Supporting information

Ag(I) complex design affording intense phosphorescence with landmarking lifetime of over 100 milliseconds

Marsel Z. Shafikov[†,‡,§], Rafał Czerwieniec[†]*, and Hartmut Yersin[†]*

[†] Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Universitätsstrasse 31, D-93053 Regensburg, Germany

[‡] Ural Federal University, Mira 19, Ekaterinburg, 620002, Russia

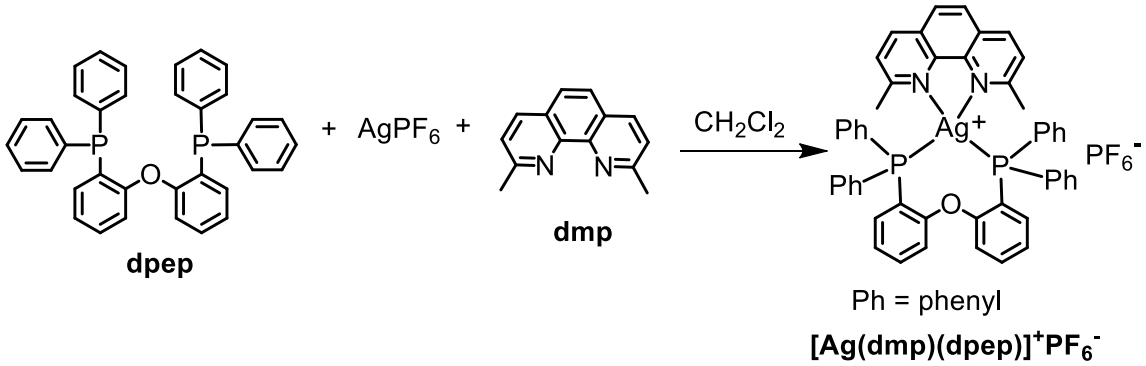
[§] Chemistry Department, University of York, Heslington, York, YO10 5DD, UK

* Corresponding authors: hartmut.yersin@ur.de (H.Y.), rafal.czerwieniec@ur.de (R.C.).

Contents **Pages**

Experimental.
NMR spectra were recorded on a Bruker AVANCE spectrometer operating at 300 MHz for ^{1}H and 121.5 MHz for ^{31}P with residual protic solvent used as internal standard.

Synthesis.



Scheme S1. Synthetic route to complex [Ag(dmp)(dpep)]$^{+}$PF$_6^{-}$

[Ag(dmp)(dpep)]$^{+}$PF$_6^{-}$ A mixture of $AgPF_6$ (150 mg, 0.587 mmol) and bis-[2-(diphenylphosphino)phenyl] ether (323 mg, 0.587 mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 4 h. Then a solution of 2,9-dimethyl-1,10-phenanthroline (129 mg, 0.587 mmol) in CH_2Cl_2 (5 mL) was added and the mixture was left to stir overnight. Afterwards the mixture was filtered, the clear yellow filtrate was concentrated to ca. 5 mL and n-hexane (10 ml) was added. The precipitated product was filtered out and dried in vacuo. Yield 65 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (2H, d, J = 8.4 Hz), 7.89 (s, 2H), 7.58 (2H, d, J = 8.4 Hz), 7.33-7.24 (5H, m), 7.19-7.03 (18H, m), 6.93-6.82 (5H, m), 2.49 (s, 6H); ^{31}P NMR (121.44 MHz, $CDCl_3$): δ -7.19, -143.62 (PF_6^-). Calc. for $C_{50}H_{40}AgF_6N_2OP_3$: C, 60.07; H, 4.03; N, 2.80. Found: C, 60.51; H, 4.12; N, 2.64.

X-ray diffraction study.

A translucent colorless irregular-shaped crystal with dimensions 0.21×0.15×0.09 mm^3 was mounted on a MITIGEN holder with inert oil. Data were collected using a SuperNova, Single source at offset, Atlas diffractometer equipped with a low-temperature device operating at T = 123.00(10) K.

Data were measured using scans 1.0° per frame for 1.0 s using Cu K$_\alpha$ radiation (micro-focus sealed X-ray tube). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent). The actually achieved resolution was Θ = 73.67. Cell parameters were retrieved using the CrysAlisPro (Agilent) software and refined using CrysAlisPro (Agilent) on 8006 reflections, 44 of the observed reflections. Data reduction was performed using the CrysAlisPro (Agilent) software which corrects for Lorentz polarization. The final completeness is 95.40 out to 73.67 in Θ. The absorption coefficient (μ) of this material is 5.954 and the minimum and maximum transmissions are 0.73717 and 1.00000.

The structure was solved in the space group P-1 (# 2) by Direct Methods using the ShelXT (Sheldrick, 2015) structure solution program and refined by Least Squares using olex2.refine (Bourhis et al., 2015). All non-hydrogen atoms were refined anizotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

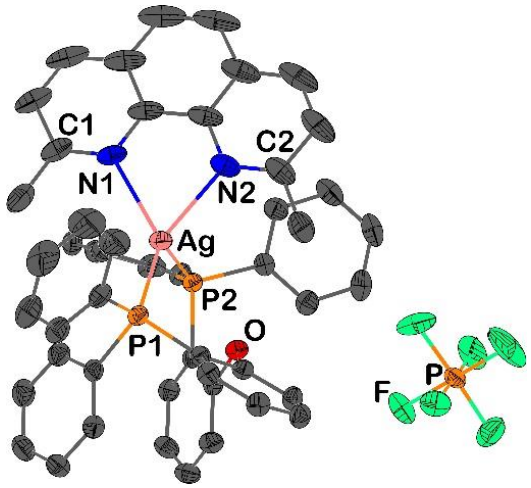


Figure S1. Perspective view (OLEX-2[1] plot with 50% probability thermal ellipsoids) of the newly synthesized complex **[Ag(dmp)(dpep)]$^{+}$PF$_6^{-}$**. Hydrogens are omitted for clarity.

Table S1. Comparison of selected geometry parameters of $[Ag(dmp)(dpep)]^+PF_6^-$ determined experimentally by an X-ray diffraction study and calculated at the M06/def2-SVP level of theory in the optimized ground state (S_0) and triplet state (T_1) geometries under gas phase conditions. Atom numbering corresponds to the one shown in Figure 1.

Parameters	X-Ray (with esd)	S_0 (M06/def2-SVP)	T_1 (M06/def2-SVP)
Bonds (Å)			
Ag-N1	2.360(3)	2.369	2.367
Ag-N2	2.351(2)	2.445	2.453
Ag-P1	2.4306(8)	2.516	2.522
Ag-P2	2.5218(7)	2.537	2.530
Angles (degree^o)			
N1-Ag-P1	126.3(1)	120.380	118.591
N1-Ag-P2	113.02(8)	122.454	124.488
N2-Ag-P1	129.54(8)	119.154	118.375
N2-Ag-P2	99.91(7)	104.927	106.147
N1-Ag-N2	71.35(11)	70.370	69.821
P1-Ag-P2	110.20(3)	111.590	111.504
Dihedral angles (degree^o)			
C1-N1-Ag-P1	50.3(3)	61.848	61.105
C1-N1-Ag-P2	90.7(3)	89.587	90.647
C2-N2-Ag-P1	56.5(3)	64.423	68.033
C2-N2-Ag-P2	70.3(3)	61.364	58.132

Photophysics.

Photophysical measurements were performed for a $[Ag(dmp)(dpep)]^+PF_6^-$ doped PMMA film deposited in a helium cryostat (Cryovac Konti Cryostat IT). Luminescence spectra were measured with a Horiba Jobin Yvon Fluorolog 3 steady-state fluorescence spectrometer. This spectrometer was modified to allow for measurements of emission decay times. The sample was excited with THORLABS M310D2 - Deep UV (λ_{exc} = 310 nm) pulsed LED equipped with a THORLABS LA4052-UV lens. The pulse duration was set to 10 μs with repetition adjusted for the full emission decay curve to be observed. The excitation source was triggered by a digital delay generator DG645 (Stanford Research Systems). The emission signal was detected with a cooled photomultiplier attached to a FAST ComTec multichannel scalar PCI card with a time resolution of 250 ps. Photoluminescence quantum yields were determined with a Hamamatsu C9920-02 system equipped with a Spectralon® integrating sphere.

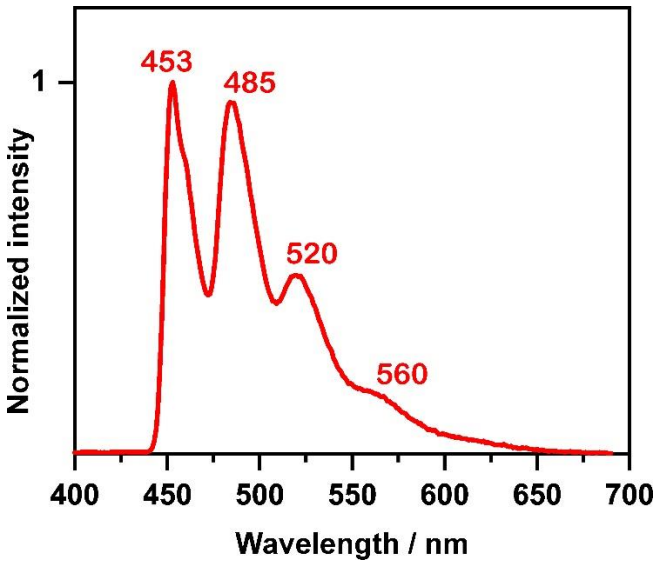


Figure S2. Emission spectrum of **[Ag(dmp)(dpep)]$^{+}$PF$_6^{-}$** measured for a doped PMMA film at T = 77 K. Dopant concentration c << 1 wt. %. The vibrational progression is of about 1400 cm^{-1}.

Calculations.

M06[2]/def2-SVP[3,4] level of theory with "tight" criteria was applied for geometry optimizations and M062X[2]/def2-SVP level of theory was applied for time-dependent calculations, all using the Gaussian 09D[5] program.

Table S2. Excited state properties of [Ag(dmp)(dpep)]$^{+}$ obtained from TD-DFT calculations (M062X/def2-SVP) for the gas phase relaxed geometry of the lowest excited triplet state (T_1).

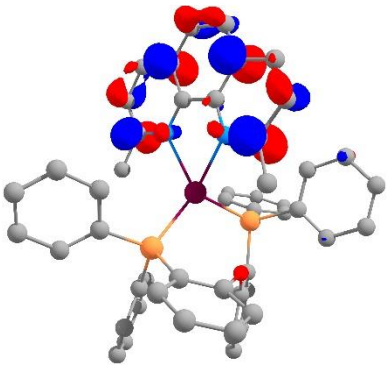
State	Energy (eV)	Main contributions	Oscillator strength	Character
S_1	3.85	HOMO−1→LUMO (67%), HOMO→LUMO (25%), HOMO−1→LUMO+1 (3%)	0.2441	$L_{dmp}C$ + $L_{dpep}L_{dmp}CT$
S_2	3.92	HOMO−1→LUMO+1 (53%), HOMO→LUMO+1 (24%), HOMO−11→LUMO (5%), HOMO−5→LUMO (4%), HOMO−1→LUMO (3%)	0.0278	$L_{dmp}C$ + $L_{dpep}L_{dmp}CT$
S_3	4.14	HOMO→LUMO (68%), HOMO−1→LUMO (26%)	0.0003	$L_{dpep}L_{dmp}CT$ + $L_{dmp}C$
S_4	4.41	HOMO→LUMO+1 (32%), HOMO−13→LUMO+1 (15%), HOMO−1→LUMO+1 (11%),	0.0258	$L_{dpep}L_{dmp}CT$ + $L_{dmp}C$

		HOMO−14→LUMO+1 (11%), HOMO→LUMO (6%).		
T_1	2.34	HOMO−1→LUMO (75%), HOMO→LUMO (19%)	0	$L_{dmp}C$ + $L_{dpep}L_{dmp}CT$
T_2	3.24	HOMO−1→LUMO+1 (68%), HOMO→LUMO+1 (21%), HOMO−17→LUMO (3 %)	0	$L_{dmp}C$ + $L_{dpep}L_{dmp}CT$
T_3	3.90	HOMO−11→LUMO (27%), HOMO−5→LUMO (21%), HOMO−1→LUMO+6 (9%), HOMO−10→LUMO (8%), HOMO−4→LUMO (5%), HOMO−12→LUMO (4%), HOMO−7→LUMO (3%), HOMO−9→LUMO (3%), HOMO−1→LUMO+1 (3%), HOMO→LUMO+6 (2%)	0	$L_{dmp}C$ + $L_{dpep}L_{dmp}CT$

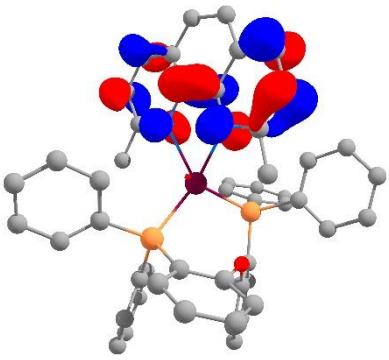
Table S3. Orbital energies and characters resulting from Mulliken population analysis calculated for $[Ag(dmp)(dpep)]^+$ at the M062X/def2-SVP level of theory at the lowest triplet state (T_1) optimized geometry.

Orbital	Energy, (eV)	Contributions, (%)			
		dmp[a]	Ag	P	Ph.[b]
LUMO+4	-2.35	2	4	12	82
LUMO+3	-2.36	1	4	14	81
LUMO+2	-2.53	1	7	10	82
LUMO+1	-3.31	96	2	0	1
LUMO	-3.81	99	0	0	0
HOMO	-9.34	17	11	32	40
HOMO−1	-9.58	83	2	5	10
HOMO−2	-10.08	3	7	16	73
HOMO−3	-10.11	2	4	9	85
HOMO−4	-10.56	6	0	1	93
a) 2,9-dimethyl-1,10-phenanthroline ligand (dmp) b) phenyl groups of the dpep ligand including diphenyl ether					

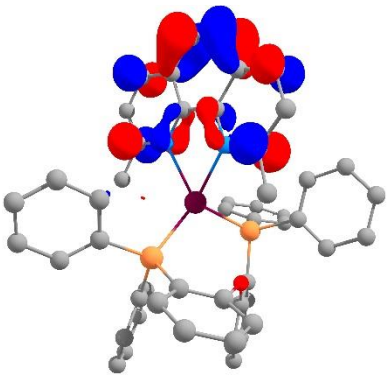
Table S4. Iso-surface contour plots (iso-value = 0.05) and energies of the molecular orbitals relevant to the lowest excited states of $[Ag(dmp)(dpep)]^+$ as calculated at the M062X/def2-SVP theory level in the lowest triplet-state (T_1) geometry. Hydrogens are omitted for clarity.



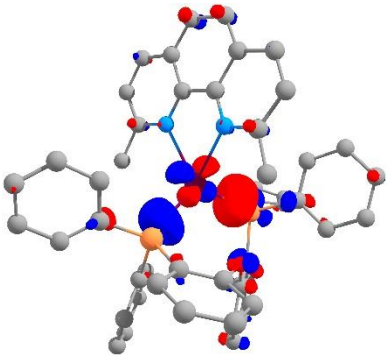
LUMO+6 (−2.04 eV)



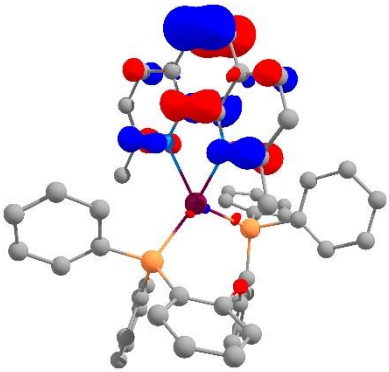
LUMO+1 (−3.31 eV)



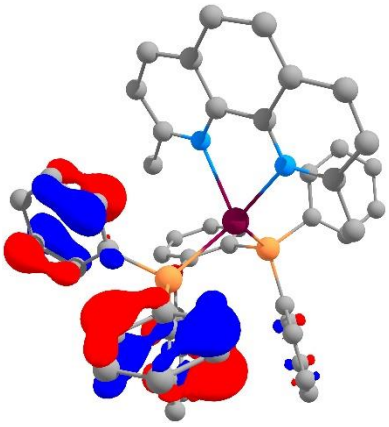
LUMO (−3.81 eV)



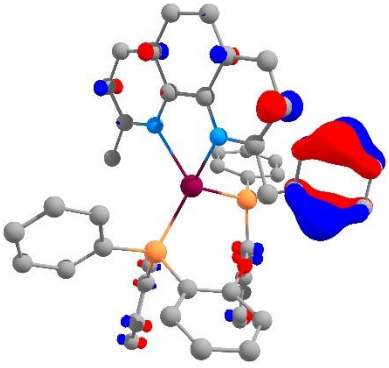
HOMO (−9.34 eV)



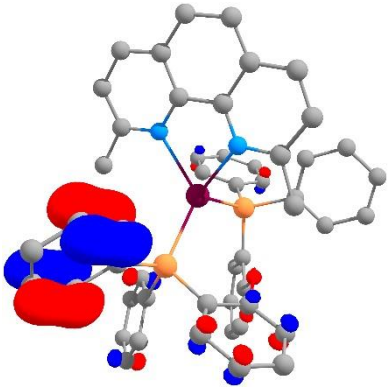
HOMO−1 (−9.58 eV)



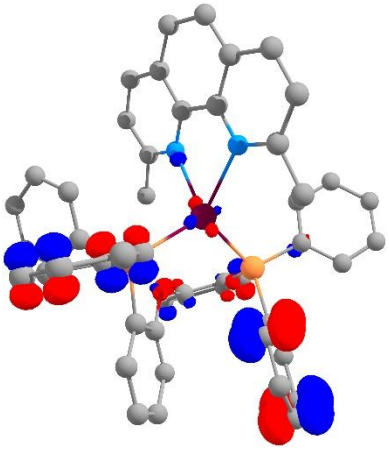
HOMO−4 (−10.56 eV)



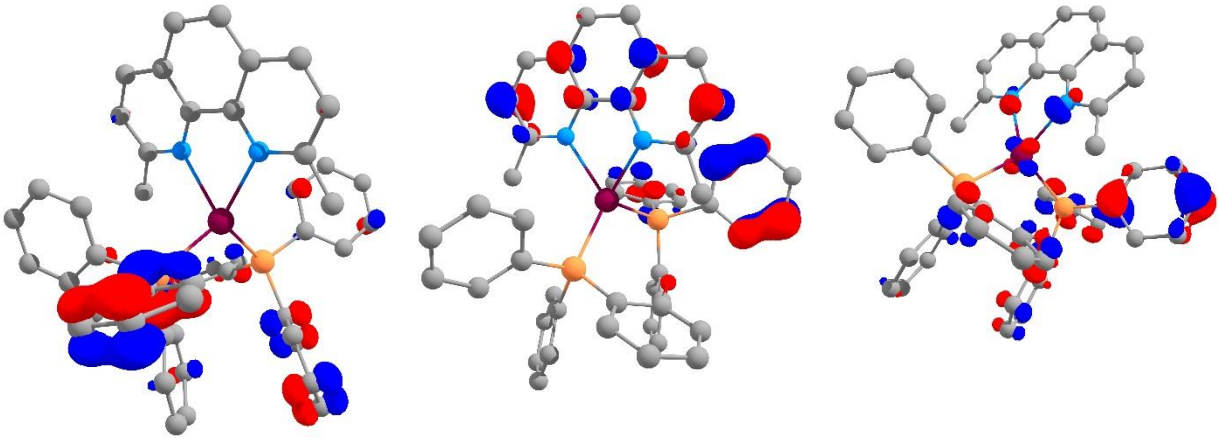
HOMO−5 (−10.59 eV)



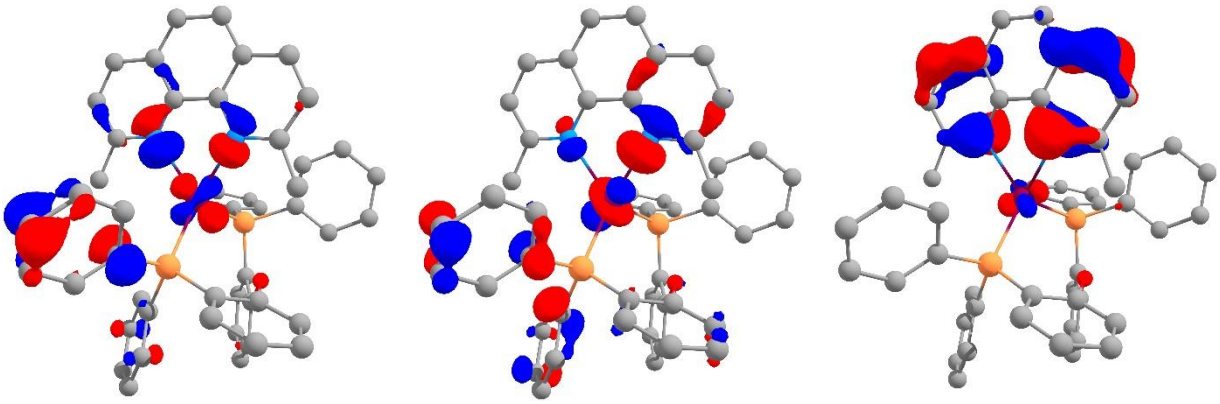
HOMO−7 (−10.68 eV)



HOMO−9 (−10.82 eV)



HOMO−10 (−10.83 eV) **HOMO−11 (−10.87 eV)** **HOMO−12 (−10.93 eV)**



HOMO−13 (−11.00 eV) **HOMO−14 (−11.11 eV)** **HOMO−17 (−12.15 eV)**

Table S5. Calculated (M06/def2-SVP) gas phase geometry of $[Ag(dmp)(dpep)]^+$ in cartesian (XYZ) coordinates

Ground state (S_0)				Lowest triplet state (T_1)			
C	-2.087482000	3.121718000	-3.903168000	C	-1.938161000	3.145146000	-3.973259000
C	-2.634824000	4.383737000	-3.683480000	C	-2.410715000	4.442578000	-3.789195000
C	-2.595454000	4.951062000	-2.409965000	C	-2.335564000	5.042795000	-2.532454000
C	-2.004824000	4.261034000	-1.355201000	C	-1.783689000	4.349824000	-1.458888000
C	-1.449555000	2.993422000	-1.569537000	C	-1.303297000	3.046550000	-1.637732000
C	-1.501788000	2.426750000	-2.847315000	C	-1.391045000	2.447427000	-2.898650000
C	-2.930035000	3.192604000	3.602447000	C	-2.772100000	3.454191000	3.530915000
C	-3.509550000	2.387935000	2.621279000	C	-3.391141000	2.649422000	2.574461000
C	-2.796329000	2.074468000	1.468423000	C	-2.697084000	2.271516000	1.429262000
C	-1.502010000	2.577485000	1.277737000	C	-1.382031000	2.709048000	1.221387000
C	-0.932953000	3.397767000	2.256197000	C	-0.772658000	3.529878000	2.174831000
C	-1.645149000	3.698045000	3.416709000	C	-1.466199000	3.894995000	3.327950000
C	2.306640000	-2.978664000	-0.257738000	C	2.125372000	-3.071477000	-0.174654000
C	1.349841000	-3.835208000	0.307186000	C	1.124835000	-3.862824000	0.409323000
C	1.487862000	-5.214568000	0.194746000	C	1.182867000	-5.249343000	0.318142000
C	2.568843000	-5.751504000	-0.504892000	C	2.226698000	-5.858428000	-0.379056000
C	3.509002000	-4.906153000	-1.087976000	C	3.209844000	-5.077717000	-0.980735000
C	3.383178000	-3.522494000	-0.964725000	C	3.164207000	-3.687293000	-0.879033000
C	2.821917000	0.389713000	-2.202038000	C	2.845051000	0.226317000	-2.177685000
C	3.255815000	-0.331721000	-1.085500000	C	3.228902000	-0.500530000	-1.046450000

C	4.621352000	-0.352340000	-0.770152000	C	4.589128000	-0.597887000	-0.722412000
C	5.535437000	0.326293000	-1.569961000	C	5.546547000	0.010350000	-1.528126000
C	5.093878000	1.040355000	-2.684159000	C	5.154606000	0.730024000	-2.657213000
C	3.737821000	1.074352000	-2.998376000	C	3.804693000	0.840392000	-2.980086000
C	2.305380000	0.391695000	2.236196000	C	2.291951000	0.345760000	2.250276000
C	2.689311000	0.705011000	3.535320000	C	2.682495000	0.666672000	3.545493000
C	3.408038000	-0.226019000	4.280884000	C	3.344540000	-0.285143000	4.316887000
C	3.729357000	-1.463216000	3.726495000	C	3.602860000	-1.549692000	3.792001000
C	3.337738000	-1.770233000	2.424779000	C	3.204942000	-1.863844000	2.493894000
C	2.623481000	-0.845503000	1.654621000	C	2.547062000	-0.919173000	1.698227000
C	1.470989000	3.854281000	-0.982311000	C	1.660641000	3.764016000	-1.061533000
C	2.794748000	4.289573000	-0.963236000	C	3.005588000	4.128744000	-1.045562000
C	3.706935000	3.693446000	-0.097046000	C	3.880384000	3.509187000	-0.157388000
C	3.305847000	2.672189000	0.762112000	C	3.421496000	2.534358000	0.726394000
C	1.980925000	2.250422000	0.737383000	C	2.076356000	2.182504000	0.703925000
C	1.041905000	2.827532000	-0.136001000	C	1.173716000	2.784947000	-0.190398000
C	-5.390050000	-2.955342000	-0.687897000	C	-5.399726000	-2.924337000	-0.724775000
C	-5.474897000	-2.634203000	0.630202000	C	-5.533607000	-2.482618000	0.668846000
C	-4.184647000	-2.715400000	-1.419952000	C	-4.217123000	-2.729645000	-1.423067000
C	-3.066103000	-2.120663000	-0.786150000	C	-3.100510000	-2.073654000	-0.789718000
N	-1.927823000	-1.855849000	-1.460229000	N	-1.982730000	-1.813554000	-1.430773000
C	-1.803706000	-2.194824000	-2.736615000	C	-1.801766000	-2.213163000	-2.724026000
C	-2.863970000	-2.812322000	-3.434854000	C	-2.823304000	-2.881173000	-3.407986000
C	-4.049169000	-3.055753000	-2.781113000	C	-4.026800000	-3.133429000	-2.778686000
C	-3.144657000	-1.807796000	0.629314000	C	-3.211873000	-1.689966000	0.647898000
C	-4.355288000	-2.067172000	1.316913000	C	-4.466441000	-1.896682000	1.329098000
C	-4.390953000	-1.762598000	2.693623000	C	-4.515807000	-1.481393000	2.695428000
C	-3.270726000	-1.262253000	3.312644000	C	-3.386670000	-0.976213000	3.298856000
C	-2.095955000	-1.045768000	2.556478000	C	-2.192004000	-0.851512000	2.567740000
N	-2.060334000	-1.305555000	1.256043000	N	-2.152050000	-1.194964000	1.252839000
Ag	-0.384292000	-0.470063000	-0.315654000	Ag	-0.426687000	-0.425131000	-0.311475000
P	-0.618226000	2.055395000	-0.239374000	P	-0.525843000	2.102750000	-0.280050000
P	2.012360000	-1.186250000	-0.047045000	P	1.931687000	-1.261565000	-0.000943000
O	1.494865000	1.265201000	1.551375000	O	1.534423000	1.246162000	1.539696000
H	-2.124090000	2.673545000	-4.899872000	H	-2.003542000	2.671375000	-4.956522000
H	-3.100538000	4.928499000	-4.509369000	H	-2.846152000	4.989653000	-4.629937000
H	-3.028650000	5.940208000	-2.237727000	H	-2.710425000	6.059835000	-2.388155000
H	-1.971829000	4.711372000	-0.356697000	H	-1.722628000	4.825403000	-0.473488000
H	-1.082307000	1.426464000	-3.011655000	H	-1.031706000	1.419917000	-3.035439000
H	-3.486534000	3.433788000	4.512387000	H	-3.313482000	3.745558000	4.435261000
H	-4.522390000	1.997217000	2.757301000	H	-4.419529000	2.307588000	2.724576000
H	-3.249814000	1.429731000	0.703537000	H	-3.181793000	1.624868000	0.685404000
H	0.073006000	3.806559000	2.112086000	H	0.250792000	3.887139000	2.017484000
H	-1.193989000	4.339592000	4.178954000	H	-0.983175000	4.535942000	4.070908000
H	0.486748000	-3.411491000	0.838952000	H	0.290944000	-3.381796000	0.938947000
H	0.742961000	-5.875535000	0.646279000	H	0.404438000	-5.859422000	0.784508000
H	2.673671000	-6.835625000	-0.601541000	H	2.268440000	-6.948152000	-0.458962000
H	4.351884000	-5.325076000	-1.644619000	H	4.023745000	-5.552913000	-1.535291000
H	4.127800000	-2.867120000	-1.427701000	H	3.942010000	-3.083182000	-1.356865000
H	1.751352000	0.433334000	-2.437094000	H	1.780484000	0.330492000	-2.420685000
H	4.971982000	-0.897633000	0.113806000	H	4.901765000	-1.148364000	0.172521000
H	6.599881000	0.302664000	-1.320300000	H	6.606338000	-0.073230000	-1.271656000
H	5.813243000	1.577870000	-3.308255000	H	5.908325000	1.211822000	-3.286246000
H	3.388497000	1.643198000	-3.864466000	H	3.494550000	1.413848000	-3.857971000
H	2.402248000	1.676806000	3.948466000	H	2.444987000	1.661206000	3.935241000
H	3.710698000	0.013988000	5.303560000	H	3.652146000	-0.039435000	5.336721000
H	4.287178000	-2.198454000	4.312170000	H	4.116063000	-2.300676000	4.398131000
H	3.585098000	-2.749289000	1.999730000	H	3.402516000	-2.863702000	2.091851000
H	0.760423000	4.313377000	-1.677232000	H	0.978741000	4.241006000	-1.772944000

H	3.112975000	5.094413000	-1.630463000	H	3.369612000	4.896969000	-1.732246000
H	4.748842000	4.025363000	-0.083350000	H	4.938328000	3.785866000	-0.145881000
H	4.018707000	2.198696000	1.443484000	H	4.104553000	2.042485000	1.425078000
H	-6.238015000	-3.404248000	-1.213620000	H	-6.246215000	-3.408930000	-1.219658000
H	-6.394168000	-2.816183000	1.194975000	H	-6.480789000	-2.634397000	1.194140000
C	-0.502209000	-1.900381000	-3.406828000	C	-0.478197000	-1.925295000	-3.338325000
H	-2.733564000	-3.082601000	-4.485711000	H	-2.658490000	-3.196807000	-4.441692000
H	-4.892581000	-3.519821000	-3.301971000	H	-4.841277000	-3.644399000	-3.300492000
H	-5.311902000	-1.943837000	3.256935000	H	-5.452513000	-1.593079000	3.249886000
H	-3.271784000	-1.031574000	4.381161000	H	-3.402319000	-0.672789000	4.349407000
C	-0.859786000	-0.514308000	3.200790000	C	-0.934304000	-0.356754000	3.186685000
H	0.331245000	-2.359140000	-2.846727000	H	0.332897000	-2.425843000	-2.776718000
H	-0.316074000	-0.812623000	-3.427172000	H	-0.258640000	-0.842255000	-3.311309000
H	-0.474590000	-2.271136000	-4.440615000	H	-0.429138000	-2.260217000	-4.383678000
H	-0.951159000	-0.476783000	4.295384000	H	-1.053898000	-0.179679000	4.264980000
H	-0.644709000	0.507099000	2.838433000	H	-0.607063000	0.589427000	2.717255000
H	0.013125000	-1.138508000	2.941140000	H	-0.111966000	-1.082173000	3.040759000

References.

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

2 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2007, **120**, 215-241.

3 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.

4 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.

5 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. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, 2009