₃), 19.7 (2 × C(O)CH₃), 19.6 (C(O)CH₃), -5.8 (s+d, br, Pt(CH₃)₃); δ_{Pt} (107 MHz, (CD₃)₂CO) –2154.

fac-[PtMe₃(ch-SPT)][BF₄] (**43**, *ch-SPT* = **6b**). v_{max} (KBr)/cm⁻¹ 2960 w, 2906 w, 1735 s, 1602 m, 1452 m, 1386 w, 1317 s, 1272 s, 1180 m, 1092 s, 1025 s, 854 w, 771, w, 710 s, 686 m; $\delta_{\rm H}$ (400 MHz, (CD₃)₂CO): 8.89 (1H, d, br, *H*6), 8.83 (1H, s, *H*_{Taz}), 8.51 (1H, d, *H*3), 8.32 (1H, t, *H*4), 8.11–7.84 (8H, m, C(O)C₆*H*₅), 7.70–7.35 (13H, m, *H*5, C(O)C₆*H*₅), 6.28 (1H, dd, *H*3_{ch}), 6.09 (1H, d, ³*J*_{H,H} = 10.4, *H*1_{ch}), 6.00 (1H, dd, *H*4_{ch}), 5.94 (1H, dd, br, *H*2_{ch}), 4.89 (1H, m, *H*5_{ch}), 4.82 (1H, m, *H*6a_{ch}), 4.72 (1H, m, *H*6b_{ch}), 1.32 (9H, s+d, br, PtC*H*₃); $\delta_{\rm C}$ (125 MHz, (CD₃)₂CO) 166.3 (*C*(O)C₆*H*₅), 166.1 (*C*(O)C₆*H*₅), 165.8 (*C*(O)C₆*H*₅), 151.7 (br, C6), 141.6

(br, C4), 134.9 (C(O) C_6H_5), 134.5 (C(O) C_6H_5), 134.4 (C(O) C_6H_5), 134.3 (C(O) C_6H_5), 130.6–129.4 (C(O) C_6H_5), 127.4 (br, C5), 125.3 (br, Ctaz), 124.5 (br, C3), 85.5 (br, C1_{ch}), 77.3 (C_{ch}), 74.4 (C_{3ch}), 71.1 (br, C2), 69.8 (C4), 63.6 (C6), –5.9 (s+d, br, Pt(CH_3)₃); δ_{Pt} (107 MHz, CD₃)₂CO): –2158.

*fac-[PtMe*₃(*ch-SPT*)][*BF*₄] (44, *ch-SPT* = 6*c*). v_{max} (KBr)/cm⁻¹ 3030 w, 2058 w, 2903 w, 2869 w, 1734 w, 1605 w, 1555 w, 1497 w, 1453 m, 1362 w, 1229 w, 1147 m, 1088 s, 1074 s, 1027 s, 745 m, 697 m; δ_{H} (400 MHz, (CD₃)₂CO) 8.93 (1H, d, br, *H*6), 8.78 (1H, s, *H*_{Taz}), 8.49 (1H, d, *H*3), 8.31 (1H, t, *H*4), 7.83 (1H, t, *H*5), 7.38–7.23 (20H, m, CH₂C₆H₅), 5.35 (1H, d, ³*J*_{H,H} = 9.5, *H*1_{ch}), 4.95–4.51 (8H, m, *C*H₂C₆H₅), 3.94 (4H, m, *H*3_{ch}, *H*5_{ch}, *H*6a_{ch}, *H*6b_{ch}), 3.85 (2H, m, *H*2_{ch}, *H*4_{ch}), 1.41 (9H, s+d, br, PtC*H*₃); δ_{C} (125 MHz, (CD₃)₂CO) 154.8 (C6), 141.5 (C4), 139.5 (CH₂C₆H₅), 139.3 (CH₂C₆H₅), 138.7 (CH₂C₆H₅), 129.2–128.0 (CH₂C₆H₅), 127.2 (C5), 124.3 (C3), 124.4 (*C*_{Taz}), 91.2 (br, *C*1_{ch}), 86.9 (*C*3_{ch}), 80.9 (br, *C*2_{ch}), 80.0 (br, *C*5_{ch}), 78.5 (*C*4_{ch}), 76.1 (*C*H₂C₆H₅), 75.8 (*C*H₂C₆H₅), 75.5 (*C*H₂C₆H₅), 73.7 (*C*H₂C₆H₅), 69.5 (br, *C*6_{ch}), -5.7 (s+d, br, Pt(*C*H₃)₃); δ_{Pt} (107 MHz, (CD₃)₂CO) –2151.

fac-[PtMe₃(ch-Sbpy)][BF₄] (**45**, *ch-Sbpy* = **7a**). v_{max} (KBr)/cm⁻¹ 2966 w, 2907 w, 2359 w, 1755 s, 1605 w, 1588 w, 1561 w, 1439 m, 1375 m, 1233 s, 1058 s, 1044 s, 913 w, 777 w; $\delta_{\rm H}$ (400 MHz, (CD₃)₂CO) 9.05 (1H, d, br, *H*6), 8.74 (1H, d, *H*3), 8.60 (1H, d, *H*3'), 8.44 (1H, t, *H*4), 8.33 (1H, t, *H*4'), 8.16 (1H, d, br, *H*5'), 7.98 (1H, t, *H*5), 6.00 (1H, d, br, *H*1_{ch}), 5.43 (1H, dd, *H*3_{ch}), 5.23 (1H, dd, br, *H*4_{ch}), 5.17 (1H, dd, *H*2_{ch}), 4.28 (3H, m, *H*5_{ch}, *H*6a_{ch}, *H*6b_{ch}), 2.05 (3H, s, C(O)C*H*₃), 2.04 (3H, s, C(O)C*H*₃), 2.02 (3H, s, C(O)C*H*₃), 1.98 (3H, s, C(O)C*H*₃), 1.45 (9H, s+d, br, ²*J*_{Pt,H} = 70.5, PtC*H*₃); $\delta_{\rm C}$ (125 MHz, (CD₃)₂CO): 170.6 (*C*(O)CH₃), 170.0 (*C*(O)CH₃), 169.8 (*C*(O)CH₃), 156.7 (br, C6), 141.9 (br, C4), 141.8 (C4'), 128.7 (br, C5), 127.8 (br, C5'), 126.3 (br, C3), 122.8 (br, C3'), 84.2 (br, C1_{ch}), 76.6 (*C*_{5ch}), 74.0 (br, *C*3_{ch}), 70.2 (br, *C*4_{ch}), 68.9 (C2_{ch}), 62.9 (C6_{ch}), 20.7 (2 × C(O)CH₃), 20.5 (2 × C(O)CH₃), -3.4 (s+d, br, Pt(*C*H₃)₃); $\delta_{\rm Pt}$ (107 MHz, (CD₃)₂CO) –2123.

*fac-[PtMe*₃(*ch-Sbpy*)][*BF*₄] (**46**, *ch-Sbpy* = **7b**). v_{max} (KBr)/ cm⁻¹ 2966 w, 2906 w, 2362 w, 2343 w 1735 s, 1602 m, 1587 w, 1561 w, 1491 w, 1452 m, 1439 m, 1366 w, 1316 m, 1268 s, 1179 m, 1087 s, 1069 s, 1026 s, 774 m, 710 s, 687 w; $\delta_{\rm H}$ (400 MHz, (CD₃)₂CO) 8.95 (1H, d, br, *H6*), 8.68 (1H, d, *H3*), 8.53 (1H, d, *H3'*), 8.40 (1H, t, *H4*), 8.26 (1H, d, br, *H5'*), 8.10–7.82 (9H, m, *H4'*, C(O)C₆*H*₅), 7.67 (1H, t, *H5*), 7.61–7.33 (12H, m, C(O)C₆*H*₅), 6.23 (1H, dd, *H3_{ch}*), 6.07 (1H, d, br, *H1_{ch}*), 5.92 (1H, dd, *H4_{ch}*), 5.81 (1H, dd, br, *H2_{ch}*), 4.88 (1H, m, br,

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*H*5_{ch}), 4.77 (1H, dd, *H*6a_{ch}), 4.65 (1H, dd, *H*6b_{ch}), 1.33 (9H, s+d, br, Pt(C*H*₃)₃); $\delta_{\rm C}$ (125 MHz, (CD₃)₂CO) 166.3 (*C*(O)C₆H₅), 166.1 (*C*(O)C₆H₅), 165.8 (*C*(O)C₆H₅), 164.9 (*C*(O)C₆H₅), 147.5 (*C*6), 141.9 (*C*4), 141.7 (*C*4'), 134.6 (*C*(O)C₆H₅), 134.5 (*C*(O)C₆H₅), 134.4 (*C*(O)C₆H₅), 134.3 (*C*(O)C₆H₅), 130.5–129.4 (*C*(O)C₆H₅), 128.7 (br, *C*5), 127.6 (br, *C*5'), 126.3 (br, *C*3'), 122.8 (br, *C*3), 85.1 (*C*1_{ch}), 76.9 (*C*5_{ch}), 74.8 (*C*3_{ch}), 71.2 (br, *C*2_{ch}), 70.1 (*C*4_{ch}), 63.9 (*C*6_{ch}), –3.5 (s+d, br, Pt(*C*H₃)₃); $\delta_{\rm Pt}$ (107 MHz, (CD₃)₂CO) –2120.