Electronic Supplementary Information

Structure, photophysical properties and computational study of a highly luminescent mixed-metal platinum(II)-silver(I) system. Potential building blocks for emissive supramolecular structures

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Experimental

Synthesis of [Pt(^{n}BuBzimb)(C≡C–C_6H_4–Carb-4)] (1)

The compound was synthesized according to a modification of a previously reported method for the synthesis of platinum(II) terpyridyl complexes except that [Pt(^{n}BuBzimb)Cl] was used instead of [Pt(trpy)(MeCN)](OTf)$_2$ to give a yellow solid.[1] Yield: 0.1 g (50 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.03 (t, *J* = 7.4 Hz, 6H, –CH_3), 1.55 (m, 4H, –CH_2–), 2.03 (m, 4H, –CH_2–), 4.65 (t, *J* = 7.4 Hz, 4H, –CH_2–), 7.32 (m, 4H, carbazole and –C_6H_4–), 7.44 (m, 7H, –C_6H_4– and benzimidazole), 7.54 (d, 2H, *J* = 8.1 Hz, carbazole), 7.57 (d, *J* = 8.3 Hz, 2H, benzimidazole), 7.68 (d, *J* = 8.1 Hz, 2H, carbazole), 7.86 (d, *J* = 8.1 Hz, 2H, carbazole), 8.17 (d, *J* = 8.1 Hz, 2H, carbazole), 9.08 (d, *J* = 8.3 Hz, 2H, benzimidazole). IR (Nujol): *ν* = 2104 cm^{-1} (w; *ν*(C≡C)). Positive FAB–MS: m/z 883 $[M + H]^+$. Anal. Calcd for $C_{48}H_{41}N_5Pt$• 0.5(CH_2Cl_2): C, 62.95; H, 4.57; N, 7.57. Found: C, 62.78; H, 4.59; N, 7.71.

Synthesis of [{η^2-Pt(^{n}BuBzimb)(C≡C–C_6H_4–Carb-4)}$_2$Ag]OTf ([{1}$_2$Ag]OTf):

To a solution of [Pt(^{n}BuBzimb)Cl] (0.3 g, 0.46 mmol), AgOTf (0.24 g, 0.94 mmol) and NEt_3 (5 ml) in THF (50 ml) was added 9-(4-ethynylphenyl)carbazole (0.25 g, 0.94 mmol) and the resultant solution was heated under reflux overnight. After filtration and evaporation of solvents, the residue was purified by column chromatography on silica gel using dichloromethane-acetone (6:1 v/v) as eluent. Slow diffusion of diethyl ether vapor into a dichloromethane solution of the product gave **[{1}$_2$Ag]OTf** as a yellowish green solid. Subsequent recrystallization by the layering of diethyl ether onto dichloromethane gave **[{1}$_2$Ag]OTf** as yellow crystals suitable for X-ray crystallography. Yield: 110 mg (26 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.98 (t, *J* = 7.3 Hz, 12H, –CH_3), 1.46 (m, 8H, –CH_2), 1.81 (m, 8H,

$-CH_2$), 4.32 (t, J = 7.3 Hz, 8H, $-CH_2$), 6.94 (t, J = 7.8 Hz, 4H, benzimidazole), 7.27 (m, 12H, benzimidazole and carbazole), 7.41 (m, 10H, $-C_6H_4-$ of ethynyl ligand, $-C_6H_4-$ and benzimidazole), 7.51 (d, J = 7.7 Hz, 4H, carbazole), 7.57 (d, J = 7.8 Hz, 4H, benzimidazole), 7.79 (d, J = 8.3 Hz, 4H, $-C_6H_4-$ of ethynyl ligand), 8.16 (d, J = 7.8 Hz, 4H, benzimidazole), 8.20 (d, J = 7.8 Hz, 4H, benzimidazole). IR (Nujol): ν = 2078 cm^{-1} (w; ν(C≡C)). Positive ESI-MS: m/z 1874 $[M-OTf]^+$. Anal. Calcd for $C_{97}H_{82}N_{10}O_3F_3SPt_2Ag$: C, 57.59; H, 4.09; N, 6.92. Found: C, 57.72; H, 4.29; N, 6.88.

Crystal Structure Determination for **[{1}$_2$Ag]OTf**: Single crystals of complex **[{1}$_2$Ag]OTf** suitable for X-ray diffraction studies were grown by layering of diethyl ether onto a dichloromethane solution of the complex. The X-ray diffraction data were collected on a Bruker SMART 1000 CCD diffractometer[2] using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). Raw frame data were integrated with SAINT[3] program. Semi-empirical absorption correction with SADABS[4] was applied. The structure was solved by direct methods employing SHELXS97[5] program and refined using SHELXL97 program[6]. Most of the non-hydrogen atoms were refined anisotropically.

According to the SHELXL-97 program,[6] all 16587 independent reflections (R_{int} equal to 0.032, 10781 reflections larger than $4\sigma(F_o)$) from a total 44341 reflections were participated in the full-matrix least-square refinement against F^2. These reflections were in the range $-16 \le h \le 16$, $-16 \le k \le 16$, $-29 \le l \le 29$ with $2\theta_{max}$ equal to 25.0°.

Convergence ($(\Delta/\sigma)_{max}$ = 0.004) for 1002 variable parameters by full-matrix least-squares refinement on F^2 reaches to R = 0.00818, wR = 0.1802 with a goodness-of-fit of 1.01.[7] The final difference Fourier map shows maximum rest peaks and holes of 1.38 and −0. 86 e $Å^{-3}$ respectively.

Crystal data for **[{1}$_2$Ag]OTf:** $C_{97}H_{82}AgN_{10}Pt_2F_3O_3S$, formula weight = 2022.84, crystal dimensions 0.49 mm × 0.42 mm × 0.39 mm, triclinic, space group $P\bar{1}$ *(No. 2)*, a = 14.002 (2) Å, b = 14.255 (2) Å, c = 24.591 (4) Å, α = 102.52 (2)°, β = 96.09 (2)°, γ = 96.61(2)°, V = 4716.1 (12) $Å^3$, Z = 2, density = 1.424 g cm^{-3}, μ(Mo-K$_\alpha$) = 3.24 mm^{-1}, F(000) = 2008, T = 301 K. Final R = 0.0559, wR =0.1652 with I > 2$\sigma(I)$; R = 0.00818, wR = 0.1802 for all data; GOF = 1.009 for 1002 variable parameters and a total of 44341 reflections, of which 16587 were independent (R_{int} = 0.032) and 10781 were larger than 4$\sigma(F_o)$. Bruker SMART 1000 CCD diffractometer, Mo-K$_\alpha$ radiation (λ = 0.71073 Å); θ range for data collection of 2.6° to 25.0°. CCDC-767390 **([{1}$_2$Ag]OTf**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details

Calculations were mainly carried out using Gaussian 03 software package.[8] Density functional theory (DFT) at the hybrid Perdew, Burke, and Ernzerhof functional (PBE0) level [9] was used to optimize the ground-state geometries of the [Pt(MeBzimb)(C≡C–C_6H_4–Carb-4)] (**1′**) and [{η^2-Pt(MeBzimb)(C≡C–C_6H_4–Carb-4)}$_2$Ag]$^+$ (**[{1′}$_2$Ag]$^+$**). On the basis of the ground state optimized geometries in the gas phase, non-equilibrium time-dependent

density functional theory (TDDFT) method[10] at the same level associated with conductor-like polarizable continuum model (CPCM)[11] was employed to compute singlet–singlet and singlet–triplet transitions for the complexes (CH_2Cl_2 as the solvent). On the basis of the major excitation in the first lowest-lying singlet–triplet transition from the TDDFT calculation, the unrestricted UPBE0 was used to optimize the lowest triplet excited state of the model complexes starting from the optimized ground-state structure. Single-point CPCM calculations using CH_2Cl_2 as the solvent were performed to compute the ground and triplet excited state energies at the optimized triplet excited state geometry and their relative differences were used to compare with the experimental emission energies. The Stuttgart effective core potentials (ECPs) and the associated basis set were applied to describe for Pt[12] with f-type polarization functions (ζ = 0.993),[13] while the 6-31G basis set[14] was used for all other atoms with d-type polarization functions for Cl (ζ = 0.75),[15a] N and C atoms of the bzimb ligand directly coordinated to the Pt center and alkynyl C atoms [ζ(C) and ζ(N) = 0.800)].[15b] All geometry optimizations were performed without any symmetry constraints. Vibrational frequency calculations were performed for all stationary points to verify that each was a minimum (NIMAG = 0) on the potential energy surface. The DFT and TDDFT calculations were performed with a pruned (99,590) grid. Mulliken population analyses were performed using MullPop[16] and Wiberg bond indices (WBI) were obtained by natural bond orbital (NBO) analysis.[17]

Optimized Geometry

The optimized structures with selected structural parameters for **1′** and **[{1′}$_2$Ag]$^+$** are given in Fig. S1. In general, the calculated bond lengths and angles in **[{1′}$_2$Ag]$^+$** are in good agreement with those observed in the X-ray crystal structure of

[{1}$_2$Ag]OTf. For the complexes, the respective Pt–N and Pt–C(bzimb) bond distances within the Pt(bzimb) unit(s) are calculated to be 2.029–2.034 and 1.922–1.963 Å. The Pt–C(alkynyl) and C≡C bond distances in **1′** (2.028 and 1.231 Å) are on average lengthened by 0.022 and 0.015 Å respectively upon π-coordination of the alkynyl units to Ag. The unsymmetrical≡C π-coordination mode to the silver atom in **[{1′}$_2$Ag]$^+$** was reproduced, in which the average Ag–C distances for the carbon atoms at the *α*- and at the *β*-positions to the Pt units are calculated to be 2.217 and 2.431 Å, respectively. The Pt···Ag separations are calculated to be 3.099 Å with the Wiberg bond indices of 0.126, suggesting an attractive Pt···Ag interaction.

Table S1. Selected singlet–singlet transitions of the model complexes computed by TDDFT/CPCM using CH_2Cl_2 as the solvent

Complex	Transition	Orbital Involved[a]	Coefficient[b]	f [c]	Vertical excitation wavelength (nm)
1′	$S_0 \rightarrow S_1$	H → L	0.66	0.018	389
	$S_0 \rightarrow S_2$	H → L+1	0.64	0.035	368
	$S_0 \rightarrow S_3$	H–1 → L	0.64	0.225	366
	$S_0 \rightarrow S_4$	H–2 → L	0.46	0.015	348
		H–1 → L+1	–0.46		
	$S_0 \rightarrow S_5$	H–2 → L+1	0.67	0.028	343
	$S_0 \rightarrow S_6$	H–2 → L	0.47	0.436	331
		H–1 → L+1	0.43		
[{1′}$_2$Ag]$^+$	$S_0 \rightarrow S_1$	H → L	0.48	0.132	377
		H → L+1	0.45		
	$S_0 \rightarrow S_{12}$	H–7 → L+2	0.35	0.373	343
		H–5 → L+1	0.39		
	$S_0 \rightarrow S_{15}$	H–3 → L	–0.43	0.432	332
		H–3 → L+1	0.36		

[a] The orbitals involved in the excitations (H = HOMO and L = LUMO)

[b] The coefficients in the configuration interaction (CI) expansion that are less than or equal to absolute value of 0.3 are not listed

[c] Oscillator strengths

Table S2. Mulliken percentage compositions[a] of selected molecular orbitals (H = HOMO and L = LUMO) in **1′**

	Pt	bzimb	C≡C–C_6H_4–Carb-4
L+1	13	83	4
L	1	99	0
H	6	2	92
H–1	26	44	30
H–2	31	69	0

[a]The compositions were expressed in terms of contributions from the Pt metal center (Pt), bzimb ligand (bzimb) and alkynyl ligand (C≡C–C_6H_4–Carb-4)

Table S3. Mulliken percentage compositions[a] of selected molecular orbitals (H = HOMO and L = LUMO in **[{1′}$_2$Ag]$^+$**

	Pt	Ag	bzimb	C≡C–C_6H_4–Carb-4
L+2	1	0	98	0
L+1	12	5	72	11
L	6	2	87	5
H	2	1	1	96
H–3	26	1	72	1
H–5	22	2	63	13
H–7	16	2	75	6

[a]The compositions were expressed in terms of contributions from the two Pt metal centers (Pt), Ag metal center, two bzimb ligands (bzimb) and two alkynyl ligands (C≡C–C_6H_4–Carb-4)

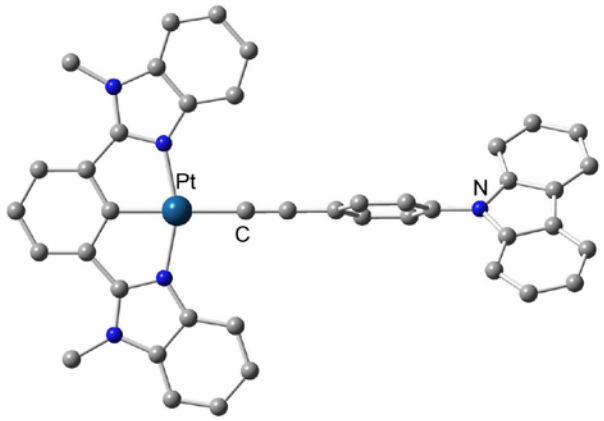
Table S4. First singlet–triplet transition[a] of the model complexes computed by TDDFT/CPCM using CH_2Cl_2 as the solvent

Complex	Transition	Orbital Involved[b]	Coefficient	Vertical excitation wavelength (nm)
1′	$S_0 \rightarrow T_1$	H–2 → L	0.63	478
[{1′}$_2$Ag]$^+$	$S_0 \rightarrow T_1$	H–3 → L+2	0.41	476

[a] The oscillator strength for all the singlet–triplet transitions are zero

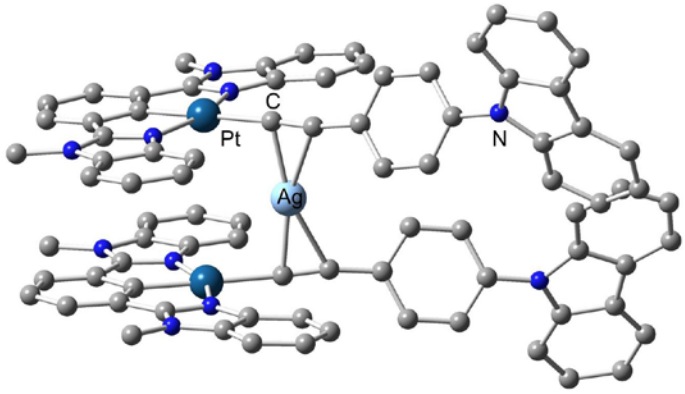
[b] The orbitals involved in the excitation (H = HOMO and L = LUMO) with the largest coefficient in the CI expansion

(a)



Pt–C(alkynyl)	2.028
Pt–N	2.029
Pt–C(bzimb)	1.963
C≡C	1.231
N–Pt–C(bzimb)	79.2
N–Pt–C(alkynyl)	100.8

(b)



Pt–C(alkynyl)	2.050
Pt–N	2.034
Pt–C(bzimb)	1.961
C≡C	1.246
Ag–C_α	2.217
Ag–C_β	2.431
N–Pt–C(bzimb)	79.3
N–Pt–C(alkynyl)	100.7

Fig. S1 The PBE0 optimized structures of (a) **1′** and (b) **[{1′}$_2$Ag]$^+$** with selected bond distances (Å) and angles (º). For clarity, all hydrogen atoms are omitted

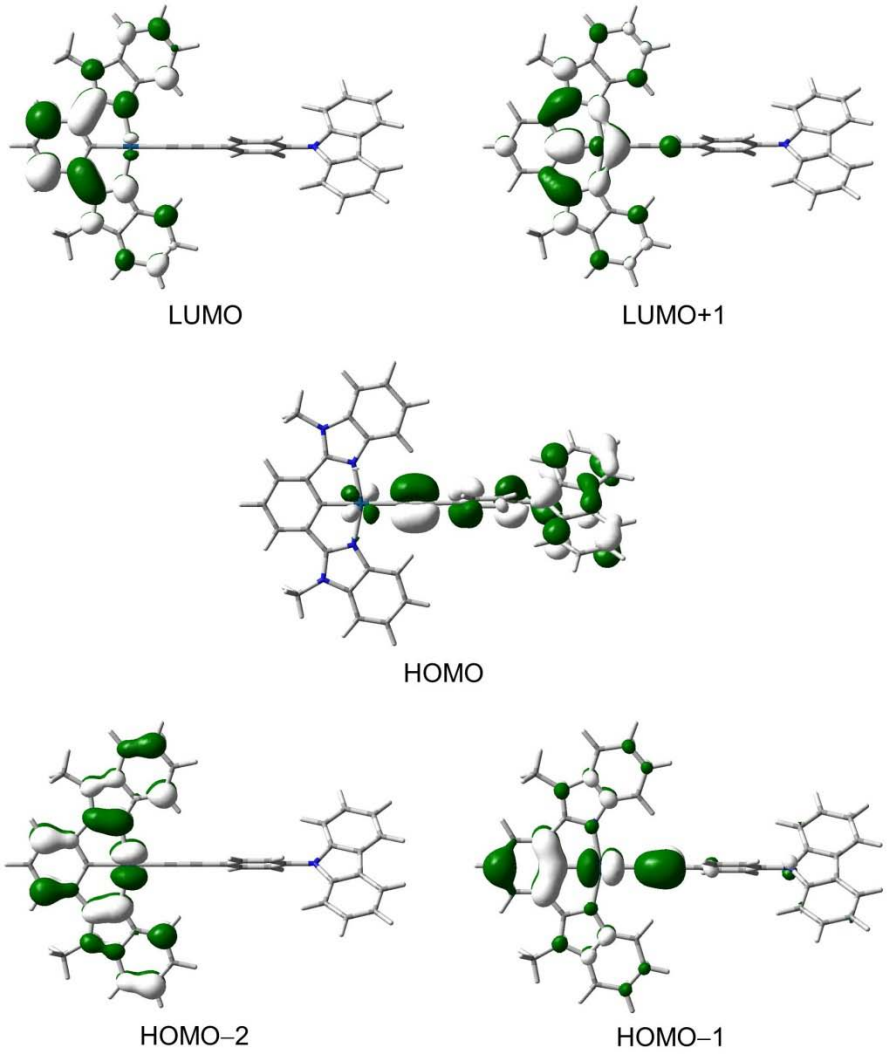


Fig. S2 Spatial plots (isovalue = 0.03) of selected TDDFT/CPCM molecular orbitals of **1′** obtained from TDDFT/CPCM calculation.

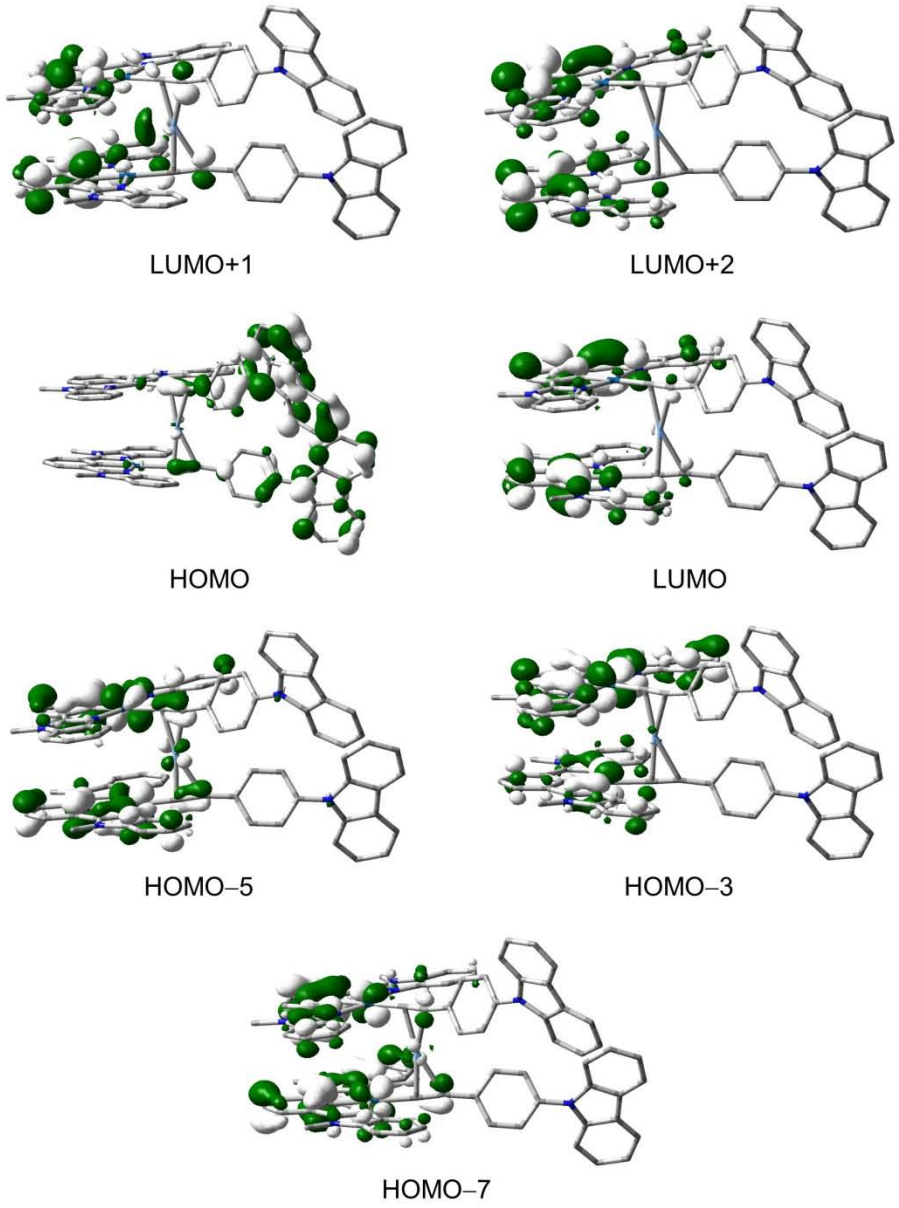


Fig. S3 Spatial plots (isovalue = 0.03) of selected molecular orbitals of **[{1′}$_2$Ag]$^+$** obtained from TDDFT/CPCM calculation. For clarity, all hydrogen atoms are omitted

Cartesian coordinates for the PBE0 optimized ground state and triplet excited state of **1′** and **[{1′}$_2$Ag]$^+$**

1′ (Singlet Ground State)					**1′** (Triplet Excited State)				
1	C	9.514758	-1.235175	1.166873	1	C	9.513859	1.141161	-1.220350
2	C	8.503034	-0.531970	0.506384	2	C	8.499589	0.484173	-0.517676
3	C	7.144451	-0.832728	0.785943	3	C	7.142263	0.759719	-0.826704
4	C	6.787368	-1.830566	1.694708	4	C	6.788579	1.689126	-1.806504
5	C	7.814371	-2.516780	2.338700	5	C	7.818060	2.330491	-2.491586
6	C	9.165076	-2.222968	2.083434	6	C	9.167702	2.059582	-2.207635
7	N	6.329045	-0.012551	-0.000230	7	N	6.323958	-0.004501	0.012135
8	C	7.146616	0.811007	-0.780699	8	C	7.139350	-0.766990	0.855366
9	C	8.504419	0.515656	-0.491736	9	C	8.497738	-0.488647	0.553577
10	C	9.517843	1.223210	-1.144939	10	C	9.509597	-1.143565	1.261637
11	C	9.170546	2.209832	-2.063665	11	C	9.160085	-2.062727	2.247054
12	C	7.820470	2.498148	-2.328366	12	C	7.809511	-2.336382	2.523842
13	C	6.791790	1.807547	-1.691780	13	C	6.782378	-1.697118	1.833289
14	C	4.909746	-0.014638	-0.004355	14	C	4.905465	-0.006539	0.007954
15	C	4.207197	-0.216283	-1.198384	15	C	4.195474	0.264847	1.183826
16	C	2.817044	-0.208670	-1.203460	16	C	2.805426	0.253322	1.181508
17	C	2.085325	-0.017764	-0.012325	17	C	2.082218	-0.011830	-0.000099
18	C	2.810051	0.174454	1.183055	18	C	2.813228	-0.273604	-1.177659
19	C	4.200070	0.185198	1.185812	19	C	4.203326	-0.280032	-1.172084
20	C	0.660284	-0.018195	-0.015504	20	C	0.656618	-0.015911	-0.004009
21	C	-0.570541	-0.013002	-0.015031	21	C	-0.573178	-0.019426	-0.007366
22	Pt	-2.598719	0.001226	-0.004652	22	Pt	-2.610693	-0.014911	-0.002080
23	N	-2.996288	-1.980375	-0.184183	23	N	-2.960683	1.974263	0.173750
24	C	-4.310872	-2.287447	-0.206729	24	C	-4.283144	2.291545	0.221140
25	N	-4.482821	-3.640876	-0.330983	25	N	-4.433479	3.643791	0.339756
26	C	-3.217874	-4.224447	-0.389820	26	C	-3.158985	4.220049	0.368304
27	C	-2.289878	-3.163452	-0.295869	27	C	-2.241207	3.151882	0.261390
28	C	-2.806493	-5.551186	-0.514012	28	C	-2.739693	5.542928	0.475006
29	C	-1.434688	-5.785440	-0.541292	29	C	-1.364171	5.772603	0.471490
30	C	-0.504554	-4.730583	-0.447543	30	C	-0.444729	4.713101	0.364601
31	C	-0.913831	-3.408388	-0.323802	31	C	-0.864761	3.390526	0.257958
32	C	-5.267157	-1.196876	-0.101392	32	C	-5.249929	1.218383	0.139860
33	C	-4.561282	0.015679	0.006829	33	C	-4.578123	0.010604	0.022464
34	C	-5.247761	1.238564	0.123522	34	C	-5.269221	-1.239901	-0.081039
35	C	-6.650140	1.249189	0.131514	35	C	-6.715766	-1.208904	-0.074675
36	C	-7.340491	0.036442	0.023302	36	C	-7.363672	0.010772	0.044553
37	C	-6.669596	-1.186471	-0.092861	37	C	-6.679008	1.238625	0.156785
38	C	-4.274461	2.314892	0.217776	38	C	-4.355318	-2.280549	-0.177827
39	N	-4.425041	3.670584	0.345523	39	N	-4.459657	-3.655865	-0.291521
40	C	-3.151090	4.235431	0.389898	40	C	-3.175289	-4.194163	-0.402181
41	C	-2.239951	3.161028	0.283974	41	C	-2.254372	-3.107476	-0.326113
42	N	-2.964931	1.988534	0.179357	42	N	-2.949683	-1.944392	-0.182761
43	C	-2.718726	5.555855	0.510065	43	C	-2.741866	-5.497182	-0.554033
44	C	-1.343434	5.769888	0.521276	44	C	-1.350789	-5.713950	-0.622138
45	C	-0.430087	4.701587	0.415597	45	C	-0.438375	-4.654342	-0.543642
46	C	-0.860267	3.385690	0.295597	46	C	-0.871741	-3.336060	-0.396258
47	C	-5.677608	4.396490	0.421144	47	C	-5.692599	-4.410238	-0.292737
48	H	-6.259339	4.079237	1.290949	48	H	-6.244559	-4.280030	-1.230436
49	C	-5.746808	-4.348382	-0.390154	49	C	-5.688319	4.366287	0.420632
50	H	-6.323672	-4.192561	0.525667	50	H	-6.286006	4.207079	-0.480866
51	H	-0.176056	2.549367	0.212461	51	H	-0.187615	-2.498360	-0.334689
52	H	0.633372	4.913360	0.428101	52	H	0.624437	-4.860144	-0.600630
53	H	-0.966743	6.782908	0.613293	53	H	-0.984184	-6.727888	-0.740792
54	H	-3.410956	6.386574	0.591717	54	H	-3.431656	-6.330209	-0.623672
55	H	-7.253516	-2.096767	-0.173316	55	H	-7.247080	2.156036	0.247412
56	H	-8.425037	0.044563	0.029566	56	H	-8.449285	0.024157	0.048395
57	H	-7.219295	2.168145	0.218874	57	H	-7.300561	-2.116392	-0.171197
58	H	-0.216408	-2.582156	-0.249775	58	H	-0.171372	2.562347	0.174251
59	H	0.555436	-4.958076	-0.472458	59	H	0.617234	4.932902	0.364847
60	H	-1.074004	-6.803947	-0.636772	60	H	-0.997417	6.790049	0.552591
61	H	-3.511798	-6.371671	-0.586782	61	H	-3.439510	6.367127	0.557574
62	H	-5.461509	5.459688	0.521554	62	H	-5.462577	-5.469257	-0.168678
63	H	-6.269041	4.248573	-0.486611	63	H	-6.327022	-4.102802	0.543097
64	H	-5.547728	-5.414651	-0.493961	64	H	-5.475444	5.430992	0.511203
65	H	-6.335492	-4.021949	-1.251817	65	H	-6.261027	4.051051	1.296890
66	H	2.275368	-0.362418	-2.130242	66	H	2.257885	0.461340	2.094109
67	H	4.758648	-0.389650	-2.116626	67	H	4.741019	0.495756	2.092773
68	H	4.746018	0.359892	2.107103	68	H	4.754941	-0.508446	-2.078001
69	H	2.262659	0.326931	2.106683	69	H	2.271858	-0.482503	-2.093800
70	H	5.752272	2.039490	-1.893045	70	H	5.742663	-1.918884	2.044645
71	H	7.571780	3.277249	-3.041843	71	H	7.558982	-3.063246	3.289817
72	H	9.946936	2.765646	-2.578690	72	H	9.935193	-2.577143	2.805161
73	H	10.561191	1.008765	-0.935363	73	H	10.553404	-0.941018	1.042907
74	H	5.747424	-2.066820	1.888619	74	H	5.749555	1.908921	-2.023245
75	H	7.563846	-3.296764	3.050560	75	H	7.570115	3.056932	-3.258798
76	H	9.940115	-2.775473	2.604063	76	H	9.944709	2.575629	-2.761578
77	H	10.558647	-1.016545	0.964458	77	H	10.556903	0.940806	-0.996029

$[\{1'\}_2Ag]^+$ (Singlet Ground State)

1	C	5.569556	-6.148503	2.284564	53	N	-5.505595	2.940360	-0.426320	105	H	-1.148496	-3.528116	0.177011
2	C	6.303903	-5.175034	1.606224	54	C	-4.551327	3.789455	0.129597	106	H	-1.330352	-5.577983	-1.237591
3	C	7.680685	-5.348908	1.319511	55	C	-3.292278	3.279931	-0.260468	107	H	-3.536366	-6.465512	-1.902303
4	C	8.334305	-6.508130	1.745728	56	C	-4.671050	4.935790	0.915681	108	H	-5.632441	-5.341361	-1.205786
5	C	7.611972	-7.475151	2.439470	57	C	-3.488958	5.560786	1.304840	109	H	-3.036760	4.380663	5.402411
6	C	6.243531	-7.295924	2.699206	58	C	-2.229115	5.056910	0.921137	110	H	-4.169597	4.161357	4.059271
7	N	5.882049	-3.951581	1.059108	59	C	-2.111234	3.916716	0.134781	111	H	-7.157640	-4.039373	-0.188042
8	C	6.979469	-3.342774	0.427984	60	C	-5.319513	0.809052	-1.857694	112	H	-7.363854	-2.282250	-0.307279
9	C	8.110450	-4.184286	0.574124	61	C	-4.218902	0.114075	-2.385719	113	H	-1.149704	3.528449	-0.176570
10	C	9.340859	-3.786583	0.044297	62	C	-4.396276	-1.053366	-3.147218	114	H	-1.332766	5.578249	1.237984
11	C	9.431241	-2.561283	-0.610654	63	C	-5.692982	-1.529816	-3.387953	115	H	-3.539322	6.465063	1.901845
12	C	8.305912	-1.729312	-0.730656	64	C	-6.784895	-0.827816	-2.862781	116	H	-5.634768	5.340244	1.204516
13	C	7.067519	-2.105354	-0.211424	65	C	-6.617234	0.333205	-2.098473	117	H	-5.877468	-2.421596	-3.975580
14	C	4.578713	-3.421070	1.135013	66	C	-3.095371	-1.553020	-3.566426	118	H	-7.788678	-1.185065	-3.066870
15	C	3.913897	-3.347021	2.367512	67	N	-2.002203	-0.849142	-3.198265	119	H	-7.495763	0.840533	-1.716593
16	C	2.629835	-2.822168	2.442822	68	C	-0.896017	-1.495650	-3.720424	120	H	0.807588	-0.296261	-3.151093
17	C	1.978485	-2.346661	1.287208	69	C	-1.346440	-2.638704	-4.417907	121	H	2.411216	-1.837464	-4.287115
18	C	2.653780	-2.424894	0.054422	70	N	-2.735418	-2.643227	-4.305037	122	H	1.610010	-3.846172	-5.474264
19	C	3.933968	-2.959828	-0.021283	71	C	0.467791	-1.187314	-3.663886	123	H	-0.802076	-4.385743	-5.595115
20	C	0.656766	-1.802321	1.386973	72	C	1.348336	-2.052222	-4.303182	124	H	-7.159162	4.037761	0.186164
21	C	-0.502782	-1.438335	1.660514	73	C	0.891393	-3.197480	-4.986255	125	H	-7.364840	2.280571	0.305332
22	Pt	-2.404599	-0.772663	2.039992	74	C	-0.462669	-3.507742	-5.057663	126	H	-4.166739	-4.161958	-4.060022
23	N	-2.003622	0.849274	3.198331	75	C	-3.626952	-3.646952	-4.859145	127	H	-3.033331	-4.380876	-5.402741
24	C	-3.097167	1.552779	3.566083	76	C	-6.944777	3.087287	-0.301405	128	H	2.122765	-2.764180	3.399728
25	N	-2.737853	2.643111	4.304821	77	C	0.656845	1.802871	-1.386354	129	H	4.419152	-3.684114	3.265555
26	C	-1.348913	2.639062	4.418198	78	C	-0.502731	1.438953	-1.659857	130	H	4.437115	-3.041386	-0.978072
27	C	-0.897846	1.496159	3.720884	79	C	1.978586	2.347161	-1.286613	131	H	2.158730	-2.077142	-0.847117
28	C	-0.465665	3.508403	5.058265	80	C	2.629861	2.822785	-2.442222	132	H	4.509744	-6.028462	2.477234
29	C	0.888527	3.198599	4.987339	81	C	3.913953	3.347570	-2.366953	133	H	5.696043	-8.067270	3.230650
30	C	1.346106	2.053496	4.304432	82	C	3.934206	2.960075	0.021792	134	H	8.106641	-8.378839	2.778135
31	C	0.466084	1.188285	3.664828	83	C	2.653989	2.425208	-0.053875	135	H	9.388460	-6.654793	1.534086
32	C	-4.397741	1.052675	3.146381	84	C	4.578875	3.421436	-1.134500	136	H	6.208905	-1.449155	-0.299484
33	C	-4.219679	-0.114707	2.384947	85	N	5.882238	3.951886	-1.058639	137	H	8.400102	-0.769672	-1.227892
34	C	-5.319850	-0.810058	1.856505	86	C	6.979686	3.342964	-0.427674	138	H	10.379567	-2.240370	-1.027531
35	C	-6.617826	-0.334651	2.096787	87	C	8.110688	4.184449	-0.573812	139	H	10.215026	-4.421144	0.148113
36	C	-6.786173	0.826312	2.861031	88	C	7.680907	5.349172	-1.319030	140	H	4.509896	6.028989	-2.476405
37	C	-5.694700	1.528683	3.386622	89	C	6.304094	5.175386	-1.605649	141	H	5.696213	8.067836	-3.229685
38	C	-4.840899	-1.960842	1.106588	90	C	7.067741	2.105469	0.211587	142	H	8.106861	8.379256	-2.777338
39	N	-3.505820	-2.149847	1.026916	91	C	8.306163	1.729321	0.730676	143	H	9.388715	6.655015	-1.533596
40	C	-3.291179	-3.280277	0.260082	92	C	9.431514	2.561262	0.610675	144	H	6.209110	1.449293	0.299647
41	C	-4.549912	-3.790215	-0.130465	93	C	9.341126	3.786639	-0.044131	145	H	8.400355	0.769623	1.227799
42	N	-5.504669	-2.941429	0.425078	94	C	5.569729	6.148963	-2.283812	146	H	10.379861	2.240266	1.027439
43	C	-2.109781	-3.916691	-0.134707	95	C	6.243715	7.296406	-2.698378	147	H	10.215307	4.421179	-0.147946
44	C	-2.226992	-5.056930	-0.921098	96	C	7.612185	7.475548	-2.438738	148	H	2.158994	2.077364	0.847658
45	C	-3.486523	-5.561215	-1.305285	97	C	8.334538	6.508418	-1.745167	149	H	4.437437	3.041491	0.978549
46	C	-4.668964	-4.936595	-0.916585	98	H	0.806362	0.297346	3.152152	150	H	4.419147	3.684755	-3.264995
47	C	-6.943755	-3.088830	0.299614	99	H	2.409066	1.839108	4.288739	151	H	2.122708	2.764944	-3.399093
48	C	-3.629932	3.646537	4.858596	100	H	1.606750	3.847539	5.475599	152	H	-7.415210	3.099573	-1.287246
49	Ag	-0.203232	0.000313	0.000333	101	H	-0.805561	4.386292	5.595592	153	H	-7.414560	-3.101278	1.285276
50	Pt	-2.404188	0.772660	-2.040046	102	H	-7.496036	-0.842278	1.714572	154	H	-4.336856	3.192904	5.557785
51	N	-3.506258	2.149440	-1.027392	103	H	-7.790156	1.183219	3.064738	155	H	-4.333770	-3.193557	-5.558594
52	C	-4.841242	1.959994	-1.107582	104	H	-5.879713	2.420400	3.974181					

$[\{1'\}_2Ag]^+$ (Triplet Excited State)

1	C	-5.631501	-6.173178	-2.179703	53	N	5.522084	2.935487	0.388288	105	H	1.109163	-3.577235	-0.228606
2	C	-6.365059	-5.178873	-1.531380	54	C	4.559158	3.782424	-0.164225	106	H	1.301369	-5.628714	1.182576
3	C	-7.742745	-5.341537	-1.242736	55	C	3.304387	3.263881	0.227279	107	H	3.510374	-6.486216	1.874807
4	C	-8.398198	-6.510981	-1.636971	56	C	4.672720	4.929271	-0.946750	108	H	5.599372	-5.333563	1.205285
5	C	-7.676655	-7.499110	-2.301139	57	C	3.486247	5.551833	-1.333662	109	H	2.962655	4.365451	-5.417887
6	C	-6.307246	-7.330516	-2.562742	58	C	2.231704	5.040909	-0.948775	110	H	4.092950	4.150916	-4.071683
7	N	-5.941610	-3.941028	-1.018410	59	C	2.120764	3.896601	-0.164455	111	H	7.119040	-3.974344	0.267983
8	C	-7.039086	-3.312371	-0.406830	60	C	5.360714	0.802536	1.809847	112	H	7.297864	-2.212058	0.298934
9	C	-8.171465	-4.155451	-0.531407	61	C	4.286783	0.111642	2.349480	113	H	1.160768	3.504956	0.146567
10	C	-9.402042	-3.740996	-0.015066	62	C	4.459953	-1.076481	3.137744	114	H	1.331434	5.558050	-1.261644
11	C	-9.491287	-2.497935	0.605666	63	C	5.812567	-1.537515	3.363511	115	H	3.532234	6.457839	-1.928272
12	C	-8.364683	-1.664982	0.704371	64	C	6.867171	-0.830043	2.813935	116	H	5.634388	5.337395	-1.237243
13	C	-7.126169	-2.057408	0.197634	65	C	6.688467	0.332670	2.027492	117	H	6.012979	-2.413333	3.969136
14	C	-4.636641	-3.416679	-1.105290	66	C	3.232173	-1.564009	3.553965	118	H	7.879940	-1.171839	3.005107
15	C	-3.965540	-3.383838	-2.336262	67	N	2.052782	-0.814160	3.174228	119	H	7.556721	0.838361	1.624647
16	C	-2.679157	-2.866410	-2.422092	68	C	0.984027	-1.435066	3.734046	120	H	-0.713297	-0.211829	3.190183
17	C	-2.031363	-2.356323	-1.279201	69	C	1.434785	-2.592510	4.444924	121	H	-2.330349	-1.709873	4.375847
18	C	-2.713472	-2.392358	-0.048289	70	N	2.820575	-2.645521	4.311820	122	H	-1.532438	-3.718392	5.568421
19	C	-3.995729	-2.920465	0.038633	71	C	-0.384166	-1.104574	3.706065	123	H	0.874979	-4.301460	5.646388
20	C	-0.707461	-1.819643	-1.390260	72	C	-1.272232	-1.945023	4.372717	124	H	7.163906	4.074620	-0.179091
21	C	0.451830	-1.464567	-1.677563	73	C	-0.817942	-3.084546	5.055196	125	H	7.385350	2.324278	-0.374640
22	Pt	2.352129	-0.794875	-2.061630	74	C	0.548388	-3.423093	5.103079	126	H	4.246023	-4.161384	4.045092
23	N	1.944314	0.825827	-3.220108	75	C	3.687794	-3.672688	4.849440	127	H	3.079868	-4.427062	5.348487
24	C	3.034889	1.535182	-3.585869	76	C	6.959491	3.101258	0.265844	128	H	-2.167598	-2.840669	-3.377994
25	N	2.670943	2.624627	-4.323458	77	C	-0.613130	1.777909	1.379015	129	H	-4.467679	-3.747133	-3.225771
26	C	1.282147	2.614217	-4.437985	78	C	0.545403	1.403342	1.643516	130	H	-4.503734	-2.969449	0.995067
27	C	0.835893	1.468178	-3.742659	79	C	-1.928615	2.339427	1.288150	131	H	-2.221718	-2.016263	0.843624
28	C	0.395331	3.480365	-5.077346	80	C	-2.569723	2.816300	2.448869	132	H	-4.570970	-6.061446	-2.373309
29	C	-0.957576	3.164424	-5.007749	81	C	-3.848253	3.355357	2.381683	133	H	-5.760366	-8.118026	-3.070558
30	C	-1.410350	2.016349	-4.326771	82	C	-3.881560	2.982008	-0.009503	134	H	-8.172693	-8.410979	-2.614926
31	C	-0.526670	1.154125	-3.687898	83	C	-2.607321	2.432564	0.058205	135	H	-9.453125	-6.649124	-1.423489
32	C	4.337123	1.042511	-3.163181	84	C	-4.517369	3.443003	1.152147	136	H	-6.266783	-1.400166	0.268613
33	C	4.164300	-0.124911	-2.401044	85	N	-5.815331	3.985732	1.084373	137	H	-8.457668	-0.691916	1.175100
34	C	5.266392	-0.809923	-1.863960	86	C	-6.918613	3.394564	0.445811	138	H	-10.439697	-2.164057	1.012037
35	C	6.561994	-0.327055	-2.100834	87	C	-8.042463	4.242943	0.605460	139	H	-10.277167	-4.376643	-0.102828
36	C	6.725731	0.832141	-2.868928	88	C	-7.602519	5.393647	1.366550	140	H	-4.424690	6.034301	2.527451
37	C	5.631952	1.526431	-3.399886	89	C	-6.226958	5.205118	1.649184	141	H	-5.594260	8.071262	3.309908
38	C	4.792642	-1.962036	-1.112897	90	C	-7.017804	2.166738	-0.210215	142	H	-8.003103	8.407068	2.865725
39	N	3.458777	-2.165911	-1.046732	91	C	-8.259985	1.808107	-0.732901	143	H	-9.299784	6.709803	1.600414
40	C	3.249270	-3.299653	-0.283398	92	C	-9.378221	2.647466	-0.599660	144	H	-6.165014	1.504472	-0.308524
41	C	4.509813	-3.794171	0.120876	93	C	-9.276839	3.862758	0.072234	145	H	-8.362744	0.856514	-1.243744
42	N	5.460039	-2.932796	-0.422584	94	C	-5.484046	6.164053	2.338758	146	H	-10.329683	2.340288	-1.019666
43	C	2.071692	-3.952984	0.094943	95	C	-6.148574	7.311090	2.769571	147	H	-10.145632	4.502859	0.186326
44	C	2.194558	-5.093837	0.879484	96	C	-7.515916	7.504142	2.514496	148	H	-2.119824	2.084875	-0.847527
45	C	3.455809	-5.582010	1.278204	97	C	-8.246636	6.552036	1.808920	149	H	-4.386607	3.075502	-0.964119
46	C	4.634230	-4.941017	0.905294	98	H	-0.863367	0.260669	-3.177245	150	H	-4.346154	3.692771	3.283642
47	C	6.899484	-3.054399	-0.272528	99	H	-2.472292	1.796807	-4.312341	151	H	-2.059297	2.749065	3.403446
48	C	3.558669	3.634144	-4.873379	100	H	-1.678338	3.810766	-5.495717	152	H	7.430223	3.073192	1.250838
49	Ag	0.185590	-0.025034	-0.014763	101	H	0.731650	4.360542	-5.613164	153	H	7.383862	-3.110156	-1.250396
50	Pt	2.459442	0.742842	2.021024	102	H	7.441506	-0.827759	-1.712943	154	H	4.270047	3.185485	-5.571215
51	N	3.529228	2.131125	0.987755	103	H	7.728235	1.194350	-3.070649	155	H	4.384797	-3.255145	5.582775
52	C	4.871414	1.947009	1.065161	104	H	5.813212	2.418275	-3.988353					

References

1 V. W. W. Yam, R. P. L. Tang, K. M. C. Wong, K. K. Cheung, *Organometallics*, 2001, **20**, 4476.

2 Bruker AXS Inc. *SMART* version 5.059, Madison, Wisconsin, USA, 1998.

3 SAINT+. SAX area detector integration program. Version 7.34A. Bruker AXS, Inc. Madison, WI.

4 G. M. Sheldrick, SADABS, Empirical Absorption Correction Program. University of Göttingen: Göttingen, Germany, 2004.

5 SHELXS97, Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Goetingen, Germany.

6 SHELXL97, Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Goetingen, Germany.

7 The weighing scheme is $w = 1/[\sigma^2(F_o^2) + (0.1144P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

8 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03 (Revision E.01), Gaussian, Inc., Wallingford CT, 2004.

9 (*a*) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; (*b*) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396; (*c*) C. Adamo and V. Barone, *J. Chem. Phys.***,** 1999, **110**, 6158.

10 (*a*) R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys.*, 1998, **109**, 8218; (*b*) R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454; (*c*) M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, *J. Chem. Phys.*, 1998, **108**, 4439.

11 (*a*) V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995; (*b*) M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669.

12 D. Andrae, U. Häussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123.

13 A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 111.

14 (*a*) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; (*b*) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (*c*) 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.

15 (*a*) 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; (*b*) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

16 R. Pis Diez, MullPop, National University of La Plata: Argentina, 2003.

17 E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, NBO Version 3.1.