Electronic Supporting Information

Platinum Trimethyl Bipyridyl Thiolates – A New Class of Tunable, Red- to Near IR Emitting Lumophores for Bioimaging Applications

Harriet L. Steel,[a] Sarah L. Allinson,[a] Jane Andre,[a] Michael P. Coogan,[b]* and James A. Platts[c]

[a] *Lancaster Biomedical Sciences, Furness Building, Lancaster University, Bailrigg, Lancaster LA1 4YG.*

[b] *Chemistry Department, Faraday Building, Lancaster University, Bailrigg, Lancaster, LA1 4YB.*

[c] *Cardiff School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT.*

Contents

S1. Experimental.

General experimental.

All starting materials, reagents and solvents were purchased from commercial suppliers and used as supplied unless otherwise stated. Toluene was dried over sodium and purified by distillation. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 and 100 MHz respectively on a Bruker Avance III 400 and referenced to residual solvent peaks unless otherwise reported. Chemical shifts are reported in ppm, and coupling constants in Hz. IR spectra were recorded on an Agilent Technologies Cary 630 FTIR Spectrometer as thin films or solids and are reported in wavenumbers (cm^{-1}). UV vis spectra were recorded on an Agilent Technologies Cary 60. Steady state emission and excitation spectra were recorded on an Agilent Technologies Cary Eclipse. Time-resolved spectra were recorded on a PicoQuant FluoTime 300 exciting with an LDH-P-C-375 and decays analysed with the program FluoFit. Melting points are uncorrected. Mass spectra were recorded at the EPSRC National Mass Spectrometry Service Centre in Swansea on a Thermo Scientific LTQ Orbitrap XL. $PtMe_3I$ was obtained from Strem.

[$PtIMe_3$(bpy)] **1**.

To a flask containing $PtIMe_3$ (500 mg, 1.36 mmol) and 2,2'bipyridine (212 mg, 1.36 mmol) was added toluene (5 ml) and the mixture heated at 100° C. for 15 minute then cooled to RT. Pale yellow crystals formed and the solution was filtered to obtain **1** (592 mg, 83%) as previously reported.

[$PtIMe_3$(4,4'dimethoxybipyridyl)] **2**.

To a flask containing $PtIMe_3$ (50 mg, 0.14 mmol) and 4,4'dimethoxybipyridine (30 mg, 0.14 mmol) was added chloroform (1 ml) and heated to reflux, at which point all the reactants passed into solution. The solution was heated at reflux for a further 10 minutes then left to cool to room temperature overnight while pale yellow crystals grew. The product was collected by filtration to give **2** (68 mg, 83%) as colourless crystals. ^{1}H (DMSO, evidence of displacement of iodide by DMSO was observed upon standing or heating, but **2** is insufficiently soluble in less coordinating solvents) δ 8.68 (2h, d, J= 6.2 Hz, satellites J_{Pt-H} = 20.0 Hz, bpyH6,6') 8.31 (2H, d, J = 2.5 Hz, bpyH3,3') 7.38 (2H, dd, J =6.2, 2.5 Hz, bpy H5,5') 4.06 (6H, s, 2 x OMe) 1.32 (6H, s satellites J_{Pt-H}= 69.7 Hz, 2 x PtMe eq) 0.56 (3H, s , satellites J_{Pt-H}= 73.9 Hz, PtMe ax); ^{13}C δ 166.3, 154.9, 146.8, 111.6, 109.9, 55.6, 6.0,

-8.8; ^{195}Pt δ – 2762; IR ν_{max} 2972, 2892, 2810, 1607, 1562, 1257, 1255, 1029, 897 cm^{-1} ; uv λ_{max} (ε) 316 (41470) 325 (39117) 383 (7823) nm; m/z isotope match on $C_{15}H_{21}IN_2O_2PtNa$ $[M+Na]^+$ (see ESI) ;HRMS $C_{15}H_{21}IN_2O_2PtNa$ calculated, 606.0189 observed 606.0191. **Crystal Data** for $C_{12}H_{9.6}I_{0.8}N_{1.6}O_{1.6}Pt_{0.8}$ (*M* =466.66 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 11.1595(10) Å, *b* = 11.6084(10) Å, *c* = 13.5382(14) Å, *β* = 103.102(10)°, *V* = 1708.2(3) $Å^3$, *Z* = 5, *T* = 100 K, μ(Mo Kα) = 10.025 mm^{-1}, *Dcalc* = 2.2681 g/cm^3, 8596 reflections measured (7.02° ≤ 2Θ ≤ 58.82°), 4058 unique (R_{int} = 0.0403, R_{sigma} = 0.0568) which were used in all calculations. The final R_1 was 0.0367 (I>=2u(I)) and wR_2 was 0.1120 (all data).

[$PtIMe_3$(4,4'dimethoxycarbonylbipyridyl)] **3**.

To a flask containing $PtIMe_3$ (50 mg, 0.14 mmol) and 4,4'dimethoxycarbonylbipyridine (40 mg, 0.15 mmol) was added chloroform (1 ml) and heated to reflux, at which point all the reactants passed into solution. The solution was heated at reflux for a further 10 minutes then left to cool to room temperature overnight. To the resulting clear red solution was then added methanol (5 ml) which induced crystallisation of the product which was collected by filtration to give **3** (76 mg, 85%) as iridescent red plates. ^{1}H ($CDCl_3$) δ 9.12 (2H, d J = 5.8 Hz, satellites J_{H-Pt} = 9.8 Hz, bpy H6,6') 8.82 (2H, d, J= 1.5 Hz, bpy H3,3') 8.12 (2H, dd J =5.8, 1.5 Hz, bpy H5,5') 4.03 (6H, s, 2 x CO_2CH_3) 1.55 (6H, s, satellites J_{H-Pt} = 70.6 Hz, 2 x Pt-CH_3 eq) 0.54 (3H, s, satellites J_{H-Pt} = 72.2 Hz, Pt-CH_3 ax); ^{13}C δ 163.7, 155.0, 148.5, 128.3, 123.5, 53.6, 8.3, -5.8; ^{195}Pt δ –2867; IR ν_{max} 3445, 2901, 1732, 1562, 1264, 1240, 1227, 959, 910 cm^{-1} ; uv λ_{max} (ε) 314 (10451) 323 (10161) 371 (5709) nm; m/z isotope match on $C_{17}H_{21}IN_2O_4PtNa$ $[M+Na]^+$ (see ESI); HRMS $_{17}H_{21}IN_2O_4PtNa$ calculated, 661.0065 observed 661.0063.

[$PtMe_3$(bpy)(Py)] PF_6 **4**.

To a flask containing **1** (100 mg, 0.191 mmol), KPF_6 (100 mg, 0.543 mmol) and pyridine (100 μL, 98.2 mg, 1.24 mmol) was added MeCN (5 ml) and the mixture heated until reflux was reached at which point all reactants dissolved and a clear solution was formed. The mixture was then cooled to 50 ° C. and stirred for 30 minutes at this temperature before the addition of water (5 ml) and cooling to room temperature for 16 hours upon which colourless crystals formed and were isolated by filtration to give **4** (86 mg, 73 %). ^{1}H δ 8.98 (2H, d, 8.0 Hz, + ^{195}Pt satellites, J_{H-Pt} = 12.0 Hz, bpy H6,6') 8.51 (2H, d, 8.0 Hz, + ^{195}Pt satellites, J_{H-Pt} = 20.0 Hz, Py H2,H6) 8.30 (2H, m, Py H3,H5) 8.19 (2H, m bpy H4,4') 7.87 (3H, m, bpy H3,3'&Py H4) 7.35 (2H, m bpy H5,5') 1.21 (6H, s, Pt satellites J_{H-Pt} = 67.0 Hz, 2 x PtCH_3 eq.) 0.51 (3H, s, Pt satellites J_{H-Pt} = 70.2 Hz, PtCH_3 ax.); ^{13}C δ 155.2, 149.0, 147.5 (+ satellites J_{C-Pt} = 8 Hz), 141.2 139.7, 128.8 (+ satellites J_{C-Pt} = 7 Hz), 127.0 (+ satellites J_{C-Pt} = 6 Hz), 125.6(+ satellites J_{C-Pt} = 4 Hz), -2.9 (+ satellites J_{C-Pt} = 688 Hz), -9.8 (+ satellites J_{Pt-C}= 662 Hz; ^{195}Pt δ -2473; IR ν_{max} 2959, 2903, 2821, 1605, 558 cm^{-1} ; uv λ_{max} (ε) 297 (21781), 309 (21906) nm; m/z 474-478 isotope match on $C_{18}H_{22}N_3Pt$ $[M-PF_6]^+$ (see ESI); HRMS, $C_{18}H_{22}N_3Pt$ calculated 472.1419, observed 472.1418. **Crystal Data** for $C_{20}H_{20}N_3F_6PPt$ (*M* =620.44 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 10.9042(2) Å, *b* = 12.0936(3) Å, *c* = 15.9712(3) Å, *β* = 93.7300(16)°, *V* = 2101.68(7) $Å^3$, *Z* = 4, *T* = 100.00(10) K, μ(Cu Kα) = 13.782 mm^{-1}, *Dcalc* = 1.9607 g/cm^3, 6810 reflections measured (8.12° ≤ 2Θ ≤ 145.98°), 3990 unique (R_{int} = 0.0315, R_{sigma} = 0.0354) which were used in all calculations. The final R_1 was 0.0394 (I>=2u(I)) and wR_2 was 0.1252 (all data).

[$PtMe_3$(bpy)(Py-3-CH_2OH)] PF_6 **5**.

To a flask containing **1** (100 mg, 0.191 mmol), KPF_6 (100 mg, 0.543 mmol) and 3-hydroxymethylpyridine (100 μL, 113 mg, 1 mmol) was added MeCN (5 ml) and the mixture heated until reflux was reached at which point all reactants dissolved and a clear solution was formed. The mixture was then cooled to 50 ° C. and stirred for 30 minutes at this temperature before the addition of water (5 ml) and cooling to room temperature for 16 hours. After this time all the volatiles were removed on a rotary evaporator and the residues recrystallised from acetone/water to give colourless crystals which were isolated by filtration to give **5** (84 mg, 68 %). ^{1}H δ 8.97 (2H, d, 5.0 Hz, satellites J_{H-Pt}=13.3 Hz bpy-H6,6') 8.49 (2H, d, 6.3 Hz, bpy H3,3') 8.29 (2H, m, bpy-H4,4') 8.14 (1H, s, satellites J_{H-Pt}= 11.5 Hz, Py H2) 8.03 (1H, d, J = 5.6 Hz, satellites J_{H-Pt} =11.0 Hz, Py-H6) 7.78 (1H, d, J = 8.5 Hz, Py-H4) 7.28 (1H, dd, J = 7.8, 5.6 Hz, Py-H5) 4.48 (2H, d, J = 5.9 Hz, PyCH_2OH) 3.56 (1H, t, J=5.9 Hz, PyCH_2O*H*) 1.22 (6H, s, satellites J_{Pt-H} = 67.7 Hz, $PtMe_{eqx2}$) 0.52 (3H, s, satellites J_{Pt-H} = 70.8 Hz, $PtMe_{ax}$); ^{13}C δ 155.1, 147.44, 147.41 (+ satellites J_{Pt-C} = 15.4 Hz) 146.8, 141.2, 140.9, 137.6, 128.7 (+ satellites J_{Pt-C} = 13.8 Hz), 126.4, 125.4 (+satellites, J_{Pt-C}=8.5 Hz) 60.8, -2.9 (+satellites, J_{Pt-C} =

688 Hz), -9.7 (+satellites, J_{Pt-C} = 656 Hz); ^{195}Pt δ -2474; IR ν $_{max}$ 2955, 2894, 1603, 555 cm^{-1} ; uv λ $_{max}$ (ε) 300 (30516), 310 (32258) nm; m/z isotope match on $C_{19}H_{24}N_3OPt$ $[M\text{-}PF_6]^+$ (see ESI) ;HRMS $C_{19}H_{24}N_3OPt$ calculated 502.1524, observed 502.1524. **Crystal Data** for $C_{18}H_{23}N_3OF_6PPt$ (*M* =648.45 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.1410(4) Å, *b* = 9.5731(4) Å, *c* = 13.2139(6) Å, *α* = 108.296(4)°, *β* = 97.486(4)°, *γ* = 95.712(3)°, *V* = 1076.32(9) Å^3, *Z* = 2, *T* = 99.98(13) K, μ(Cu Kα) = 13.529 mm^{-1}, *Dcalc* = 2.0007 g/cm^3, 6376 reflections measured (7.16° ≤ 2Θ ≤ 146.02°), 4066 unique (R_{int} = 0.0205, R_{sigma} = 0.0304) which were used in all calculations. The final R_1 was 0.0211 (I>=2u(I)) and wR_2 was 0.0755 (all data).

[$PtMe_3$(bpy)(Py-4-CO_2Et)] PF_6 **6**.

To a flask containing **1** (100 mg, 0.191 mmol), KPF_6 (100 mg, 0.543 mmol) and ethylisonicotinate (100 μL, 111 mg, 0.733 mmol) was added MeCN (5 ml) and heated to 50 ° C. The mixture which contained solid material throughout the procedure was stirred for 30 minutes at this temperature before the addition of water (5 ml) and cooling to room temperature for 16 hours. The resultant large colourless blocks were isolated by filtration to give **6** (98 mg, 74 %). ^{1}H δ 8.83 (2H, d, 5.8 Hz, satellites J_{H-Pt}=12.2, Hz bpy-H6,6') 8.38 (2H, d, 8.0 Hz, bpy H3,3') 8.22 (2H, m, PyH 2,6) 8.17 (2H, m, bpy H4,4') 7.75 (2H, m, bpy H5,5') 7.64 (2H, m, PyH3,5) 4.18 (2H, q, 7.3 Hz, $CO_2CH_2CH_3$) 1.16 (3H, t, 7.3 Hz, $CO_2CH_2CH_3$) 1.08 (6H, s, Pt satellites J_{H-Pt} = 66.4 Hz, 2 x PtCH_3 eq.) 0.41 (3H, s, Pt satellites J_{H-Pt} = 71.2 Hz, PtCH_3 ax.); ^{13}C δ 164.1, 155.3, 151.2, 150.2, 147.3 (Pt satellites J_{Pt-H}= 14.6 Hz) 141.3, 128.8 (Pt satellites J_{Pt-H} =12.2 Hz) 125.9 (Pt satellites J_{Pt-H} =10.2 Hz) 125.6 (Pt satellites J_{Pt-H} =8.4 Hz) 63.0, 13.8, -2.8 (Pt satellites J_{Pt-H} = 687.0 Hz) -9.4 (Pt satellites J_{Pt-H} =662.2 Hz); ^{195}Pt δ -2473; IR ν $_{max}$ 2978, 2905, 1730, 1603, 558 cm^{-1} ; uv λ $_{max}$ (ε) 278 (26666) 290 (27750) 298 (29083) 309 (24666) nm; m/z isotope match on $C_{21}H_{26}N_3O_2Pt$ $[M\text{-}PF_6]^+$ (see ESI); HRMS $C_{21}H_{26}N_3O_2Pt$ calculated 544.1630, observed 544.1626. **Crystal Data** for $C_{21}H_{26}N_3O_2F_6PPt$ (*M* =677.47 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 10.94969(19) Å, *b* = 14.3600(2) Å, *c* = 15.7460(3) Å, *β* = 96.7748(17)°, *V* = 2458.57(8) Å^3, *Z* = 4, *T* = 289.33(10) K, μ(Cu Kα) = 11.910 mm^{-1}, *Dcalc* = 1.8301 g/cm^3, 8172 reflections measured (8.36° ≤ 2Θ ≤ 148.4°), 4766 unique (R_{int} = 0.0252, R_{sigma} = 0.0371) which were used in all calculations. The final R_1 was 0.0366 (I>=2u(I)) and wR_2 was 0.1323 (all data).

[$PtMe_3$(bpy)(PPh_3)] PF_6 **7**.

To a flask containing **1** (100 mg, 0.191 mmol), KPF_6 (100 mg, 0.543 mmol) and triphenylphosphine (50 mg, 0.191 mmol) was added MeCN (3 ml) and heated to reflux, at which point all the reactants passed into solution. The pale yellow solution was stirred as it cooled to room temperature over 30 minutes, then treated with 5 ml of water. A flocculent white solid immediately precipitated from solution which was collected by filtration then recrystallised from acetone to give **7** as colourless blocks (89 mg, 58 %). ^{1}H δ 8.42 (2H, d, J = 6.2 Hz, satellites J_{Pt-H} = 19.7 Hz, bpyH6,6') 8.32 (2H, d, J = 8.1 Hz, bpy H3,3') 8.14 (2H, m, bpyH4,4') 7.57 (2H, m, bpy H5,5') 7.42 (3H, m, 3 x H-Ar) 7.29 (6H, m, 6 x H-Ar) 7.05, (6H, m, 6 x H-Ar) 1.36 (6H, d, J_{H-P} = 7.5 Hz, satellites, J_{Pt-H} = 67.6 Hz, 2 x Pt-Me ax) 0.51 (3H, d, J_{P-H} = 7.9 Hz, satellites J_{Pt-H} = 59.0 Hz, Pt-Me ax); ^{13}C δ 154.6, 147.9 (satellites, J_{Pt-C} = 12.5 Hz), 140.7, 133.5, 133.4, 131.3, 131.3, 129.4, 129.3, 128.5 (satellites, J $_{Pt-C}$ = 12.4 Hz), 128.1 (satellites, J $_{Pt-C}$ = 11.7 Hz), 125.3 (satellites, J $_{Pt-C}$ = 8.4 Hz) 11.5 (d, J $_{P-C}$ = 112 Hz, satellites, J $_{Pt-C}$ = 429 Hz) -5.5 (d, J $_{P-C}$ = 3.9 Hz, satellites J $_{Pt-C}$ = 641 Hz); ^{195}Pt δ - 3062 (d, J_{Pt-P} = 993 Hz); ^{31}P δ -3.77 (s, satellites, J_{Pt-P} = 993 Hz, Pt-PPh_3) -146.87, (sept, J_{P-F} = 707 Hz); IR ν $_{max}$ 2963, 2913, 2825, 1478, 558 cm^{-1} ; uv λ $_{max}$ (ε) nm 302 (18112) 313 (19644); m/z isotope match on [M-PF_6] (see ESI) ;HRMS $C_{31}H_{32}N_2PPt$ calculated, 658.1948 observed 658.1948.

[$PtMe_3$(bpy)($PhNH_2$)] PF_6 **8**.

To a flask containing **1** (50 mg, 0.0955 mmol), KPF_6 (100 mg, 0.543 mmol) and aniline (0.1 ml, 102 mg, 1.09 mmol) was added MeCN (2.5 ml) and heated to reflux, at which point all the reactants passed into solution. The colourless solution was set aside overnight as it cooled to room temperature, during which time crystallisation occurred spontaneously, and the product was collected by filtration to give **8** (451 mg, 68 %) as pale yellow crystals.NMR showed the poresence of 2 rotamers: ^{1}H 8.90 (2H (minor rotamer) d, J = 6.1 Hz, satellites J_{Pt-H} = 19.1 Hz) bpyH6,6') 8.71 (2H (major rotamer) d, J = 6.1 Hz, satellites J $_{Pt-H}$ = 18.2 Hz) 8.56 (2H (minor rotamer) d, J = 8.0 Hz, bpyH3,3') 8.30 (2H (minor rotamer) + 2H (major rotamer), m, bpyH3,3' (major rotamer) + bpyH4,4' minor rotamer) 8.18 (2H major rotamer, m, bpyH4,4') 7.86 (2H minor rotamer, m, bpyH5,5') 7.71(2H major rotamer, m,

bpyH5,5') 7.10 (2H minor rotamer, m, N-ArH3,5) 6.83 (2H major rotamer, m, NArH3,5) 6.77 (1H major rotamer, m, NArH4) 6.64 (3H minor rotamer, m, NArH4 + NArH2,6) 6.16 (2H major rotamer, d, J = 7.0 Hz, NArH2,6) 5.17 (s, broad, NH2, major rotamer, under integrates) 4.13 (s, broad, NH_2 minor rotamer, under integrates) 1.20 (6H, minor rotamer, s, satellites J_{Pt-H} = 68.1 Hz, 2 x PtMe eq) 1.15 (6H , major rotamer, s, satellites J_{Pt-H} = 67.5 Hz, 2 x PtMe eq) 0.55 (3H, minor rotamer, s, satellites J_{Pt-H} = 76.9 Hz, PtMe ax) 0.46 (3H, major rotamer, s, satellites J_{Pt-H} = 73.0 Hz, PtMe ax); ^{13}C δ 155.5, 155.2, 147.8 147.7, 147.6, 147.5, 141.2, 140.8, 129.6, 129.2, 128.4 (satellites J_{Pt-C} = 13.1 Hz), 128.1 (satellites J_{Pt-C} = 14.2 Hz), 125.2 (satellites J_{Pt-C} = 8.2 Hz), 125.0 (satellites J_{Pt-C} = 8.6 Hz), 124.9, 124.3, 119.5, 115.0, -5.5 (satellites J_{Pt-C} = 686.5 Hz) -6.1, - 8.7 (satellites J_{Pt-C} = 679.7 Hz) – 8.9; ^{195}Pt δ -2521; IR ν_{max} 3341, 3291, 2898, 2818, 1603, 1495, 828 cm^{-1} ; uv λ_{max} (ε) 288 (25935) 296 (26032) 310 (20806) nm; m/z isotope match on $C_{19}H_{24}N_3Pt$ [M-PF_6] (see ESI) ;HRMS $C_{19}H_{24}N_3Pt$ calculated, 489.1614 observed 489.1612.

[Pt(S-4-C_6H_4-CO_2Me)Me_3(bipyridyl)] **9**.

To a flask containing **1** (50 mg, 0.096 mmol), 4-mercaptomethylbenzoate (24 mg, 0.14 mmol) and sodium t-butoxide (10 mg, 0.10 mmol) was added acetonitrile (1 ml) and heated to 70 C with the immediate formation of a cloudy yellow solution. The mixture was maintained at 70 C for a further 35 minutes, and then cooled to ambient temperature before the addition of water (10 ml). After standing overnight the solid yellow product was collected by filtration then recrystallised from acetonitrile/water to give **9** (29 mg, 53 %) as yellow needles. ^1H δ 8.76 (2H, d, J = 5.5 Hz, satellites J_{Pt-H} = 14.2 Hz, bpy H6,6') 7.85-7.954H, m, bpyH3,3',4,4') 7.49-7.56 (1H, m, bpyH 5,5') 7.16 (2H, d, J = 8.5 Hz, S-$C_6H_4CO_2Me$, H3,5) 6.56 (2H, d, J = 8.5 Hz, S-$C_6H_4CO_2Me$, H2,6) 3.81 (3H, s, S-$C_6H_4CO_2$*Me*) 1.24 (6H, s, satellites J_{Pt-H} = 70.5 Hz, 2 x Pt-CH_3 eq) 0.28 (3H, s, satellites J_{Pt-H} = 65.5 Hz, Pt-CH_3 ax); ^{13}C δ 153.9, 152.4, 148.8 (satellites J_{Pt-C} = 14.0 Hz), 137.9, 134.5 (satellites J_{Pt-C} = 5.2 Hz) , 127.7 (satellites $J_{Pt-C\ =\ 8.0}$ Hz) , 126.4 (satellites J_{Pt-C} = 14.6 Hz), 123.8, 122.8 (satellites J_{Pt-C} = 8.0 Hz), 51.6, 0.0 (satellites J_{Pt-C} = 615.7 Hz), -5.1 (satellites J_{Pt-C} = 681.5 Hz); ^{195}Pt δ 2956; IR ν_{max} 2946, 2888, 2812, 1704, 1586, 1436, 1277, 1260, 1111, 1085, 763 cm^{-1} ; uv λ_{max} (ε) 299 (41471) 308 (42944) 353 (12290) nm; m/z molecular ion not observed, m/z $C_{13}H_{17}N_2Pt$ [M-S-$C_6H_4CO_2Me$], HRMS $C_{13}H_{17}N_2Pt$ calculated, 396.1039 observed 396.1034. **Crystal Data** for $C_{20}H_{27}N_2O_2PtS$ (*M* =563.58 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 14.3479(5) Å, *b* = 9.0481(3) Å, *c* = 16.1964(11) Å, *β* = 109.574(8)°, *V* = 1981.12(19) $Å^3$, *Z* = 4, *T* = 100 K, μ(Mo Kα) = 7.205 mm^{-1}, *Dcalc* = 1.8894 g/cm^3, 15341 reflections measured (6.02° ≤ 2Θ ≤ 54.98°), 4503 unique (R_{int} = 0.0245, R_{sigma} = 0.0243) which were used in all calculations. The final R_1 was 0.0184 (I>=2u(I)) and wR_2 was 0.0736 (all data).

[Pt(S-4-C_6H_4-CO_2Me)Me_3(4,4'-dimethoxycarbonylbipyridyl)] **10**.

To a flask containing **8** (33 mg, 0.052 mmol), 4-mercaptomethylbenzoate (10 mg, 0.059 mmol) and sodium t-butoxide (5 mg, 0.052 mmol) was added acetonitrile (5 ml) and heated to 65 C with the immediate formation of a pale yellow-orange solution. The mixture was maintained at 65 C for a further 40 minutes, during which the solution turned red-orange. The solution was then concentrated to 1 ml, re-heated to 65 C and the clear solution was treated dropwise with water until it remained cloudy at this temperature. After the addition of 1 drop of acetonitrile returned a clear solution the mixture was allowed to cool to room temperature overnight before the solid product was collected by filtration to give **10** (22 mg, 62 %) as blood-red blocks. ^1H δ 8.90 (2H, d, J = 5.5 Hz, satellites J_{Pt-H} = 13.5 Hz, bpy-H 6,6') 8.52 (2H, s, bpy-H3,3') 8.06 (2H, d, J = 5.5 Hz, bpy5,5') 7.16 (2H, d, J = 8.2 Hz, S-C_6H_4-CO_2CH_3 H2,6) 6.52 (2H, d, J = 8.2 Hz, S-C_6H_4-CO_2CH_3 H3,5) 4.10 (6H, s, 2 x bpy-CO_2C*H*$_3$) 3.82 (3H, s, S-C_6H_4-CO_2C*H*$_3$) 1.29 (6H, s, satellites J_{Pt-H} = 70.5 Hz, 2 x Pt-CH_3 eq) 0.28 (3H, s, satellites J_{Pt-H} = 65.0 Hz, Pt-CH_3 ax); ^{13}C δ 166.9, 163.4, 154.0, 151.6, 147.4 (satellites, J_{Pt-C} = 14.1 Hz) , 139.1, 134.3, 127.6, 125.8 (satellites, J_{Pt-C} = 14.6 Hz), 124.1, 122.8 (satellites, J_{Pt-H} = 7.8 Hz), 53.3, 51.4, 0.1 (satellites, J_{Pt-C} = 609.4 Hz), -4.8 (satellites, J_{Pt-H} =679.8 Hz); ^{195}Pt δ; IR ν_{max} 2954, 2890, 2814, 1735, 1709, 1586, 1437, 1402, 1279, 1260, 1110, 1087, 1016, 763, 704 cm^{-1} ; uv λ_{max} (ε) 309 (55862) 423 (5793) nm; m/z molecular ion not observed, m/z $C_{17}H_{21}N_2O_4Pt$ [M-S-$C_6H_4CO_2Me$], HRMS $C_{17}H_{21}N_2O_4Pt$ calculated, 512.1149 observed 512.1142. **Crystal Data** for $C_{25}H_{27}N_2O_6PtS$ (*M* =678.65 g/mol): triclinic, space group P-1 (no. 2), *a* = 7.2201(5) Å, *b* = 13.2276(9) Å, *c* = 14.0336(10) Å, *α* = 70.675(5)°, *β* = 80.551(6)°, *γ* = 84.130(6)°, *V* = 1245.94(16) $Å^3$, *Z* = 2, *T* = 100 K, μ(Mo Kα) = 5.756 mm^{-1}, *Dcalc* = 1.8088 g/cm^3, 21239 reflections measured (5.18° ≤ 2Θ ≤ 55.02°), 5677 unique (R_{int} = 0.2641, R_{sigma} = 0.1575) which were used in all calculations. The final R_1 was 0.0804 (I>=2u(I)) and wR_2 was 0.2041 (all data).

S2. Crystallographic data.

Crystal data for **2.**

Table 1 Crystal data and structure refinement for 2.

Identification code	2
Empirical formula	$C_{12}H_{9.6}I_{0.8}N_{1.6}O_{1.6}Pt_{0.8}$
Formula weight	466.66
Temperature/K	100 K
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.1595(10)
b/Å	11.6084(10)
c/Å	13.5382(14)
α/°	90
β/°	103.102(10)
γ/°	90
Volume/Å^3	1708.2(3)
Z	5
ρ_{calc}g/cm^3	2.2681
μ/mm^{-1}	10.025
F(000)	1080.7
Crystal size/mm^3	0.15 x 0.15 x 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	7.02 to 58.82
Index ranges	$-13 \leq h \leq 14$, $-11 \leq k \leq 15$, $-18 \leq l \leq 13$
Reflections collected	8596
Independent reflections	4058 [R_{int} = 0.0403, R_{sigma} = 0.0568]
Data/restraints/parameters	4058/0/194
Goodness-of-fit on F^2	0.775
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.1041
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.1120
Largest diff. peak/hole / e Å^{-3}	2.12/-2.46

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pt1	466.60(19)	3691.42(18)	2865.26(17)	14.91(10)
I1	-1493.2(4)	2542.5(3)	1614.6(3)	19.61(13)
N2	1485(5)	3678(4)	1691(4)	16.1(11)
N4	39(4)	5338(4)	2120(4)	14(1)
C0aa	1453(5)	4647(5)	1157(4)	11.5(10)
C9	654(5)	5581(5)	1395(4)	12.5(11)
C10	-517(8)	3839(6)	3975(6)	29.6(17)
C13	-681(6)	6165(5)	2377(5)	20.0(13)

C14	1070(6)	2150(5)	3544(5)	22.5(13)
C17	2934(6)	2867(6)	830(5)	24.7(14)
C2aa	2221(6)	2813(5)	1531(5)	21.7(13)
O3	3634(4)	3904(4)	-396(4)	26.0(11)
C4	561(5)	6637(5)	920(5)	17.8(12)
C1aa	2152(5)	4784(5)	425(5)	15.2(11)
C6	-166(6)	7498(5)	1203(5)	17.1(12)
C7	-811(6)	7244(6)	1953(5)	21.0(13)
C8	2914(6)	3888(5)	276(5)	17.3(12)
O2	-185(5)	8507(4)	729(4)	23.7(10)
C3	3621(6)	4921(5)	-1003(5)	24.7(14)
C5	-806(7)	9448(6)	1083(6)	32.0(17)
C18	1930(6)	4485(6)	3835(5)	28.5(15)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 7. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Pt1	20.46(15)	9.02(15)	17.42(16)	-0.79(7)	8.86(10)	1.61(8)
I1	25.0(2)	15.3(2)	20.7(2)	-1.87(14)	9.63(17)	-0.22(15)
N2	18(3)	11(3)	21(3)	1.6(17)	10(2)	-1.2(19)
N4	18(2)	8(2)	19(2)	-1.1(18)	12.3(19)	0(2)
C0aa	10(2)	6(2)	19(3)	6.1(19)	4(2)	3(2)
C9	15(2)	8(3)	17(3)	2(2)	7(2)	3(2)
C10	52(5)	20(3)	22(4)	-2(3)	19(3)	-6(3)
C13	29(3)	14(3)	24(3)	-1(2)	20(3)	-1(2)
C14	29(3)	18(3)	22(3)	6(3)	9(3)	14(3)
C17	28(3)	14(3)	36(4)	13(3)	16(3)	2(3)
C2aa	32(3)	11(3)	27(3)	5(2)	16(3)	5(3)
O3	34(3)	16(2)	37(3)	9.1(19)	27(2)	2(2)
C4	17(3)	17(3)	23(3)	-1(2)	11(2)	1(3)
C1aa	18(3)	8(3)	19(3)	0(2)	6(2)	-4(2)
C6	20(3)	11(3)	21(3)	2(2)	6(2)	-2(2)
C7	24(3)	16(3)	29(3)	4(3)	17(3)	-3(3)
C8	20(3)	16(3)	19(3)	1(2)	11(2)	-5(2)
O2	39(3)	11(2)	29(3)	8.6(18)	24(2)	7.5(19)
C3	35(3)	21(3)	24(3)	5(3)	20(3)	0(3)
C5	52(4)	13(3)	41(4)	12(3)	31(4)	2(3)
C18	39(4)	24(4)	22(3)	-8(3)	5(3)	1(3)

Table 4 Bond Lengths for 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	I1	2.7839(5)	C9	C4	1.377(8)
Pt1	N2	2.154(5)	C13	C7	1.371(9)
Pt1	N4	2.164(5)	C17	C2aa	1.372(8)
Pt1	C10	2.059(7)	C17	C8	1.401(9)
Pt1	C14	2.054(6)	O3	C8	1.343(7)
Pt1	C18	2.066(7)	O3	C3	1.436(8)
N2	C0aa	1.333(7)	C4	C6	1.394(8)
N2	C2aa	1.346(7)	C1aa	C8	1.387(8)
N4	C9	1.349(6)	C6	C7	1.403(8)
N4	C13	1.347(8)	C6	O2	1.333(7)
C0aa	C9	1.485(7)	O2	C5	1.433(7)
C0aa	C1aa	1.402(7)			

Table 5 Bond Angles for 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Pt1	I1	91.19(14)	C9	C0aa	N2	116.3(5)
N4	Pt1	I1	94.58(13)	C1aa	C0aa	N2	121.9(5)
N4	Pt1	N2	76.08(17)	C1aa	C0aa	C9	121.9(5)
C10	Pt1	I1	90.5(2)	C0aa	C9	N4	115.8(5)
C10	Pt1	N2	175.6(2)	C4	C9	N4	121.9(5)
C10	Pt1	N4	99.7(2)	C4	C9	C0aa	122.3(5)
C14	Pt1	I1	89.29(19)	C7	C13	N4	123.7(6)
C14	Pt1	N2	98.6(2)	C8	C17	C2aa	117.9(5)
C14	Pt1	N4	173.5(2)	C17	C2aa	N2	123.2(6)
C14	Pt1	C10	85.5(3)	C3	O3	C8	118.0(5)
C18	Pt1	I1	177.6(2)	C6	C4	C9	119.8(5)
C18	Pt1	N2	89.9(2)	C8	C1aa	C0aa	118.4(5)
C18	Pt1	N4	87.8(2)	C7	C6	C4	118.3(5)
C18	Pt1	C10	88.6(3)	O2	C6	C4	116.4(5)
C18	Pt1	C14	88.4(3)	O2	C6	C7	125.3(5)
C0aa	N2	Pt1	116.1(4)	C6	C7	C13	118.2(6)
C2aa	N2	Pt1	124.5(4)	O3	C8	C17	115.8(5)
C2aa	N2	C0aa	119.1(5)	C1aa	C8	C17	119.5(6)
C9	N4	Pt1	115.4(4)	C1aa	C8	O3	124.7(6)
C13	N4	Pt1	126.2(4)	C5	O2	C6	117.7(5)
C13	N4	C9	118.1(5)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2.

Atom	*x*	*y*	*z*	U(eq)
H2aa	2247(6)	2145(5)	1915(5)	26.0(16)
H17	3416(6)	2245(6)	726(5)	29.6(17)
H1aa	2106(5)	5460(5)	49(5)	18.2(14)
H13	-1115(6)	5995(5)	2870(5)	24.0(16)
H7	-1313(6)	7792(6)	2157(5)	25.3(16)
H4	982(5)	6776(5)	413(5)	21.4(14)
H5a	-680(40)	10139(11)	730(30)	48(3)
H5b	-1671(9)	9290(20)	960(40)	48(3)
H5c	-490(30)	9550(30)	1798(10)	48(3)
H3a	2815(13)	5030(20)	-1430(20)	37(2)
H3b	3830(40)	5579(8)	-568(5)	37(2)
H3c	4210(30)	4839(17)	-1420(30)	37(2)
H10a	33(10)	3780(40)	4630(6)	44(2)
H10b	-930(40)	4571(18)	3910(20)	44(2)
H10c	-1110(30)	3230(30)	3900(20)	44(2)
H14a	1830(20)	1940(20)	3370(30)	34(2)
H14b	1200(40)	2227(12)	4267(5)	34(2)
H14c	460(20)	1566(10)	3310(30)	34(2)
H18a	2470(20)	3910(6)	4210(30)	43(2)
H18b	2380(30)	4940(30)	3448(6)	43(2)
H18c	1629(7)	4970(30)	4300(20)	43(2)

Experimental

Single crystals of $C_{12}H_{9.6}I_{0.8}N_{1.6}O_{1.6}Pt_{0.8}$ [2] were grown from MeCN. A suitable crystal was selected and mounted on a diffractometer. The crystal was kept at100 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

Crystal structure determination of [2]

Crystal Data for $C_{12}H_{9.6}I_{0.8}N_{1.6}O_{1.6}Pt_{0.8}$ (M =466.66 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 11.1595(10) Å, b = 11.6084(10) Å, c = 13.5382(14) Å, β = 103.102(10)°, V = 1708.2(3) Å^3, Z = 5, T = 100 K, μ(Mo Kα) = 10.025 mm^{-1}, *Dcalc* = 2.2681 g/cm^3, 8596 reflections measured (7.02° ≤ 2Θ ≤ 58.82°), 4058 unique (R_{int} = 0.0403, R_{sigma} = 0.0568) which were used in all calculations. The final R_1 was 0.0367 (I>=2u(I)) and wR_2 was 0.1120 (all data).

Refinement model description

Number of restraints - 0, number of constraints - 32.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C2aa(H2aa), C17(H17), C1aa(H1aa), C13(H13), C7(H7), C4(H4)
2.b Idealised Me refined as rotating group:
 C5(H5a,H5b,H5c), C3(H3a,H3b,H3c), C10(H10a,H10b,H10c),
C14(H14a,H14b,H14c),
 C18(H18a,H18b,H18c)
```

Crystallographic data for **4.**

Table 1. Crystal data and structure refinement for **4**

Identification code	**4**
Empirical formula	$C_{20}H_{20}N_3F_6PPt$
Formula weight	620.44
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.9042(2)
b/Å	12.0936(3)
c/Å	15.9712(3)
α/°	90
β/°	93.7300(16)
γ/°	90
Volume/Å^3	2101.68(7)
Z	4
ρ_{calc}g/cm^3	1.9607
μ/mm^{-1}	13.782
F(000)	1179.6
Crystal size/mm^3	0.15 x 0.15 x 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.12 to 145.98
Index ranges	$-13 \leq h \leq 12$, $-14 \leq k \leq 12$, $-19 \leq l \leq 18$
Reflections collected	6810
Independent reflections	3990 [R_{int} = 0.0315, R_{sigma} = 0.0354]
Data/restraints/parameters	3990/0/264
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.1235
Final R indexes [all data]	R_1 = 0.0407, wR_2 = 0.1252

Largest diff. peak/hole / e Å^{-3} 2.14/-2.61

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 4. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	7468.49(18)	6364.07(16)	5669.24(11)	7.34(13)
N0aa	7619(4)	7709(4)	6575(3)	11.3(9)
C0aa	8712(5)	8206(5)	6755(3)	11.9(10)
C1aa	7826(5)	9482(5)	7686(3)	15.3(11)
C15	8835(6)	9101(5)	7303(4)	17.0(12)
C19	6692(6)	8973(5)	7498(3)	16.8(11)
C20	6628(5)	8082(5)	6949(3)	12.5(11)
P1	7373.4(12)	12853.5(11)	8134.1(8)	10.6(3)
F5	8541(3)	12035(3)	8176(2)	24.8(8)
F6	6455(3)	11812(3)	8125(3)	26.7(8)
F9	7341(3)	12829(4)	7138(2)	28.3(9)
C2aa	8763(5)	5452(5)	6347(3)	14.0(11)
C8	6204(5)	5547(5)	6335(3)	14.6(11)
C3aa	7332(5)	5088(5)	4834(3)	16.4(11)
N4	8707(4)	7207(4)	4876(3)	11.1(9)
N6	6262(4)	7420(4)	4897(2)	9.9(9)
C5	6828(5)	8082(5)	4357(3)	12.6(11)
C6	9916(5)	7003(5)	4860(3)	14.3(11)
C7	10638(5)	7468(5)	4269(4)	18.2(12)
C9	5026(5)	7552(5)	4959(4)	16.7(11)
C10	8165(6)	7909(4)	4306(3)	12.2(11)
C11	10080(6)	8186(5)	3685(4)	21.5(13)
C12	4936(6)	8987(6)	3956(4)	29.5(15)
C13	6174(6)	8884(6)	3884(4)	23.2(14)
C14	4352(6)	8296(6)	4495(4)	25.8(14)
C4	8832(6)	8405(5)	3704(4)	18.7(12)
F1	8285(4)	13895(3)	8147(3)	26.3(8)
F2	6218(4)	13668(3)	8097(3)	24.7(9)
F3	7420(3)	12873(4)	9136(2)	32.8(10)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 4. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt1	9.98(18)	8.78(19)	3.17(18)	-0.17(6)	-0.31(11)	0.64(6)
N0aa	14(2)	13(2)	7(2)	0.8(18)	-0.7(16)	1.7(17)
C0aa	11(2)	18(3)	7(2)	-2(2)	1.1(18)	-2(2)
C1aa	21(3)	14(3)	11(2)	-4(2)	-4(2)	-7(2)

C15	24(3)	13(3)	13(3)	-5(2)	-5(2)	-1(2)
C19	22(3)	18(3)	10(3)	7(3)	0(2)	0(2)
C20	9(2)	21(3)	7(2)	6(2)	-0.7(18)	-1(2)
P1	11.1(6)	11.0(7)	10.0(6)	0.5(5)	2.8(5)	1.4(5)
F5	15.4(17)	17.0(17)	42(2)	4.5(14)	1.7(15)	2.2(16)
F6	18.8(18)	15.1(18)	46(2)	-3.8(15)	0.9(16)	3.7(17)
F9	30(2)	46(2)	9.4(16)	0.5(18)	3.7(14)	-2.9(16)
C2aa	15(3)	18(3)	9(2)	2(2)	-0.7(19)	-1(2)
C8	20(3)	14(3)	10(2)	-2(2)	2(2)	3(2)
C3aa	21(3)	18(3)	9(2)	-4(2)	-1(2)	-1(2)
N4	14(2)	14(2)	5.9(19)	3.7(18)	2.1(16)	-2.5(17)
N6	14(2)	10(2)	5.1(19)	3.3(17)	-4.0(15)	2.2(17)
C5	14(3)	19(3)	5(2)	6(2)	-1.3(19)	0(2)
C6	18(3)	15(3)	10(2)	-1(2)	2(2)	1(2)
C7	11(3)	20(3)	24(3)	0(2)	5(2)	-5(2)
C9	11(2)	20(3)	19(3)	0(2)	-0.2(19)	7(2)
C10	25(3)	7(3)	5(2)	4(2)	2(2)	-1.8(19)
C11	29(3)	21(3)	16(3)	0(3)	11(2)	3(2)
C12	28(3)	37(4)	24(3)	14(3)	-1(3)	16(3)
C13	25(4)	28(3)	16(3)	3(3)	6(3)	13(3)
C14	15(3)	38(4)	24(3)	5(3)	-6(2)	10(3)
C4	25(3)	14(3)	17(3)	4(3)	0(2)	5(2)
F1	21.0(19)	20.1(17)	38(2)	-8.0(16)	2.1(16)	0.5(18)
F2	17(2)	16(2)	41(2)	5.8(13)	1.1(17)	1.1(14)
F3	34(2)	55(3)	9.9(15)	-3.7(19)	6.8(14)	-0.3(18)

Table 4 Bond Lengths for 4.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pt1	N0aa	2.176(5)	P1	F2	1.597(4)
Pt1	C2aa	2.045(5)	P1	F3	1.598(4)
Pt1	C8	2.050(5)	N4	C6	1.342(7)
Pt1	C3aa	2.039(6)	N4	C10	1.352(7)
Pt1	N4	2.166(4)	N6	C5	1.355(7)
Pt1	N6	2.162(4)	N6	C9	1.367(7)
N0aa	C0aa	1.349(7)	C5	C10	1.480(9)
N0aa	C20	1.347(7)	C5	C13	1.396(9)
C0aa	C15	1.392(8)	C6	C7	1.387(8)
C1aa	C15	1.373(9)	C7	C11	1.385(9)
C1aa	C19	1.397(8)	C9	C14	1.352(9)
C19	C20	1.389(8)	C10	C4	1.380(8)
P1	F5	1.610(4)	C11	C4	1.389(9)
P1	F6	1.609(4)	C12	C13	1.368(10)

P1	F9	1.589(3)	C12	C14	1.385(10)
P1	F1	1.604(4)			

Table 5 Bond Angles for 4.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2aa	Pt1	N0aa	91.81(19)	F2	P1	F5	179.7(2)
C8	Pt1	N0aa	92.26(19)	F2	P1	F6	89.63(19)
C8	Pt1	C2aa	86.0(2)	F2	P1	F9	90.5(2)
C3aa	Pt1	N0aa	179.19(19)	F2	P1	F1	90.2(2)
C3aa	Pt1	C2aa	87.5(2)	F3	P1	F5	89.7(2)
C3aa	Pt1	C8	87.3(2)	F3	P1	F6	90.0(2)
N4	Pt1	N0aa	90.82(16)	F3	P1	F9	179.4(2)
N4	Pt1	C2aa	97.36(19)	F3	P1	F1	89.8(2)
N4	Pt1	C8	175.38(19)	F3	P1	F2	90.1(2)
N4	Pt1	C3aa	89.70(19)	C6	N4	Pt1	125.1(4)
N6	Pt1	N0aa	87.42(16)	C10	N4	Pt1	115.3(4)
N6	Pt1	C2aa	173.87(19)	C10	N4	C6	119.3(5)
N6	Pt1	C8	100.1(2)	C5	N6	Pt1	115.3(3)
N6	Pt1	C3aa	93.31(19)	C9	N6	Pt1	126.4(4)
N6	Pt1	N4	76.57(17)	C9	N6	C5	118.0(5)
C0aa	N0aa	Pt1	120.2(3)	C10	C5	N6	116.3(5)
C20	N0aa	Pt1	121.1(4)	C13	C5	N6	121.1(5)
C20	N0aa	C0aa	118.7(5)	C13	C5	C10	122.6(5)
C15	C0aa	N0aa	121.8(5)	C7	C6	N4	122.7(5)
C19	C1aa	C15	118.7(5)	C11	C7	C6	117.9(5)
C1aa	C15	C0aa	119.6(5)	C14	C9	N6	122.8(5)
C20	C19	C1aa	119.0(5)	C5	C10	N4	116.2(5)
C19	C20	N0aa	122.1(5)	C4	C10	N4	121.0(5)
F6	P1	F5	90.52(19)	C4	C10	C5	122.8(5)
F9	P1	F5	89.8(2)	C4	C11	C7	119.6(5)
F9	P1	F6	90.2(2)	C14	C12	C13	119.5(6)
F1	P1	F5	89.7(2)	C12	C13	C5	119.4(6)
F1	P1	F6	179.7(2)	C12	C14	C9	119.1(6)
F1	P1	F9	90.0(2)	C11	C4	C10	119.6(6)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4.

Atom	*x*	*y*	*z*	U(eq)
H9	4633(5)	7112(5)	5337(4)	20.1(14)
H14	3507(6)	8342(6)	4537(4)	31.0(16)
H13	6576(6)	9343(6)	3524(4)	27.9(16)
H6	10284(5)	6531(5)	5261(3)	17.2(13)

H7	11471(5)	7303(5)	4264(4)	21.8(14)
H11	10538(6)	8520(5)	3284(4)	25.8(15)
H4	8448(6)	8883(5)	3313(4)	22.4(14)
H0aa	9404(5)	7943(5)	6507(3)	14.3(12)
H20	5876(5)	7732(5)	6835(3)	15.0(13)
H19	5989(6)	9227(5)	7738(3)	20.2(14)
H1aa	7897(5)	10067(5)	8064(3)	18.3(13)
H15	9595(6)	9439(5)	7408(4)	20.4(15)
H3aa	8040(20)	5090(20)	4502(18)	24.5(17)
H3ab	7300(40)	4401(5)	5132(3)	24.5(17)
H3ac	6600(20)	5170(20)	4473(18)	24.5(17)
H2aa	8365(5)	4970(30)	6726(19)	21.0(16)
H2ab	9220(30)	5010(30)	5972(4)	21.0(16)
H2ac	9310(20)	5939(5)	6660(20)	21.0(16)
H8a	6360(20)	4766(5)	6320(20)	21.8(17)
H8b	6270(30)	5790(30)	6908(7)	21.8(17)
H8c	5392(6)	5700(30)	6094(17)	21.8(17)
H12	4489(6)	9518(6)	3645(4)	35.4(18)

Experimental

Single crystals of $C_{20}H_{20}N_3F_6PPt$ **4** were grown from MeCN/water. A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

Crystal structure determination of **4**

Crystal Data for $C_{20}H_{20}N_3F_6PPt$ (M =620.44 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 10.9042(2) Å, b = 12.0936(3) Å, c = 15.9712(3) Å, β = 93.7300(16)°, V = 2101.68(7) Å^3, Z = 4, T = 100.00(10) K, μ(Cu Kα) = 13.782 mm^{-1}, *Dcalc* = 1.9607 g/cm^3, 6810 reflections measured (8.12° ≤ 2Θ ≤ 145.98°), 3990 unique (R_{int} = 0.0315, R_{sigma} = 0.0354) which were used in all calculations. The final R_1 was 0.0394 (I>=2u(I)) and wR_2 was 0.1252 (all data).

Refinement model description

Number of restraints - 0, number of constraints - 38.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C9(H9), C14(H14), C13(H13), C6(H6), C7(H7), C11(H11), C4(H4),
C0aa(H0aa),
 C20(H20), C19(H19), C1aa(H1aa), C15(H15), C12(H12)
2.b Idealised Me refined as rotating group:
 C3aa(H3aa,H3ab,H3ac), C2aa(H2aa,H2ab,H2ac), C8(H8a,H8b,H8c)
```

Crystallographic data for **5**

Table 1 Crystal data and structure refinement for **5**.

Identification code	**5**
Empirical formula	$C_{18}H_{23}N_3OF_6PPt$
Formula weight	648.45
Temperature/K	99.98(13)
Crystal system	triclinic
Space group	P-1
a/Å	9.1410(4)
b/Å	9.5731(4)
c/Å	13.2139(6)
α/°	108.296(4)
β/°	97.486(4)
γ/°	95.712(3)
Volume/Å^3	1076.32(9)
Z	2
ρ_{calc}g/cm^3	2.0007
μ/mm^{-1}	13.529
F(000)	617.9
Crystal size/mm^3	0.1742 × 0.1256 × 0.0673
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.16 to 146.02
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-10 \leq l \leq 16$
Reflections collected	6376
Independent reflections	4066 [R_{int} = 0.0205, R_{sigma} = 0.0304]
Data/restraints/parameters	4066/0/283
Goodness-of-fit on F^2	0.673
Final R indexes [I>=2σ (I)]	R_1 = 0.0211, wR_2 = 0.0723
Final R indexes [all data]	R_1 = 0.0227, wR_2 = 0.0755
Largest diff. peak/hole / e Å^{-3}	1.01/-1.48

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 5. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	-35.63(12)	481.42(12)	7476.61(9)	14.37(8)
N5	-924(3)	1898(3)	6612(2)	14.9(6)
N6	714(3)	2406(4)	8926(2)	14.7(6)
N7	-1944(4)	651(3)	8288(3)	15.9(6)
C2aa	-3280(4)	-209(4)	7887(3)	18.8(7)
C3aa	-4342(4)	1235(4)	9346(3)	21.1(7)
C4aa	157(4)	3698(4)	10663(3)	18.0(7)
C0aa	-263(4)	2659(4)	9622(3)	15.9(6)
C16	-2957(4)	2099(4)	9785(3)	18.6(7)
C1aa	-1767(4)	1793(4)	9234(3)	15.2(6)
C20	-4491(4)	47(4)	8401(3)	20.7(7)
C5aa	2087(4)	3180(4)	9235(3)	18.2(7)
C6aa	2580(4)	4229(4)	10250(3)	19.9(7)
C18	-874(5)	-1451(5)	6219(3)	24.8(8)
C19	841(5)	-807(5)	8313(3)	24.1(8)
C10	-52(4)	3115(4)	6629(3)	17.7(7)
C11	-2937(4)	2554(4)	5591(3)	17.1(7)
C12	-2341(4)	1613(4)	6087(3)	15.7(6)
C13	-570(4)	4110(4)	6146(3)	19.9(7)
C14	1832(5)	432(5)	6769(3)	23.0(8)
C15	1608(4)	4472(4)	10988(3)	22.5(7)
C17	-2045(4)	3839(4)	5633(3)	17.5(7)
P1	5849.5(9)	4441.8(9)	12699.8(7)	15.47(17)
F5	7271(3)	4601(3)	12133.2(18)	34.4(6)
F6	4439(3)	4275(3)	13273(2)	35.5(6)
F1	6743(2)	5635(2)	13806.3(17)	24.5(5)
F2	4969(2)	3240(2)	11592.9(17)	24.4(4)
F3	6485(3)	3134(2)	13063.1(18)	28.6(5)
F4	5240(3)	5765(3)	12355(2)	37.5(6)
O1	-5497(3)	1494(3)	5540(2)	23.4(5)
C2	-4540(4)	2110(4)	4981(3)	20.2(7)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 5. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt1	16.40(11)	14.98(11)	13.09(11)	4.48(7)	3.72(7)	5.44(7)
N5	17.6(15)	16.9(15)	12.1(14)	4.9(11)	3.6(11)	6.2(11)
N6	12.6(14)	18.6(15)	13.4(14)	3.7(11)	1.8(11)	5.7(11)
N7	20.1(15)	13.8(14)	14.9(14)	2.4(12)	5.0(12)	5.4(12)
C2aa	20.2(17)	15.1(16)	18.9(16)	-2.4(13)	0.3(13)	5.4(13)

C3aa	20.0(17)	22.2(18)	24.7(18)	2.3(14)	7.4(14)	11.8(15)
C4aa	22.1(17)	19.9(17)	14.0(15)	3.0(13)	1.6(13)	9.2(13)
C0aa	17.8(16)	16.9(16)	16.4(15)	4.3(13)	0.9(12)	10.7(13)
C16	26.8(18)	18.5(16)	11.2(15)	4.9(13)	3.7(13)	5.3(13)
C1aa	15.6(16)	15.7(16)	17.0(15)	3.5(12)	4.5(12)	8.4(13)
C20	20.6(17)	19.1(17)	20.2(17)	-3.3(13)	1.1(14)	6.3(14)
C5aa	15.7(16)	19.4(17)	21.1(17)	2.7(13)	3.3(13)	9.0(14)
C6aa	15.3(16)	26.0(18)	19.7(17)	0.2(13)	-1.3(13)	12.1(14)
C18	32(2)	20.4(19)	20.8(19)	8.4(16)	3.6(16)	4.8(15)
C19	33(2)	25(2)	22(2)	11.6(17)	3.8(16)	15.9(17)
C10	18.3(16)	20.7(17)	12.6(15)	2.8(13)	1.0(12)	4.2(13)
C11	18.0(16)	18.2(16)	14.8(15)	4.5(13)	4.5(13)	4.0(13)
C12	18.3(16)	14.9(15)	14.2(15)	3.4(12)	5.4(12)	4.1(12)
C13	21.6(17)	18.5(17)	18.7(16)	-1.7(13)	2.2(13)	6.7(13)
C14	20.9(19)	32(2)	19.9(18)	10.4(16)	11.7(15)	8.6(16)
C15	23.6(18)	20.1(17)	20.1(17)	-2.3(14)	-2.9(14)	5.6(14)
C17	19.7(17)	16.2(16)	18.5(16)	2.9(13)	5.8(13)	7.1(13)
P1	15.6(4)	13.9(4)	14.2(4)	2.0(3)	1.2(3)	1.5(3)
F5	31.9(12)	35.8(13)	26.0(12)	-10(1)	14.3(10)	-2.1(10)
F6	25.3(12)	39.9(14)	38.4(14)	1.3(10)	17.3(10)	5.1(11)
F1	26.7(11)	21.9(11)	19(1)	4.0(9)	2.8(8)	-1.3(8)
F2	25.0(11)	21.1(11)	20.9(10)	-0.2(8)	-3.7(8)	2.5(8)
F3	35.6(13)	22.1(11)	26.0(11)	9.2(9)	-1.9(9)	6.6(9)
F4	54.4(15)	21.5(11)	31.1(13)	6.9(11)	-9.2(11)	7.5(10)
O1	18.6(12)	20.6(13)	28.9(14)	1.1(10)	7.3(10)	4.6(10)
C2	13.9(16)	25.5(18)	21.5(17)	2.8(13)	1.8(13)	8.8(14)

Table 4 Bond Lengths for 5.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pt1	N5	2.180(3)	C0aa	C1aa	1.471(5)
Pt1	N6	2.174(3)	C16	C1aa	1.391(5)
Pt1	N7	2.157(3)	C5aa	C6aa	1.385(5)
Pt1	C18	2.056(4)	C6aa	C15	1.385(5)
Pt1	C19	2.051(4)	C10	C13	1.389(5)
Pt1	C14	2.048(4)	C11	C12	1.383(5)
N5	C10	1.337(5)	C11	C17	1.389(5)
N5	C12	1.346(5)	C11	C2	1.527(5)
N6	C0aa	1.349(5)	C13	C17	1.388(5)
N6	C5aa	1.335(5)	P1	F5	1.599(2)
N7	C2aa	1.345(5)	P1	F6	1.597(2)
N7	C1aa	1.356(5)	P1	F1	1.601(2)
C2aa	C20	1.375(5)	P1	F2	1.601(2)

C3aa	C16	1.387(5)	P1	F3	1.608(2)
C3aa	C20	1.380(5)	P1	F4	1.600(3)
C4aa	C0aa	1.398(5)	O1	C2	1.413(4)
C4aa	C15	1.396(5)			

Table 5 Bond Angles for 5.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N6	Pt1	N5	90.47(11)	C0aa	C1aa	N7	115.9(3)
N7	Pt1	N5	88.58(12)	C16	C1aa	N7	120.8(3)
N7	Pt1	N6	76.58(11)	C16	C1aa	C0aa	123.3(3)
C18	Pt1	N5	93.58(14)	C3aa	C20	C2aa	119.3(3)
C18	Pt1	N6	173.18(13)	C6aa	C5aa	N6	123.3(3)
C18	Pt1	N7	98.01(15)	C15	C6aa	C5aa	118.4(3)
C19	Pt1	N5	178.54(12)	C13	C10	N5	122.3(3)
C19	Pt1	N6	88.28(15)	C17	C11	C12	119.0(3)
C19	Pt1	N7	91.86(15)	C2	C11	C12	118.6(3)
C19	Pt1	C18	87.73(17)	C2	C11	C17	122.3(3)
C14	Pt1	N5	91.03(15)	C11	C12	N5	122.4(3)
C14	Pt1	N6	100.25(14)	C17	C13	C10	119.0(3)
C14	Pt1	N7	176.80(12)	C6aa	C15	C4aa	118.7(3)
C14	Pt1	C18	85.18(17)	C13	C17	C11	118.6(3)
C14	Pt1	C19	88.45(18)	F6	P1	F5	179.44(16)
C10	N5	Pt1	119.3(2)	F1	P1	F5	89.76(12)
C12	N5	Pt1	122.1(2)	F1	P1	F6	90.03(12)
C12	N5	C10	118.6(3)	F2	P1	F5	89.93(12)
C0aa	N6	Pt1	114.3(2)	F2	P1	F6	90.28(13)
C5aa	N6	Pt1	125.7(2)	F2	P1	F1	179.50(13)
C5aa	N6	C0aa	119.2(3)	F3	P1	F5	89.65(14)
C2aa	N7	Pt1	124.9(2)	F3	P1	F6	89.83(14)
C1aa	N7	Pt1	115.4(2)	F3	P1	F1	89.51(12)
C1aa	N7	C2aa	119.5(3)	F3	P1	F2	90.10(12)
C20	C2aa	N7	121.9(3)	F4	P1	F5	90.05(16)
C20	C3aa	C16	119.2(3)	F4	P1	F6	90.46(16)
C15	C4aa	C0aa	119.6(3)	F4	P1	F1	89.48(12)
C4aa	C0aa	N6	120.7(3)	F4	P1	F2	90.92(12)
C1aa	C0aa	N6	116.9(3)	F4	P1	F3	178.94(13)
C1aa	C0aa	C4aa	122.3(3)	O1	C2	C11	112.1(3)
C1aa	C16	C3aa	119.2(3)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5.

Atom	*x*	*y*	*z*	U(eq)
H10	935(4)	3303(4)	6976(3)	21.2(8)
H12	-2941(4)	752(4)	6056(3)	18.8(8)
H17	-2427(4)	4504(4)	5324(3)	21.0(8)
H13	63(4)	4945(4)	6166(3)	23.9(8)
H5aa	2745(4)	3006(4)	8743(3)	21.8(8)
H6aa	3540(4)	4758(4)	10432(3)	23.8(8)
H15	1916(4)	5138(4)	11686(3)	27.0(9)
H4aa	-526(4)	3873(4)	11135(3)	21.6(8)
H2aa	-3389(4)	-1000(4)	7243(3)	22.5(8)
H16	-2825(4)	2874(4)	10439(3)	22.3(8)
H3aa	-5162(4)	1455(4)	9684(3)	25.3(9)
H20	-5399(4)	-575(4)	8116(3)	24.8(8)
H18a	-1480(30)	-1224(6)	5660(11)	37.2(13)
H18b	-64(5)	-1917(19)	5934(17)	37.2(13)
H18c	-1460(30)	-2113(15)	6476(6)	37.2(13)
H14a	1581(8)	500(30)	6059(10)	34.4(12)
H14b	2578(13)	1255(19)	7202(13)	34.4(12)
H14c	2210(20)	-484(15)	6710(20)	34.4(12)
H19a	1745(19)	-265(13)	8789(18)	36.1(13)
H19b	134(14)	-1060(30)	8728(19)	36.1(13)
H19c	1060(30)	-1702(16)	7812(4)	36.1(13)
H1	-5700(50)	2163(6)	6040(30)	35.1(8)

Experimental

Single crystals of $C_{18}H_{23}N_3OF_6PPt$ [5] were grown from MeCN water. A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 99.98(13) K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

Crystal structure determination of [5]

Crystal Data for $C_{18}H_{23}N_3OF_6PPt$ (M =648.45 g/mol): triclinic, space group P-1 (no. 2), a = 9.1410(4) Å, b = 9.5731(4) Å, c = 13.2139(6) Å, α = 108.296(4)°, β = 97.486(4)°, γ = 95.712(3)°, V = 1076.32(9) Å^3, Z = 2, T = 99.98(13) K, μ(Cu Kα) = 13.529 mm^{-1}, *Dcalc* = 2.0007 g/cm^3, 6376 reflections measured (7.16° ≤ 2Θ ≤ 146.02°), 4066 unique (R_{int} = 0.0205, R_{sigma} = 0.0304) which were used in all calculations. The final R_1 was 0.0211 (I>=2u(I)) and wR_2 was 0.0755 (all data).

Refinement model description

Number of restraints - 0, number of constraints - 38.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C10(H10), C12(H12), C17(H17), C13(H13), C5aa(H5aa), C6aa(H6aa),
C15(H15),
 C4aa(H4aa), C2aa(H2aa), C16(H16), C3aa(H3aa), C20(H20)
2.b Idealised Me refined as rotating group:
 C18(H18a,H18b,H18c), C14(H14a,H14b,H14c), C19(H19a,H19b,H19c)
2.c Idealised tetrahedral OH refined as rotating group:
```

Crystallographic data for 6.

Table 1 Crystal data and structure refinement for 6.

Identification code	6
Empirical formula	$C_{21}H_{26}N_3O_2F_6PPt$
Formula weight	677.47
Temperature/K	289.33(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.94969(19)
b/Å	14.3600(2)
c/Å	15.7460(3)
α/°	90
β/°	96.7748(17)
γ/°	90
Volume/Å^3	2458.57(8)
Z	4
ρ_{calc}g/cm^3	1.8301
μ/mm^{-1}	11.910
F(000)	1296.1
Crystal size/mm^3	0.15 x 0.2 x 0.25
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.36 to 148.4
Index ranges	$-9 \leq h \leq 13$, $-11 \leq k \leq 17$, $-19 \leq l \leq 19$
Reflections collected	8172
Independent reflections	4766 [R_{int} = 0.0252, R_{sigma} = 0.0371]
Data/restraints/parameters	4766/0/301
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.1226

Final R indexes [all data] $R_1 = 0.0421$, $wR_2 = 0.1323$
Largest diff. peak/hole / e Å^{-3} 6.63/-0.85

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for 6. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pt1	3963.26(19)	6664.78(15)	2732.22(13)	10.96(13)
N0aa	1996(5)	6533(3)	2750(3)	13.4(10)
C0aa	5797(6)	6855(5)	2648(4)	20.7(13)
N13	3880(4)	7888(3)	3546(3)	14.6(10)
N1aa	3196(4)	7517(3)	1669(3)	13.1(9)
C2aa	4547(5)	5836(4)	3751(4)	16.7(11)
C10	1377(6)	8256(4)	1006(4)	18.2(13)
C11	1966(5)	7623(4)	1596(3)	12.1(10)
C22	4101(6)	9539(4)	3778(4)	18.1(12)
C1aa	1284(5)	7059(4)	2172(4)	16.2(11)
C15	3845(5)	7974(4)	1139(4)	16.3(11)
C17	2065(6)	8733(5)	466(4)	20.8(13)
C19	3349(6)	8580(5)	540(4)	21.6(13)
C20	1456(6)	5997(4)	3283(4)	18.7(12)
C24	4295(5)	8733(4)	3320(4)	15.5(12)
C25	3069(6)	8614(5)	4735(4)	21.3(12)
C27	26(6)	7043(4)	2118(4)	18.9(12)
C30	3298(6)	7841(4)	4247(4)	18.7(12)
C33	193(6)	5943(5)	3278(4)	21.1(13)
C3aa	3464(6)	9481(4)	4490(4)	17.0(12)
C14	4037(6)	5509(4)	1981(4)	19.7(12)
O9	3524(5)	11114(3)	4727(3)	29.1(11)
O10	2587(5)	10193(4)	5596(3)	35.0(12)
C12	3210(6)	10360(5)	4941(4)	22.8(13)
C13	2173(9)	11013(7)	6061(6)	50(3)
C9	-536(6)	6472(5)	2687(4)	21.7(13)
P1	7289.2(14)	9046.6(10)	1153.2(9)	14.0(3)
F0aa	6331(3)	9015(3)	1845(2)	22.3(8)
F8	6179(4)	9170(3)	406(2)	32.0(9)
F1aa	7383(3)	10157(2)	1253(2)	21.4(7)
F3	8411(3)	8923(3)	1898(2)	28.5(9)
F4	7189(4)	7937(3)	1044(3)	32.9(10)
F1	8244(3)	9078(3)	453(2)	24.4(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 6. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka*b*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt1	7.85(17)	12.72(17)	12.31(18)	0.39(7)	1.16(11)	2.86(7)
N0aa	9(2)	14(2)	17(3)	-1.0(18)	-0.0(19)	3.7(19)
C0aa	9(3)	27(3)	26(3)	-3(2)	1(2)	6(3)
N13	14(2)	13(2)	16(2)	0.1(19)	-1.2(18)	2.4(19)
N1aa	14(2)	13(2)	12(2)	1.8(18)	-0.6(18)	1.8(18)
C2aa	17(3)	20(3)	13(3)	6(2)	1(2)	4(2)
C10	15(3)	18(3)	20(3)	0(2)	-3(2)	3(2)
C11	12(3)	10(2)	14(3)	-1(2)	1(2)	-1(2)
C22	21(3)	13(3)	21(3)	-1(2)	0(2)	6(2)
C1aa	14(3)	15(3)	18(3)	3(2)	1(2)	-3(2)
C15	15(3)	19(3)	14(3)	-4(2)	3(2)	0(2)
C17	18(3)	20(3)	23(3)	1(2)	-2(2)	6(3)
C19	21(3)	27(3)	15(3)	-4(3)	-5(2)	5(3)
C20	15(3)	21(3)	21(3)	0(2)	5(2)	4(2)
C24	18(3)	13(3)	16(3)	-1(2)	5(2)	3(2)
C25	22(3)	24(3)	18(3)	0(3)	3(2)	2(3)
C27	14(3)	17(3)	26(3)	4(2)	0(2)	5(2)
C30	20(3)	16(3)	20(3)	-3(2)	3(2)	6(2)
C33	16(3)	25(3)	22(3)	-5(2)	7(2)	-2(3)
C3aa	20(3)	18(3)	12(3)	5(2)	-3(2)	0(2)
C14	19(3)	17(3)	22(3)	5(2)	2(2)	-2(2)
O9	42(3)	20(2)	24(2)	1(2)	-1(2)	-2.3(19)
O10	49(3)	31(3)	26(3)	0(2)	14(2)	-8(2)
C12	27(3)	24(3)	16(3)	6(3)	-6(2)	-3(2)
C13	67(7)	49(6)	38(5)	-15(5)	24(5)	-31(4)
C9	13(3)	24(3)	29(4)	2(3)	6(3)	-1(3)
P1	13.8(7)	14.4(7)	14.7(7)	-0.7(5)	5.1(5)	-0.6(5)
F0aa	24.5(18)	24.4(19)	20.7(17)	-2.2(15)	13.3(15)	-1.7(14)
F8	25(2)	48(3)	21.0(19)	-2.3(19)	-3.1(16)	1.2(18)
F1aa	18.3(17)	14.2(16)	33(2)	-0.4(14)	9.5(15)	-2.6(14)
F3	24(2)	39(2)	21.1(19)	11.9(17)	-2.4(15)	2.7(16)
F4	43(2)	15.2(18)	45(2)	-6.3(18)	27(2)	-8.4(17)
F1	26.7(19)	26.0(19)	24.0(19)	-4.9(16)	16.9(16)	-5.0(15)

Table 4 Bond Lengths for 6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	N0aa	2.166(5)	C15	C19	1.350(9)
Pt1	C0aa	2.046(6)	C17	C19	1.414(9)
Pt1	N13	2.182(5)	C20	C33	1.385(8)
Pt1	N1aa	2.162(5)	C25	C30	1.389(9)

Pt1	C2aa	2.038(5)	C25	C3aa	1.388(9)
Pt1	C14	2.046(6)	C27	C9	1.409(9)
N0aa	C1aa	1.356(8)	C33	C9	1.380(9)
N0aa	C20	1.327(8)	C3aa	C12	1.490(8)
N13	C24	1.358(8)	O9	C12	1.197(8)
N13	C30	1.340(8)	O10	C12	1.325(8)
N1aa	C11	1.347(7)	O10	C13	1.485(9)
N1aa	C15	1.330(7)	P1	F0aa	1.600(4)
C10	C11	1.401(8)	P1	F8	1.599(4)
C10	C17	1.383(9)	P1	F1aa	1.605(4)
C11	C1aa	1.482(8)	P1	F3	1.605(4)
C22	C24	1.392(8)	P1	F4	1.605(4)
C22	C3aa	1.392(9)	P1	F1	1.607(4)
C1aa	C27	1.371(8)			

Table 5 Bond Angles for 6.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C0aa	Pt1	N0aa	176.0(2)	C19	C15	N1aa	123.8(6)
N13	Pt1	N0aa	87.26(18)	C19	C17	C10	118.7(6)
N13	Pt1	C0aa	92.3(2)	C17	C19	C15	118.1(6)
N1aa	Pt1	N0aa	76.33(18)	C33	C20	N0aa	123.2(6)
N1aa	Pt1	C0aa	99.7(2)	C22	C24	N13	122.1(5)
N1aa	Pt1	N13	87.73(17)	C3aa	C25	C30	118.7(6)
C2aa	Pt1	N0aa	99.1(2)	C9	C27	C1aa	118.8(6)
C2aa	Pt1	C0aa	84.8(2)	C25	C30	N13	123.4(6)
C2aa	Pt1	N13	92.2(2)	C9	C33	C20	118.1(6)
C2aa	Pt1	N1aa	175.4(2)	C25	C3aa	C22	118.6(6)
C14	Pt1	N0aa	92.5(2)	C12	C3aa	C22	118.2(6)
C14	Pt1	C0aa	88.0(3)	C12	C3aa	C25	123.1(6)
C14	Pt1	N13	179.3(2)	C13	O10	C12	117.1(6)
C14	Pt1	N1aa	92.8(2)	O9	C12	C3aa	123.8(6)
C14	Pt1	C2aa	87.2(2)	O10	C12	C3aa	111.1(6)
C1aa	N0aa	Pt1	115.8(4)	O10	C12	O9	125.1(6)
C20	N0aa	Pt1	125.2(4)	C33	C9	C27	119.2(6)
C20	N0aa	C1aa	118.9(5)	F8	P1	F0aa	90.1(2)
C24	N13	Pt1	121.8(4)	F1aa	P1	F0aa	90.05(19)
C30	N13	Pt1	120.1(4)	F1aa	P1	F8	89.8(2)
C30	N13	C24	117.8(5)	F3	P1	F0aa	90.3(2)
C11	N1aa	Pt1	115.0(4)	F3	P1	F8	179.6(2)
C15	N1aa	Pt1	125.3(4)	F3	P1	F1aa	90.2(2)
C15	N1aa	C11	119.5(5)	F4	P1	F0aa	90.2(2)
C17	C10	C11	119.1(6)	F4	P1	F8	89.7(3)

C10	C11	N1aa	120.5(5)	F4	P1	F1aa	179.4(2)
C1aa	C11	N1aa	117.2(5)	F4	P1	F3	90.3(2)
C1aa	C11	C10	122.3(5)	F1	P1	F0aa	179.6(2)
C3aa	C22	C24	119.3(5)	F1	P1	F8	89.5(2)
C11	C1aa	N0aa	115.1(5)	F1	P1	F1aa	90.0(2)
C27	C1aa	N0aa	121.8(6)	F1	P1	F3	90.0(2)
C27	C1aa	C11	123.1(5)	F1	P1	F4	89.8(2)

Table 6 Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 6.

Atom	***x***	***y***	***z***	**U(eq)**
H20	1951(6)	5639(4)	3678(4)	22.4(15)
H33	-154(6)	5561(5)	3662(4)	25.3(15)
H9	-1388(6)	6451(5)	2665(4)	26.0(16)
H27	-448(6)	7403(4)	1713(4)	22.7(14)
H24	4722(5)	8775(4)	2845(4)	18.5(14)
H30	3034(6)	7262(4)	4416(4)	22.5(14)
H22	4394(6)	10109(4)	3609(4)	21.8(14)
H15	4688(5)	7869(4)	1185(4)	19.5(14)
H19	3839(6)	8888(5)	186(4)	25.9(15)
H17	1691(6)	9147(5)	62(4)	25.0(15)
H10	533(6)	8353(4)	978(4)	21.8(15)
H0aa	5954(9)	6780(30)	2066(7)	31.0(19)
H0ab	6033(11)	7472(12)	2840(30)	31.0(19)
H0ac	6265(6)	6410(20)	3000(20)	31.0(19)
H14a	3262(16)	5190(19)	1940(30)	29.6(19)
H14b	4210(40)	5693(5)	1420(10)	29.6(19)
H14c	4680(30)	5101(16)	2231(16)	29.6(19)
H2aa	4810(40)	6218(4)	4239(8)	25.0(17)
H2ab	3884(13)	5440(20)	3877(18)	25.0(17)
H2ac	5220(30)	5460(20)	3616(11)	25.0(17)
H13a	1970(70)	11510(20)	5664(10)	75(4)
H13b	1460(40)	10848(17)	6330(40)	75(4)
H13c	2820(30)	11210(30)	6490(30)	75(4)

Experimental

Single crystals of $C_{21}H_{26}N_3O_2F_6PPt$ [6] were grown from MeCN/water. A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 289.33(10) K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

Crystal structure determination of [6]

Crystal Data for $C_{21}H_{26}N_3O_2F_6PPt$ (M =677.47 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.94969(19) Å, b = 14.3600(2) Å, c = 15.7460(3) Å, β = 96.7748(17)°, V = 2458.57(8) Å^3, Z = 4, T = 289.33(10) K, μ(Cu Kα) = 11.910 mm^{-1}, *Dcalc* = 1.8301 g/cm^3, 8172 reflections measured (8.36° ≤ 2Θ ≤ 148.4°), 4766 unique (R_{int} = 0.0252, R_{sigma} = 0.0371) which were used in all calculations. The final R_1 was 0.0366 (I>=2u(I)) and wR_2 was 0.1323 (all data).

Refinement model description

Number of restraints - 0, number of constraints - 38.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C20(H20), C33(H33), C9(H9), C27(H27), C24(H24), C30(H30), C22(H22),
C15(H15),
 C19(H19), C17(H17), C10(H10)
2.b Idealised Me refined as rotating group:
 C0aa(H0aa,H0ab,H0ac), C14(H14a,H14b,H14c), C2aa(H2aa,H2ab,H2ac),
C13(H13a,
 H13b,H13c)
 O1(H1)
```

Crystal data for **9.**

Table 1 Crystal data and structure refinement for 9.

Identification code	9
Empirical formula	$C_{20}H_{27}N_2O_2PtS$
Formula weight	563.58
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.3479(5)
b/Å	9.0481(3)
c/Å	16.1964(11)
α/°	90
β/°	109.574(8)
γ/°	90
Volume/Å^3	1981.12(19)
Z	4

ρ_{calc}g/cm^3	1.8894
μ/mm^{-1}	7.205
F(000)	1090.6
Crystal size/mm^3	0.2 × 0.2× 0.2
Radiation	Mo Kα (λ = 0.71075)
2Θ range for data collection/°	6.02 to 54.98
Index ranges	-18 ≤ h ≤ 18, -11 ≤ k ≤ 11, -21 ≤ l ≤ 18
Reflections collected	15341
Independent reflections	4503 [R_{int} = 0.0245, R_{sigma} = 0.0243]
Data/restraints/parameters	4503/0/247
Goodness-of-fit on F^2	0.648
Final R indexes [I>=2σ (I)]	R_1 = 0.0184, wR_2 = 0.0699
Final R indexes [all data]	R_1 = 0.0205, wR_2 = 0.0736
Largest diff. peak/hole / e Å^{-3}	0.76/-0.97

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 9. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pt1	8036.15(7)	974.57(11)	6802.40(6)	10.15(7)
S1	8196.7(5)	3616.7(9)	7183.5(4)	12.98(14)
N4	7028.9(16)	1343(3)	5510.9(15)	10.8(4)
N5	9003.4(18)	1299(3)	6064.0(16)	11.8(5)
C13	6971(2)	669(4)	7376(2)	16.1(6)
C16	9122(2)	531(4)	7966.3(18)	17.1(6)
C6	9995(2)	1373(3)	6390(2)	14.9(5)
C7	10570(2)	1685(3)	5881.2(19)	18.0(6)
C10	8545.0(19)	1543(3)	5197.0(17)	12.2(5)
C14	9081(2)	1844(3)	4648.5(19)	15.9(6)
C1	10105(2)	1930(4)	4990(2)	18.7(6)
C2	5435(2)	1575(4)	4418.7(19)	17.0(6)
C9	6039.6(19)	1391(3)	5277.3(18)	13.0(5)
C12	5861(2)	1719(3)	3775.0(19)	18.8(6)
C3	7461.8(19)	1500(3)	4891.6(16)	11.3(5)
C4	6886(2)	1675(3)	4006.7(18)	16.2(6)
C5	7635(2)	4561(3)	6179.8(17)	12.2(5)
C8	8207.8(19)	5031(3)	5676.6(17)	12.3(5)
C11	6622.6(19)	4864(3)	5879.3(17)	12.9(5)
C15	6190(2)	5635(3)	5101.4(19)	12.6(5)
C17	6769(2)	6121(3)	4614(2)	11.9(6)
C18	7783(2)	5796(3)	4898(2)	14.1(6)
O1	6907.4(14)	7707(2)	3514.5(12)	16.1(4)

C19	6269(2)	6968(3)	3799.2(19)	14.8(6)
C1a	7997(2)	-1281(4)	6579(2)	17.1(6)
O2	5386.3(16)	6994(3)	3431.3(14)	23.7(5)
C1b	6488(2)	8522(4)	2704.1(18)	17.8(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 9. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Pt1	11.43(9)	10.54(9)	8.56(9)	-0.15(3)	3.45(6)	0.14(3)
S1	15.8(3)	12.5(3)	9.0(3)	-0.1(3)	1.9(2)	-0.8(3)
N4	9.4(10)	10.6(10)	10.3(10)	-1.8(9)	0.6(8)	-1.4(9)
N5	15.8(11)	12.1(10)	9.6(11)	-0.2(10)	6.8(9)	-0.8(10)
C13	17.3(14)	19.7(14)	15.6(14)	-3.3(12)	11.3(11)	1.9(12)
C16	17.4(13)	21.2(15)	11.0(13)	3.6(12)	2.4(10)	3.6(12)
C6	10.4(12)	14.8(13)	17.2(13)	1.9(11)	1.7(10)	0.6(12)
C7	12.4(12)	19.0(15)	22.7(15)	-1.3(11)	6.2(11)	0.1(12)
C10	16.5(12)	9.2(12)	11.5(12)	-1.8(10)	5.5(10)	-2.0(11)
C14	18.5(13)	17.5(14)	12.5(13)	-0.2(11)	6.2(10)	0.2(11)
C1	15.6(13)	24.6(16)	19.2(13)	-2.0(11)	10.3(11)	0.7(12)
C2	11.6(12)	19.9(15)	15.9(13)	-1.3(11)	-0.2(10)	-3.4(12)
C9	11.3(12)	13.0(13)	14.4(13)	-2.0(11)	3.7(10)	-3.7(11)
C12	17.4(13)	19.1(14)	16.4(13)	0.2(12)	0.9(10)	1.8(12)
C3	17.4(13)	8.0(12)	9.2(11)	0.6(11)	5.2(10)	-0.9(10)
C4	18.2(13)	16.8(14)	11.6(12)	0.1(11)	2.1(10)	0.8(11)
C5	15.3(12)	5.2(12)	14.7(12)	-1.6(10)	3.1(10)	-0.8(11)
C8	12.5(11)	12.3(13)	12.6(11)	0.4(10)	4.9(9)	-0.7(10)
C11	14.6(12)	13.2(13)	12.4(12)	-0.2(10)	6.5(9)	1.1(10)
C15	10.6(12)	12.0(12)	15.5(13)	-0.6(11)	4.8(10)	-4.0(12)
C17	11.5(13)	11.1(13)	12.8(14)	-0.1(9)	3.7(11)	-1.4(10)
C18	13.9(13)	13.8(13)	15.5(14)	-0.4(10)	6.2(11)	-0.6(11)
O1	17.6(9)	17(1)	12.7(9)	-2.6(8)	4.0(7)	5.1(8)
C19	16.0(13)	14.7(14)	13.7(13)	-0.1(11)	4.9(10)	1.5(11)
C1a	23.5(16)	8.9(13)	20.2(14)	-1.1(11)	9.2(11)	-1.9(13)
O2	13.4(10)	34.9(14)	20.2(10)	-1.6(9)	2.3(8)	9.8(10)
C1b	18.9(13)	20.8(15)	13.4(13)	-2.6(12)	5.2(11)	6.7(12)

Table 4 Bond Lengths for 9.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pt1	S1	2.4604(8)	C14	C1	1.388(4)
Pt1	N4	2.133(2)	C2	C9	1.380(4)
Pt1	N5	2.134(2)	C2	C12	1.380(4)

Pt1	C13	2.055(3)	C12	C4	1.391(4)
Pt1	C16	2.043(3)	C3	C4	1.403(3)
Pt1	C1a	2.070(3)	C5	C8	1.403(4)
S1	C5	1.773(3)	C5	C11	1.396(4)
N4	C9	1.342(3)	C8	C18	1.388(4)
N4	C3	1.353(4)	C11	C15	1.391(4)
N5	C6	1.343(4)	C15	C17	1.394(4)
N5	C10	1.354(3)	C17	C18	1.402(4)
C6	C7	1.377(4)	C17	C19	1.487(4)
C7	C1	1.390(4)	O1	C19	1.334(3)
C10	C14	1.382(4)	O1	C1b	1.449(3)
C10	C3	1.465(4)	C19	O2	1.206(4)

Table 5 Bond Angles for 9.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N4	Pt1	S1	94.00(7)	C3	C10	N5	115.9(2)
N5	Pt1	S1	89.02(7)	C3	C10	C14	122.9(2)
N5	Pt1	N4	77.47(9)	C1	C14	C10	119.8(3)
C13	Pt1	S1	92.23(9)	C14	C1	C7	118.8(3)
C13	Pt1	N4	95.87(11)	C12	C2	C9	119.0(3)
C13	Pt1	N5	173.29(10)	C2	C9	N4	122.4(3)
C16	Pt1	S1	88.91(10)	C4	C12	C2	119.3(3)
C16	Pt1	N4	172.86(10)	C10	C3	N4	116.8(2)
C16	Pt1	N5	96.09(11)	C4	C3	N4	120.7(2)
C16	Pt1	C13	90.52(12)	C4	C3	C10	122.5(2)
C1a	Pt1	S1	175.20(10)	C3	C4	C12	119.1(3)
C1a	Pt1	N4	90.74(12)	C8	C5	S1	120.3(2)
C1a	Pt1	N5	91.30(11)	C11	C5	S1	121.0(2)
C1a	Pt1	C13	88.01(13)	C11	C5	C8	118.8(2)
C1a	Pt1	C16	86.30(13)	C18	C8	C5	121.0(3)
C5	S1	Pt1	105.22(9)	C15	C11	C5	120.7(2)
C9	N4	Pt1	125.93(19)	C17	C15	C11	120.1(3)
C3	N4	Pt1	114.52(17)	C18	C17	C15	119.8(3)
C3	N4	C9	119.5(2)	C19	C17	C15	117.6(3)
C6	N5	Pt1	126.0(2)	C19	C17	C18	122.5(3)
C10	N5	Pt1	114.98(18)	C17	C18	C8	119.6(3)
C10	N5	C6	118.8(2)	C1b	O1	C19	116.3(2)
C7	C6	N5	122.9(3)	O1	C19	C17	112.5(2)
C1	C7	C6	118.6(3)	O2	C19	C17	124.2(3)
C14	C10	N5	121.1(2)	O2	C19	O1	123.2(3)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 9.

Atom	*x*	*y*	*z*	U(eq)
H11	6233.1(19)	4547(3)	6202.5(17)	15.5(6)
H15	5514(2)	5826(3)	4905.9(19)	15.1(6)
H18	8168(2)	6092(3)	4567(2)	16.9(7)
H8	8881.9(19)	4826(3)	5867.6(17)	14.8(6)
H9	5750.3(19)	1297(3)	5709.7(18)	15.7(6)
H2	4752(2)	1601(4)	4276.2(19)	20.4(7)
H12	5467(2)	1844(3)	3192.5(19)	22.6(7)
H4	7186(2)	1761(3)	3580.8(18)	19.5(7)
H6	10307(2)	1206(3)	6986(2)	17.8(6)
H14	8756(2)	1988(3)	4052.5(19)	19.1(7)
H1	10473(2)	2147(4)	4629(2)	22.4(7)
H7	11256(2)	1731(3)	6128.3(19)	21.5(7)
H1ba	6321(15)	7848(5)	2218(2)	26.6(9)
H1bb	5902(9)	9030(20)	2710(6)	26.6(9)
H1bc	6962(6)	9228(17)	2647(7)	26.6(9)
H13a	6562(10)	-157(15)	7106(9)	24.1(9)
H13b	7283(2)	480(20)	7990(3)	24.1(9)
H13c	6571(10)	1542(9)	7299(12)	24.1(9)
H16a	9497(10)	1413(7)	8182(7)	25.7(8)
H16b	8827(2)	190(20)	8384(4)	25.7(8)
H16c	9552(9)	-221(17)	7880(3)	25.7(8)
H1aa	8566(9)	-1566(5)	6432(14)	25.6(9)
H1ab	7999(16)	-1795(4)	7098(5)	25.6(9)
H1ac	7407(8)	-1526(5)	6104(10)	25.6(9)

Experimental

Single crystals of $C_{20}H_{27}N_2O_2PtS$ [9] were grown from toluene. A suitable crystal was selected and mounted on a diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2013). in preparation.
3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2013). in preparation.

Crystal structure determination of [9]

Crystal Data for $C_{20}H_{27}N_2O_2PtS$ (*M* =563.58 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 14.3479(5) Å, b = 9.0481(3) Å, c = 16.1964(11) Å, β = 109.574(8)°, V = 1981.12(19) Å^3, Z = 4, T = 100 K, μ(Mo Kα) = 7.205 mm^{-1}, *Dcalc* = 1.8894 g/cm^3, 15341 reflections measured (6.02° ≤ 2Θ ≤ 54.98°), 4503 unique (R_{int} = 0.0245, R_{sigma} = 0.0243) which were used in all calculations. The final R_1 was 0.0184 (I>=2u(I)) and wR_2 was 0.0736 (all data).

Refinement model description

Number of restraints - 0, number of constraints - 40.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C11(H11), C15(H15), C18(H18), C8(H8), C9(H9), C2(H2), C12(H12),
C4(H4),
 C6(H6), C14(H14), C1(H1), C7(H7)
2.b Idealised Me refined as rotating group:
 C1b(H1ba,H1bb,H1bc), C13(H13a,H13b,H13c), C16(H16a,H16b,H16c),
C1a(H1aa,H1ab,
```

Crystal data for **10**

Table 1 Crystal data and structure refinement for 10.

Identification code	10
Empirical formula	$C_{25}H_{27}N_2O_6PtS$
Formula weight	678.65
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	7.2201(5)
b/Å	13.2276(9)
c/Å	14.0336(10)
α/°	70.675(5)
β/°	80.551(6)
γ/°	84.130(6)
Volume/Å^3	1245.94(16)
Z	2
ρ_{calc}g/cm^3	1.8088
μ/mm^{-1}	5.756
F(000)	663.4
Crystal size/mm^3	0.2 x 0.2 x 0.2
Radiation	Mo Kα (λ = 0.71075)
2Θ range for data collection/°	5.18 to 55.02
Index ranges	$-9 \le h \le 9$, $-17 \le k \le 14$, $-18 \le l \le 18$
Reflections collected	21239
Independent reflections	5677 [R_{int} = 0.2641, R_{sigma} = 0.1575]
Data/restraints/parameters	5677/0/321
Goodness-of-fit on F^2	1.121
Final R indexes [I>=2σ (I)]	R_1 = 0.0804, wR_2 = 0.1866

Final R indexes [all data] $R_1 = 0.0928$, $wR_2 = 0.2041$
Largest diff. peak/hole / e $Å^{-3}$ 7.68/-4.66

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 10. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pt1	3401.8(4)	3839.0(3)	7504.4(2)	24.32(17)
S2	6547(4)	3435(2)	6657.0(19)	29.0(5)
N6	2768(11)	2185(8)	8220(6)	23.6(17)
N9	2192(11)	3460(8)	6352(6)	25.6(19)
C8	1583(13)	665(8)	7993(7)	24.3(19)
C9	1707(12)	2460(8)	6608(6)	21.3(18)
C10	1649(13)	-1171(8)	9368(7)	25.0(19)
C11	2048(14)	4140(8)	5413(7)	27(2)
C15	1973(12)	1725(8)	7651(7)	22.8(18)
C19	998(12)	2073(8)	5936(7)	22.0(19)
C20	1969(14)	3(9)	8964(7)	28(2)
C1	1419(13)	3818(9)	4683(7)	27(2)
C2	873(13)	2772(8)	4950(7)	25.1(19)
C3	5863(13)	1802(9)	5959(7)	29(2)
C14	2761(12)	480(8)	9555(7)	22.4(18)
C16	3133(13)	1561(9)	9148(7)	28(2)
O2	169(11)	2961(6)	3285(5)	32.0(16)
O3	928(11)	-1503(6)	8715(5)	29.1(16)
O4	1974(13)	-1726(7)	10203(6)	40.5(19)
O5	-307(9)	1392(6)	4541(5)	26.5(14)
O6	5701(10)	-1544(7)	6329(5)	33.2(17)
O7	5971(11)	-1891(6)	7987(5)	35.0(17)
C4	5721(13)	734(9)	6044(7)	26(2)
C5	201(13)	2411(8)	4161(7)	23.3(18)
C6	5921(13)	-1228(8)	7028(8)	27(2)
C7	6176(13)	-92(8)	6928(7)	25(2)
C13	4504(17)	4043(11)	8691(8)	38(3)
C12	6433(13)	2081(8)	6737(7)	23.0(18)
C17	6797(12)	182(8)	7692(7)	24.1(19)
C18	512(18)	-2609(10)	9063(8)	39(3)
C1a	5705(17)	-2996(9)	8144(8)	36(2)
C1b	3898(16)	5414(10)	6758(9)	36(3)
C1c	-1089(14)	1019(9)	3843(8)	33(2)
C1d	6936(13)	1246(8)	7604(7)	24.6(19)
C1e	761(16)	4296(10)	8103(10)	39(3)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 10. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka*b*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt1	33.1(3)	28.2(3)	13.8(2)	-5.62(16)	-4.49(15)	-7.84(17)
S2	33.1(13)	33.2(14)	20.9(12)	-6.6(10)	-1.4(9)	-8.7(10)
N6	23(4)	40(5)	13(4)	-7(3)	-2(3)	-12(3)
N9	24(4)	40(5)	12(4)	-8(4)	-2(3)	-6(4)
C8	29(5)	31(5)	14(4)	-1(4)	-9(3)	-5(4)
C9	27(4)	25(5)	10(4)	-8(3)	1(3)	-2(3)
C10	34(5)	27(5)	15(4)	-5(4)	-2(3)	-7(4)
C11	34(5)	27(5)	15(4)	-9(4)	-2(4)	1(4)
C15	24(4)	31(5)	12(4)	4(4)	-8(3)	-4(4)
C19	25(4)	31(5)	8(4)	-8(4)	2(3)	-4(4)
C20	32(5)	46(6)	8(4)	-8(4)	-3(3)	-11(4)
C1	25(5)	40(6)	12(4)	-3(4)	-3(3)	-2(4)
C2	30(5)	35(5)	9(4)	-2(4)	1(3)	-7(4)
C3	32(5)	43(6)	17(5)	-2(4)	-8(4)	-13(4)
C14	28(5)	26(5)	14(4)	-10(4)	-5(3)	-4(4)
C16	30(5)	46(6)	16(4)	-2(4)	-2(3)	-21(4)
O2	47(4)	37(4)	13(3)	1(3)	-16(3)	-4(3)
O3	48(4)	30(4)	11(3)	-7(3)	-13(3)	-3(3)
O4	68(5)	37(5)	19(4)	-5(4)	-20(4)	-4(3)
O5	35(4)	32(4)	14(3)	-1(3)	-11(3)	-5(3)
O6	41(4)	47(5)	22(4)	-7(3)	-9(3)	-22(3)
O7	52(4)	40(5)	17(3)	-9(3)	-3(3)	-14(3)
C4	26(5)	42(6)	10(4)	0(4)	-4(3)	-6(4)
C5	25(4)	25(5)	16(4)	3(3)	-12(3)	0(4)
C6	33(5)	32(5)	23(5)	-4(4)	-7(4)	-15(4)
C7	33(5)	35(6)	12(4)	-5(4)	-2(3)	-13(4)
C13	49(6)	58(8)	19(5)	-21(6)	-1(4)	-25(5)
C12	26(4)	28(5)	16(4)	0(4)	-6(3)	-8(4)
C17	24(4)	33(5)	18(4)	1(4)	-5(3)	-12(4)
C18	61(7)	38(7)	22(5)	-12(5)	-9(5)	-10(5)
C1a	56(7)	29(6)	25(5)	-9(5)	-11(5)	-7(4)
C1b	41(6)	44(7)	25(6)	-7(5)	-7(4)	-10(5)
C1c	31(5)	46(7)	26(5)	-9(4)	-7(4)	-15(5)
C1d	33(5)	34(6)	10(4)	-7(4)	-3(3)	-10(4)
C1e	38(6)	32(6)	52(8)	2(5)	-11(5)	-17(6)

Table 4 Bond Lengths for 10.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

Pt1	S2	2.478(3)	C19	C2	1.398(13)
Pt1	N6	2.145(9)	C20	C14	1.411(12)
Pt1	N9	2.173(8)	C1	C2	1.389(15)
Pt1	C13	2.063(10)	C2	C5	1.504(12)
Pt1	C1b	2.037(13)	C3	C4	1.391(15)
Pt1	C1e	2.069(12)	C3	C12	1.394(12)
S2	C12	1.766(10)	C14	C16	1.389(14)
N6	C15	1.371(11)	O2	C5	1.207(11)
N6	C16	1.343(13)	O3	C18	1.427(13)
N9	C9	1.319(13)	O5	C5	1.341(12)
N9	C11	1.341(13)	O5	C1c	1.443(10)
C8	C15	1.366(14)	O6	C6	1.224(11)
C8	C20	1.409(13)	O7	C6	1.346(13)
C9	C15	1.495(12)	O7	C1a	1.433(13)
C9	C19	1.395(12)	C4	C7	1.416(14)
C10	C20	1.494(15)	C6	C7	1.490(14)
C10	O3	1.333(11)	C7	C17	1.389(12)
C10	O4	1.205(12)	C12	C1d	1.417(14)
C11	C1	1.385(13)	C17	C1d	1.385(13)

Table 5 Bond Angles for 10.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N6	Pt1	S2	94.3(2)	C9	C15	N6	114.3(8)
N9	Pt1	S2	88.0(2)	C9	C15	C8	123.4(8)
N9	Pt1	N6	76.7(3)	C2	C19	C9	117.8(9)
C13	Pt1	S2	92.6(4)	C10	C20	C8	123.3(8)
C13	Pt1	N6	97.6(4)	C14	C20	C8	117.4(10)
C13	Pt1	N9	174.2(4)	C14	C20	C10	119.3(9)
C1b	Pt1	S2	86.4(4)	C2	C1	C11	118.6(9)
C1b	Pt1	N6	176.4(3)	C1	C2	C19	119.4(9)
C1b	Pt1	N9	99.8(4)	C5	C2	C19	121.5(9)
C1b	Pt1	C13	85.9(5)	C5	C2	C1	119.0(8)
C1e	Pt1	S2	175.0(4)	C12	C3	C4	121.1(10)
C1e	Pt1	N6	89.9(4)	C16	C14	C20	118.6(9)
C1e	Pt1	N9	90.4(4)	C14	C16	N6	123.6(8)
C1e	Pt1	C13	89.5(5)	C18	O3	C10	115.5(8)
C1e	Pt1	C1b	89.2(5)	C1c	O5	C5	114.6(7)
C12	S2	Pt1	102.8(3)	C1a	O7	C6	115.4(7)
C15	N6	Pt1	116.0(6)	C7	C4	C3	120.0(8)
C16	N6	Pt1	126.2(6)	O2	C5	C2	124.2(9)
C16	N6	C15	117.7(9)	O5	C5	C2	111.8(8)
C9	N9	Pt1	115.1(7)	O5	C5	O2	123.9(9)

C11	N9	Pt1	124.5(7)	O7	C6	O6	122.7(10)
C11	N9	C9	120.3(8)	C7	C6	O6	125.1(10)
C20	C8	C15	120.5(8)	C7	C6	O7	112.3(8)
C15	C9	N9	117.9(8)	C6	C7	C4	119.1(8)
C19	C9	N9	122.2(9)	C17	C7	C4	119.0(9)
C19	C9	C15	119.8(8)	C17	C7	C6	121.8(9)
O3	C10	C20	112.1(8)	C3	C12	S2	121.6(8)
O4	C10	C20	122.6(9)	C1d	C12	S2	120.1(7)
O4	C10	O3	125.3(9)	C1d	C12	C3	118.3(9)
C1	C11	N9	121.6(9)	C1d	C17	C7	120.8(9)
C8	C15	N6	122.2(8)	C17	C1d	C12	120.7(9)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 10.

Atom	***x***	***y***	***z***	**U(eq)**
H18a	140(120)	-2790(20)	8520(20)	58(4)
H18b	1610(40)	-3042(10)	9280(60)	58(4)
H18c	-490(80)	-2735(17)	9620(40)	58(4)
H1aa	6820(50)	-3310(20)	7850(60)	54(4)
H1ab	5470(120)	-3374(16)	8862(8)	54(4)
H1ac	4650(80)	-3047(9)	7830(60)	54(4)
H1d	7364(13)	1414(8)	8121(7)	29(2)
H17	7122(12)	-356(8)	8270(7)	29(2)
H4	5327(13)	562(9)	5520(7)	32(2)
H3	5572(13)	2339(9)	5372(7)	35(3)
H1	1363(13)	4291(9)	4028(7)	32(3)
H19	621(12)	1373(8)	6137(7)	26(2)
H16	3665(13)	1869(9)	9539(7)	34(3)
H8	1059(13)	379(8)	7582(7)	29(2)
H14	3027(12)	79(8)	10204(7)	27(2)
H1ca	-240(50)	1150(60)	3220(20)	49(3)
H1cb	-1270(100)	264(15)	4140(30)	49(3)
H1cc	-2280(50)	1400(50)	3710(50)	49(3)
H1ea	800(30)	4330(70)	8770(30)	59(4)
H1eb	380(60)	4990(30)	7670(40)	59(4)
H1ec	-120(30)	3780(40)	8140(60)	59(4)
H13a	4680(120)	4791(13)	8550(30)	57(4)
H13b	3660(60)	3780(70)	9312(15)	57(4)
H13c	5690(60)	3650(60)	8760(50)	57(4)
H1ba	3100(80)	5851(11)	7100(40)	55(4)
H1bb	5190(30)	5531(17)	6750(50)	55(4)
H1bc	3630(110)	5601(19)	6070(20)	55(4)

Experimental

Single crystals of $C_{25}H_{27}N_2O_6PtS$ [10] were grown from toluene. A suitable crystal was selected and mounted on a diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2013). in preparation.
3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2013). in preparation.

Crystal structure determination of [10]

Crystal Data for $C_{25}H_{27}N_2O_6PtS$ (M =678.65 g/mol): triclinic, space group P-1 (no. 2), a = 7.2201(5) Å, b = 13.2276(9) Å, c = 14.0336(10) Å, α = 70.675(5)°, β = 80.551(6)°, γ = 84.130(6)°, V = 1245.94(16) Å^3, Z = 2, T = 100 K, μ(Mo Kα) = 5.756 mm^{-1}, *Dcalc* = 1.8088 g/cm^3, 21239 reflections measured (5.18° ≤ 2Θ ≤ 55.02°), 5677 unique (R_{int} = 0.2641, R_{sigma} = 0.1575) which were used in all calculations. The final R_1 was 0.0804 (I>=2u(I)) and wR_2 was 0.2041 (all data). This was a challenging sample to handle with crystal disintegrating on handling, and redisolving if allowed to warm reflected in the large R_{int}.

Refinement model description

Number of restraints - 0, number of constraints - 42.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C1d(H1d), C17(H17), C4(H4), C3(H3), C1(H1), C19(H19), C16(H16),
C8(H8),
 C14(H14)
2.b Idealised Me refined as rotating group:
 C18(H18a,H18b,H18c), C1a(H1aa,H1ab,H1ac), C1c(H1ca,H1cb,H1cc),
C1e(H1ea,H1eb,
 H1ec), C13(H13a,H13b,H13c), C1b(H1ba,H1bb,H1bc)
```

S3. Flow cytometry

HeLa human cervical carcinoma cells were grown in DMEM (Lonza) supplemented with 10% fetal calf serum (Labtech) and 100 U/ml penicillin and 100 µg/ml streptomycin (Lonza) at 37°C in a humidified incubator with 5% carbon dioxide. The cells were trypsinised according to standard procedures and re-suspended in ice-cold PBS at a concentration of 1 x 10^6 cells/ml. **9** dissolved to 20 mg/ml in DMSO was added to obtain the indicated final concentrations. The cells were then incubated on ice at 0-4° C for 10 minutes before analysis using a BD FACSCanto II flow cytometer.

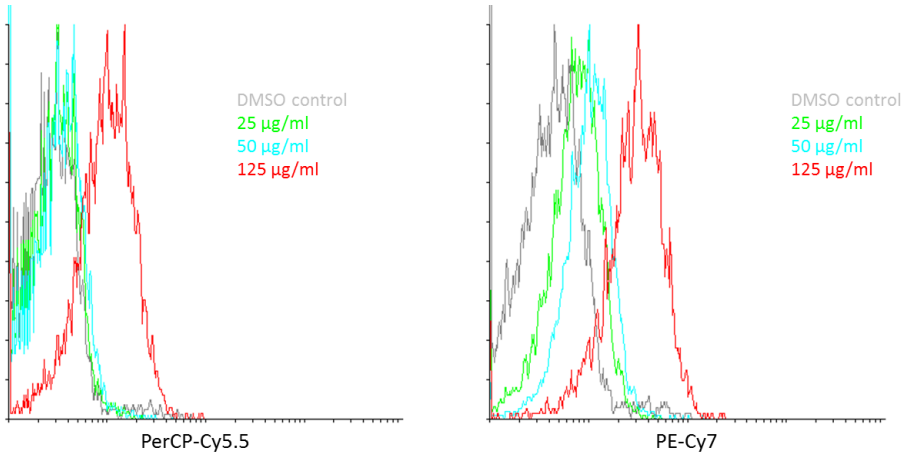

Figure S1. Flow cytometric analysis of **9** uptake by HeLa cells. Flow cytometry histograms of gated cells treated with the indicated concentrations of MC51 for 10 minutes. The PerCP-Cy5.5 channel detects fluorescence between 655 and 735 nm and the PE-Cy7 channel detects fluorescence between 750 and 810 nm

Back and Side Scatter Profiles

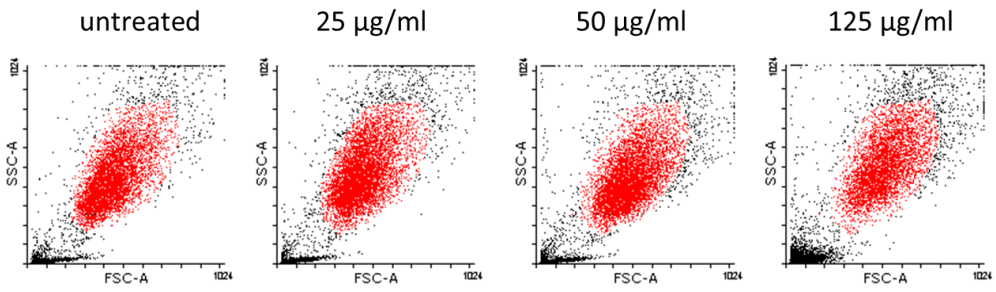

Figure S2. Dot plots of forward scatter (FSC) versus side scatter (SSC) for HeLa cells treated with **9**. Populations of cells selected for fluorescence histogram analysis are shown in red.

S4. Confocal microscopy

HeLa S3 cells were grown on glass coverslips under the same conditions as in **S3**. The coverslips were washed briefly in PBS and then incubated in PBS containing **9** at the indicated concentrations for 10 minutes at 4°C. The coverslips were then washed in PBS and mounted by inversion on a glass slide. Images were captured on a Zeiss LSM 510 Meta laser scanning confocal microscope.

S5. DFT calculations

DFT geometry optimisation and orbital calculations were performed in Gaussian09 [i] using the B3LYP functional[ii] with Stuttgart-Dresden basis set and effective core potential for Pt,[iii] along with 6-31+G(d,p) on all non-metal atoms,[iv] and also included a simulated MeCN environment using the polarised continuum model (PCM) approach.[v]

Table S1

Orbital make-up of selected absorptions

1

```
Excited State   1: Singlet-A 3.0526 eV, 406.3 nm f=0.0003: Orbitals 67 -> 68
Excited State   2: Singlet-A 3.0565 eV, 405.6 nm f=0.0007: Orbitals 66 -> 68
Excited State   3: Singlet-A 3.4605 eV, 358.3 nm f=0.0276: Orbitals 65 -> 68
Excited State   9: Singlet-A 4.2172 eV, 294.0 nm f=0.0835: Orbitals 64 -> 68
```

4

```
Excited State   1: Singlet-A 4.2176 eV, 294.0 nm f=0.1834: Orbitals 84 -> 85
Excited State   4: Singlet-A 4.3720 eV, 283.6 nm f=0.1377: Orbitals 81 -> 85
```

SH

```
Excited State   1: Singlet-A 2.5430 eV, 487.6 nm f=0.0004: Orbitals 72 -> 73
Excited State   2: Singlet-A 3.1548 eV, 393.0 nm f=0.0213: Orbitals 71 -> 73
Excited State   7: Singlet-A 4.1161 eV, 301.2 nm f=0.0364: Orbitals 68 -> 73
```

9

```
Excited State   1: Singlet-A 2.4650 eV, 503.0 nm f=0.0017: Orbitals 107 -> 108
Excited State   2: Singlet-A 2.8278 eV, 438.4 nm f=0.0599: Orbitals 106 -> 108
Excited State   6: Singlet-A 3.6334 eV, 341.2 nm f=0.0974: Orbitals 106 -> 109
Excited State   7: Singlet-A 3.8131 eV, 325.2 nm f=0.6042: Orbitals 106 -> 110
```

---

[i] Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[ii] a) A. D. Becke, *J. Chem. Phys.*, 1993, **98,** 5648-52. b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-89.

[iii] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, and H. Preuss, *Theor. Chem. Acc.*, 1990, **77**, 123-41.

[iv] a) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257-2261. b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654-3665. c) T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294-301.

[v] J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999-3093, and references cited therein.