Excited States of $Pt(PF_3)_4$ and Their Role in Focused Electron-Beam Nanofabrication

SUPPLEMENTARY INFORMATION

Matija Zlatar,[*,†] Michael Allan,[*,‡] and Juraj Fedor[*,¶]

†*Department of Chemistry, Institute of Chemistry, Technology and Metallurgy (IChTM), University of Belgrade, Njegoševa 12, P.O. Box 815, 11001 Belgrade, Serbia*

‡*Departement of Chemistry, University of Fribourg, Chemin du musée 9, 1700 Fribourg, Switzerland*

¶*J. Heyrovský Institute of Physical Chemistry v.v.i., The Czech Academy of Sciences, Dolejškova 3, 18223 Prague, Czech Republic*

E-mail: matijaz@chem.bg.ac.rs; michael.allan@unifr.ch; juraj.fedor@jh-inst.cas.cz

Table S1: Pt-P bond lengths (Å) and at different levels of theory and comparison with previously reported results.

Present results			Previous results			
	Relativistic	Non-relativistic	Theory		Experiment	
LDA	2.222	2.332	MP2[1]	2.239		
B3LYP	2.279	2.457	BP86[2]	2.276	X-ray[1]	2.224
B3LYP-D3	2.266	2.428	MPW91PW91[2]	2.255	El. diffr[3]	2.229

Comparison of calculated molecular properties with experimental data

In order to test the performance of theoretical methods we have calculated the basic properties of $Pt(PF_3)_4$ and compared them to available experimental data. Table S1 shows the comparison for the Pt-P bond length. The experimental values are 2.229 Å as determined by electron diffraction and 2.224 Å as determined by X-ray scattering. In the Table S1 the results of previous calculation[1] at MP2 level with relativistic corrected core potentials are included as well. The best agreement with experimental bond lengths have been achieved with scalar relativistic (SR) LDA/TZP level of theory. SR-B3LYP/TZP and SR-B3LYP-D3/TZP give slightly longer Pt-P bond lengths. Inclusion of relativistic corrections is indispensable for reasonable agreement with the experiment.

Table S2 shows the calculated vibrational frequencies and their comparison with experimental data. SR calculations show better agreement with experimentally determined frequencies. Non-relativistic (NR) calculations give lower frequencies, corroborating longer bond lengths, Table S1.

Bonding analysis

Results for the energy decomposition analysis of $Pt(PF_3)_4$ at different levels of theory are summarized in Table S3. This nature of bonding, in principle, does not change at different level of theory, however interaction energy between two fragments is significantly lower if

Table S2: Selected vibrational frequencies of $Pt(PF_3)_4$ (meV) at different levels of theory and comparison with previously reported results.

Description	Present results						Previous work	
	Relativistic			Non-relativistic				
	LDA	B3LYP	B3LYP-D3	LDA	B3LYP	B3LYP-D3	Exp.[4]	Exp.[5]
P−F symm str	109	107	108	108	106	106	119	113
P−F asymm str	104	102	103	103	102	102	106	107
PF_3 symm def	60	60	60	57	57	57	68	65
PF_3 asymm def	43	44	44	41	42	42	41	48
PF_3 rock	26	24	25	19	14	16	35	35
Pt−P asymm str	28	26	27	23	18	19	27	26
PtP_4 def	6	7	6	3	4	4	6	6

NR calculations are employed. This is in accordance with longer Pt−P equilibrium bond lengths in non-relativistic situation, Table S1.

Table S3: Energy decomposition analysis of $Pt(PF_3)_3{-}{-}PF_3$ (energy components given in eV; values in parentheses give the percentage of the total attractive interactions: $E_{\mathbf{elst}} + E_{\mathbf{orb}} + E_{\mathbf{disp}}$)

	Relativistic		Non-relativistic	
	B3LYP	B3LYP-D3	B3LYP	B3LYP-D3
$E_{\mathrm{def}}(Pt(PF_3)_3)$	0.7183	0.6812	0.4341	0.4113
$E_{\mathrm{def}}(PF_3)$	0.0128	0.0153	0.0057	0.0069
E_{prep}	0.7311	0.6965	0.4398	0.4182
E_{Pauli}	7.3848	7.7207	4.1519	4.5791
E_{elst}	-5.8000 (67 %)	-6.0468 (65 %)	-3.3163 (67 %)	-3.6266 (64 %)
E_{orb}	-2.8337 (33 %)	-2.9196 (31 %)	-1.6200 (33 %)	-1.7259 (31 %)
E_{disp}	–	-0.3567 (4 %)	–	-0.3001 (5 %)
E_{int}	-1.2488	-1.6025	-0.7844	-1.0735
BDE	0.5178	0.9060	0.3446	0.6553

Excited states

Tables S4, S5, S6 list the calculated excited states, their energies and oscillator strengths. The excitation energies were calculated at the SR-LDA/TZP ground state geometry using the SR-SAOP/TZP method (see Figure 1 in the main text). Ground electronic state of $Pt(PF_3)_4$ is $^1A_1$, with electronic configuration: $...(7e)^4(6t_1)^6(20t_2)^6(8e)^4(7t_1)^6(14a_1)^2(8t_1)^6(1a_2)^2(21t_2)^6(9e)^4$

$(22t_2)^6(23t_2)^0(10e)^0(9t_1)^0(15a_1)^0(16a_1)^0(24t_2)^0(25t_2)^0(11e)^0(17a_1)^0(26t_2)^0(10t_1)^0(27t_2)^0$ ... Description of electronic states by TDDFT is given by linear combination of single excitations, as given in Tables S4, S5 and S6.

Dipole allowed transitions are to the excited $^1T_2$ states, Table S4. Spin allowed, dipole forbidden transitions are given in Table S5, while singlet-triplet transitions are collected in Table S6.

Table S4: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) spin and dipole allowed transitions, the corresponding oscillator strenghts (f), and description of the dominant one-electron excitations (contributions greater than 10 %) of $Pt(PF_3)_4$

E (eV)	f	Assignment	%	E (eV)	f	Assignment	%
5.885	0.44364E-01	$22t_2 \rightarrow 23t_2$	77.11	10.599	0.37307E-01	$22t_2 \rightarrow 17a_1$	69.66
		$22t_2 \rightarrow 10e$	18.55			$8t_1 \rightarrow 10e$	10.94
6.525	0.12539	$22t_2 \rightarrow 10e$	70.30	10.648	0.11706E-01	$8t_1 \rightarrow 10e$	76.79
		$22t_2 \rightarrow 15a_1$	14.28	10.779	0.43323E-02	$22t_2 \rightarrow 26t_2$	85.41
		$22t_2 \rightarrow 23t_2$	11.44	10.937	0.98605E-02	$7t_1 \rightarrow 10e$	90.51
6.904	0.94420E-01	$22t_2 \rightarrow 15a_1$	54.71	10.971	0.11875E-02	$9e \rightarrow 24t_2$	94.55
		$22t_2 \rightarrow 9t_1$	37.68	11.058	0.81334E-04	$20t_2 \rightarrow 10e$	91.94
7.236	0.28466	$22t_2 \rightarrow 9t_1$	54.09	11.094	0.26430E-03	$1a_2 \rightarrow 9t_1$	47.15
		$22t_2 \rightarrow 15a_1$	26.22			$8t_1 \rightarrow 9t_1$	49.17
8.246	0.17888E-01	$22t_2 \rightarrow 16a_1$	46.85	11.107	0.72610E-02	$21t_2 \rightarrow 9t_1$	51.98
		$22t_2 \rightarrow 24t_2$	46.27			$8t_1 \rightarrow 9t_1$	19.75
8.350	0.73354E-03	$22t_2 \rightarrow 16a_1$	45.25	11.190	0.50058E-02	$21t_2 \rightarrow 15a_1$	22.98
		$22t_2 \rightarrow 24t_2$	50.75			$1a_2 \rightarrow 9t_1$	18.08
8.568	0.12845	$9e \rightarrow 23t_2$	85.91			$22t_2 \rightarrow 10t_1$	34.20
9.551	0.18121	$9e \rightarrow 9t_1$	85.25			$8t_1 \rightarrow 9t_1$	14.11
9.655	0.31007E-01	$22t_2 \rightarrow 25t_2$	98.80	11.196	0.10471	$21t_2 \rightarrow 15a_1$	36.79
10.056	0.78400E-01	$21t_2 \rightarrow 23t_2$	76.32			$22t_2 \rightarrow 10t_1$	51.33
		$8t_1 \rightarrow 23t_2$	11.42	11.227	0.73014E-01	$1a_2 \rightarrow 9t_1$	18.88
10.110	0.52105E-01	$8t_1 \rightarrow 23t_2$	84.16			$21t_2 \rightarrow 15a_1$	11.36
10.224	0.38502E-01	$14a_1 \rightarrow 23t_2$	82.79			$21t_2 \rightarrow 9t_1$	14.97
10.409	0.79109E-02	$7t_1 \rightarrow 23t_2$	84.85			$22t_2 \rightarrow 27t_2$	13.76
10.468	0.44058E-02	$22t_2 \rightarrow 11e$	77.17			$22t_2 \rightarrow 10t_1$	10.96
		$8e \rightarrow 23t_2$	11.31			$8t_1 \rightarrow 9t_1$	10.80
10.506	0.24861E-02	$21t_2 \rightarrow 10e$	45.37	11.391	0.15589E-02	$6t_1 \rightarrow 23t_2$	86.73
		$20t_2 \rightarrow 23t_2$	35.93	11.416	0.54315E-04	$7e \rightarrow 23t_2$	39.26
10.530	0.36624E-03	$8e \rightarrow 23t_2$	46.26			$19t_2 \rightarrow 23t_2$	53.19
		$21t_2 \rightarrow 10e$	16.39	11.463	0.19230E-03	$7t_1 \rightarrow 9t_1$	76.50
		$20t_2 \rightarrow 23t_2$	19.76			$20t_2 \rightarrow 9t_1$	13.41
10.538	0.10297E-01	$8e \rightarrow 23t_2$	38.55				
		$20t_2 \rightarrow 23t_2$	28.47				
		$21t_2 \rightarrow 10e$	16.48				

Table S5: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) spin allowed, dipole forbidden transitions, their symmetry label, the corresponding oscillator strenghts (f), and description of the dominant one-electron excitations (contributions greater than 10 %) of $Pt(PF_3)_4$

Symmetry	E (eV)	f	Assignment	%

Table S5: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) dipole forbidden transitions

Symmetry	E (eV)	f	Assignment	%
A_1	5.9241	0.0000	$22t_2 \rightarrow 23t_2$	96.45
	8.4208	0.0000	$22t_2 \rightarrow 24t_2$	94.98
	9.3659	0.0000	$9e \rightarrow 10e$	62.74
			$21t_2 \rightarrow 23t_2$	33.85
	9.6158	0.0000	$22t_2 \rightarrow 25t_2$	99.83
	10.511	0.0000	$20t_2 \rightarrow 23t_2$	71.67
			$2t_2 \rightarrow 26t_2$	12.01
			$21t_2 \rightarrow 23t_2$	11.17
	10.701	0.0000	$22t_2 \rightarrow 26t_2$	53.93
			$20t_2 \rightarrow 23t_2$	20.74
			$21t_2 \rightarrow 23t_2$	10.72
	11.017	0.0000	$8e \rightarrow 10e$	49.20
			$14a_1 \rightarrow 15a_1$	20.64
			$22t_2 \rightarrow 26t_2$	18.13
	11.099	0.0000	$8t_1 \rightarrow 9t_1$	99.97
	11.152	0.0000	$14a_1 \rightarrow 15a_1$	43.48
			$8e \rightarrow 10e$	34.14
	11.420	0.0000	$22t_2 \rightarrow 27t_2$	57.34
			$19t_2 \rightarrow 23t_2$	34.63
	11.436	0.0000	$19t_2 \rightarrow 23t_2$	63.13
			$22t_2 \rightarrow 27t_2$	28.00
	11.568	0.0000	$7t_1 \rightarrow 9t_1$	68.78
A_2	6.6127	0.0000	$22t_2 \rightarrow 9t_1$	100.00
	8.7871	0.0000	$9e \rightarrow 10e$	100.00

Table S5: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) dipole forbidden transitions

Symmetry	E (eV)	f	Assignment	%
	10.068	0.0000	$8t_1 \rightarrow 23t_2$	99.70
	10.369	0.0000	$7t_1 \rightarrow 23t_2$	99.76
	10.929	0.0000	$21t_2 \rightarrow 9t_1$	99.83
	11.004	0.0000	$8e \rightarrow 10e$	99.37
	11.187	0.0000	$22t_2 \rightarrow 10t_1$	99.92
	11.234	0.0000	$1a_2 \rightarrow 15a_1$	97.16
	11.393	0.0000	$6t_1 \rightarrow 23t_2$	97.48
E	5.8437	0.0000	$22t_2 \rightarrow 23t_2$	96.36
	6.9036	0.0000	$22t_2 \rightarrow 9t_1$	95.67
	8.2597	0.0000	$22t_2 \rightarrow 24t_2$	99.97
	9.0108	0.0000	$9e \rightarrow 10e$	97.08
	9.5683	0.0000	$9e \rightarrow 15a_1$	91.34
	9.6728	0.0000	$22t_2 \rightarrow 25t_2$	93.37
	10.024	0.0000	$21t_2 \rightarrow 23t_2$	84.99
			$8t_1 \rightarrow 23t_2$	10.48
	10.116	0.0000	$8t_1 \rightarrow 23t_2$	85.94
	10.376	0.0000	$7t_1 \rightarrow 23t_2$	98.77
	10.524	0.0000	$20t_2 \rightarrow 23t_2$	95.51
	10.620	0.0000	$1a_2 \rightarrow 10e$	80.71
			$14a_1 \rightarrow 10e$	13.60
	10.682	0.0000	$14a_1 \rightarrow 10e$	49.71
			$22t_2 \rightarrow 26t_2$	37.98
	10.725	0.0000	$22t_2 \rightarrow 26t_2$	55.65
			$14a_1 \rightarrow 10e$	23.72

Table S5: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) dipole forbidden transitions

Symmetry	E (eV)	f	Assignment	%
	10.853	0.0000	$9e \rightarrow 16a_1$	90.16
	11.026	0.0000	$8e \rightarrow 10e$	96.69
	11.100	0.0000	$21t_2 \rightarrow 9t_1$	65.26
			$8t_1 \rightarrow 9t_1$	20.21
	11.188	0.0000	$22t_2 \rightarrow 10t_1$	85.27
			$8t_1 \rightarrow 9t_1$	13.30
	11.234	0.0000	$8t_1 \rightarrow 9t_1$	52.41
			$19t_2 \rightarrow 23t_2$	13.97
			$21t_2 \rightarrow 9t_1$	14.75
	11.389	0.0000	$6t_1 \rightarrow 23t_2$	89.09
	11.408	0.0000	$22t_2 \rightarrow 27t_2$	92.56
T_1	5.7151	0.20106e-33	$22t_2 \rightarrow 23t_2$	92.97
	6.1971	0.33217e-32	$22t_2 \rightarrow 10e$	92.13
	6.7380	0.83888e-34	$22t_2 \rightarrow 9t_1$	95.54
	8.2606	0.49880e-35	$22t_2 \rightarrow 24t_2$	99.74
	8.3061	0.12464e-32	$9e \rightarrow 23t_2$	99.60
	9.3172	0.14140e-32	$9e \rightarrow 9t_1$	99.83
	9.6414	0.18301e-35	$22t_2 \rightarrow 25t_2$	98.76
	9.9405	0.18501e-36	$21t_2 \rightarrow 23t_2$	94.83
	10.062	0.62807e-36	$1a_2 \rightarrow 23t_2$	49.36
			$8t_1 \rightarrow 23t_2$	50.25
	10.098	0.10198e-35	$1a_2 \rightarrow 23t_2$	47.30
			$8t_1 \rightarrow 23t_2$	48.02
	10.390	0.39794e-37	$7t_1 \rightarrow 23t_2$	98.19

Table S5: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) dipole forbidden transitions

Symmetry	E (eV)	f	Assignment	%
	10.448	0.22650e-34	$21t_2 \rightarrow 10e$	63.25
			$22t_2 \rightarrow 11e$	28.77
	10.473	0.22395e-34	$8e \rightarrow 23t_2$	49.52
			$22t_2 \rightarrow 11e$	45.21
	10.493	0.40701e-34	$8e \rightarrow 23t_2$	38.19
			$21t_2 \rightarrow 10e$	26.53
			$22t_2 \rightarrow 11e$	20.88
	10.500	0.50353e-35	$20t_2 \rightarrow 23t_2$	88.07
	10.641	0.21616e-39	$8t_1 \rightarrow 10e$	90.58
	10.698	0.11680e-37	$22t_2 \rightarrow 26t_2$	98.56
	10.904	0.99746e-34	$7t_1 \rightarrow 10e$	98.27
	10.959	0.20640e-35	$9e \rightarrow 24t_2$	63.73
			$21t_2 \rightarrow 9t_1$	33.28
	10.980	0.22762e-35	$21t_2 \rightarrow 9t_1$	52.53
			$9e \rightarrow 24t_2$	34.95
	11.027	0.31398e-34	$20t_2 \rightarrow 10e$	96.78
	11.184	0.24337e-35	$8t_1 \rightarrow 9t_1$	77.16
			$14a_1 \rightarrow 9t_1$	11.39
	11.186	0.51450e-38	$22t_2 \rightarrow 10t_1$	91.04
	11.248	0.32106e-35	$8t_1 \rightarrow 15a_1$	96.90
	11.294	0.64323e-36	$14a_1 \rightarrow 9t_1$	55.04
			$22t_2 \rightarrow 27t_2$	18.10
			$6t_1 \rightarrow 23t_2$	10.63
	11.388	0.10163e-33	$7e \rightarrow 23t_2$	28.53

Table S5: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) dipole forbidden transitions

Symmetry	E (eV)	f	Assignment	%
			$22t_2 \rightarrow 27t_2$	40.94
			$6t_1 \rightarrow 23t_2$	26.29
	11.403	0.31738e-33	$7e \rightarrow 23t_2$	65.31
			$22t_2 \rightarrow 27t_2$	23.51
	11.419	0.55380e-35	$7t_1 \rightarrow 9t_1$	47.20

Table S6: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) singlet-triplet transitions, their symmetry label, the corresponding oscillator strenghts (f), and description of the dominant one-electron excitations (contributions greater than 10 %) of $Pt(PF_3)_4$

Symmetry	E (eV)	f	Assignment	%
A_1	5.3835	0.0000	$22t_2 \rightarrow 23t_2$	99.72
	8.2005	0.0000	$22t_2 \rightarrow 24t_2$	99.72
	8.5016	0.0000	$9e \rightarrow 10e$	98.40
	9.5889	0.0000	$22t_2 \rightarrow 25t_2$	99.42
	9.7101	0.0000	$21t_2 \rightarrow 23t_2$	98.08
	10.402	0.0000	$20t_2 \rightarrow 23t_2$	97.77
	10.598	0.0000	$22t_2 \rightarrow 26t_2$	98.59
	10.938	0.0000	$8e \rightarrow 10e$	96.71
	11.099	0.0000	$8t_1 \rightarrow 9t_1$	99.98
	11.212	0.0000	$14a_1 \rightarrow 15a_1$	93.55
	11.305	0.0000	$22t_2 \rightarrow 27t_2$	87.42
	11.345	0.0000	$7t_1 \rightarrow 9t_1$	82.80
			$19t_2 \rightarrow 23t_2$	14.41
A_2	6.6120	0.0000	$22t_2 \rightarrow 9t_1$	100.00

Table S6: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) singlet-triplet transitions

Symmetry	E (eV)	f	Assignment	%
	8.7859	0.0000	$9e \rightarrow 10e$	100.00
	10.021	0.0000	$8t_1 \rightarrow 23t_2$	99.73
	10.346	0.0000	$7t_1 \rightarrow 23t_2$	99.79
	10.928	0.0000	$21t_2 \rightarrow 9t_1$	99.68
	10.979	0.0000	$8e \rightarrow 10e$	99.18
	11.167	0.0000	$1a_2 \rightarrow 15a_1$	94.83
	11.186	0.0000	$22t_2 \rightarrow 10t_1$	99.53
	11.316	0.0000	$6t_1 \rightarrow 23t_2$	95.31
E	5.4175	0.0000	$22t_2 \rightarrow 23t_2$	99.68
	6.4855	0.0000	$22t_2 \rightarrow 9t_1$	99.58
	8.2430	0.0000	$22t_2 \rightarrow 24t_2$	99.95
	8.6493	0.0000	$9e \rightarrow 10e$	99.54
	9.3530	0.0000	$9e \rightarrow 15a_1$	99.03
	9.5944	0.0000	$22t_2 \rightarrow 25t_2$	96.66
	9.7641	0.0000	$21t_2 \rightarrow 23t_2$	95.56
	9.9994	0.0000	$8t_1 \rightarrow 23t_2$	98.95
	10.338	0.0000	$7t_1 \rightarrow 23t_2$	99.42
	10.434	0.0000	$20t_2 \rightarrow 23t_2$	98.57
	10.520	0.0000	$1a_2 \rightarrow 10e$	97.98
	10.563	0.0000	$14a_1 \rightarrow 10e$	93.00
	10.659	0.0000	$22t_2 \rightarrow 26t_2$	92.49
	10.739	0.0000	$9e \rightarrow 16a_1$	92.86
	10.857	0.0000	$21t_2 \rightarrow 9t_1$	94.78
	10.959	0.0000	$8e \rightarrow 10e$	98.66
	11.046	0.0000	$8t_1 \rightarrow 9t_1$	97.84

Table S6: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) singlet-triplet transitions

Symmetry	E (eV)	f	Assignment	%
	11.172	0.0000	$22t_2 \rightarrow 10t_1$	99.63
	11.320	0.0000	$6t_1 \rightarrow 23t_2$	84.38
			$19t_2 \rightarrow 23t_2$	10.93
	11.335	0.0000	$22t_2 \rightarrow 27t_2$	96.19
T_1	5.4149	0.0000	$22t_2 \rightarrow 23t_2$	97.81
	6.0224	0.0000	$22t_2 \rightarrow 10e$	98.39
	6.5170	0.0000	$22t_2 \rightarrow 9t_1$	98.89
	8.1942	0.0000	$9e \rightarrow 23t_2$	99.71
	8.2545	0.0000	$22t_2 \rightarrow 24t_2$	99.93
	9.2941	0.0000	$9e \rightarrow 9t_1$	99.80
	9.6031	0.0000	$22t_2 \rightarrow 25t_2$	98.53
	9.8198	0.0000	$21t_2 \rightarrow 23t_2$	97.56
	9.9892	0.0000	$1a_2 \rightarrow 23t_2$	85.98
			$8t_1 \rightarrow 23t_2$	13.10
	10.018	0.0000	$8t_1 \rightarrow 23t_2$	86.40
			$1a_2 \rightarrow 23t_2$	13.32
	10.321	0.0000	$7t_1 \rightarrow 23t_2$	98.68
	10.340	0.0000	$21t_2 \rightarrow 10e$	95.66
	10.437	0.0000	$22t_2 \rightarrow 11e$	85.65
			$8e \rightarrow 23t_2$	10.05
	10.445	0.0000	$8e \rightarrow 23t_2$	85.53
			$22t_2 \rightarrow 11e$	12.00
	10.459	0.0000	$20t_2 \rightarrow 23t_2$	95.67
	10.534	0.0000	$8t_1 \rightarrow 10e$	97.47
	10.677	0.0000	$22t_2 \rightarrow 26t_2$	99.07

Table S6: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) singlet-triplet transitions

Symmetry	E (eV)	f	Assignment	%
	10.864	0.0000	$7t_1 \rightarrow 10e$	87.06
	10.882	0.0000	$21t_2 \rightarrow 9t_1$	79.62
			$7t_1 \rightarrow 10e$	11.98
	10.949	0.0000	$9e \rightarrow 24t_2$	97.94
	10.984	0.0000	$20t_2 \rightarrow 10e$	97.78
	11.045	0.0000	$8t_1 \rightarrow 9t_1$	97.35
	11.091	0.0000	$14a_1 \rightarrow 9t_1$	91.39
	11.180	0.0000	$22t_2 \rightarrow 10t_1$	85.14
			$8t_1 \rightarrow 15a_1$	12.87
	11.181	0.0000	$8t_1 \rightarrow 15a_1$	82.49
			$22t_2 \rightarrow 10t_1$	13.45
	11.306	0.0000	$6t_1 \rightarrow 23t_2$	84.62
			$7e \rightarrow 23t_2$	10.32
	11.329	0.0000	$7e \rightarrow 23t_2$	78.71
			$6t_1 \rightarrow 23t_2$	10.43
	11.361	0.0000	$19t_2 \rightarrow 23t_2$	75.78
			$22t_2 \rightarrow 27t_2$	15.92
T_2	5.4183	0.0000	$22t_2 \rightarrow 23t_2$	99.25
	5.9203	0.0000	$22t_2 \rightarrow 10e$	97.97
	6.4289	0.0000	$22t_2 \rightarrow 9t_1$	98.37
	6.6579	0.0000	$22t_2 \rightarrow 15a_1$	99.58
	7.9813	0.0000	$22t_2 \rightarrow 16a_1$	97.85
	8.1576	0.0000	$9e \rightarrow 23t_2$	98.65
	8.2282	0.0000	$22t_2 \rightarrow 24t_2$	99.13
	9.2594	0.0000	$9e \rightarrow 9t_1$	99.74

Table S6: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) singlet-triplet transitions

Symmetry	E (eV)	f	Assignment	%
	9.5997	0.0000	$22t_2 \rightarrow 25t_2$	99.54
	9.7810	0.0000	$21t_2 \rightarrow 23t_2$	98.93
	9.9997	0.0000	$8t_1 \rightarrow 23t_2$	96.03
	10.013	0.0000	$14a_1 \rightarrow 23t_2$	93.22
	10.309	0.0000	$7t_1 \rightarrow 23t_2$	94.73
	10.339	0.0000	$21t_2 \rightarrow 10e$	91.56
	10.411	0.0000	$8e \rightarrow 23t_2$	92.05
	10.420	0.0000	$22t_2 \rightarrow 11e$	73.29
			$20t_2 \rightarrow 23t_2$	17.55
	10.446	0.0000	$20t_2 \rightarrow 23t_2$	77.35
			$22t_2 \rightarrow 11e$	18.61
	10.468	0.0000	$22t_2 \rightarrow 17a_1$	97.15
	10.534	0.0000	$8t_1 \rightarrow 10e$	97.98
	10.637	0.0000	$22t_2 \rightarrow 26t_2$	99.06
	10.837	0.0000	$21t_2 \rightarrow 9t_1$	77.20
			$7t_1 \rightarrow 10e$	18.38
	10.855	0.0000	$7t_1 \rightarrow 10e$	79.59
			$21t_2 \rightarrow 9t_1$	18.45
	10.943	0.0000	$9e \rightarrow 24t_2$	97.53
	10.968	0.0000	$20t_2 \rightarrow 10e$	96.84
	10.996	0.0000	$21t_2 \rightarrow 15a_1$	98.06
	11.035	0.0000	$1a_2 \rightarrow 9t_1$	74.60
			$8t_1 \rightarrow 9t_1$	22.99
	11.095	0.0000	$8t_1 \rightarrow 9t_1$	76.12
			$1a_2 \rightarrow 9t_1$	23.82

Table S6: TDDFT (SR-SAOP/TZP//SR-LDA/TZP) singlet-triplet transitions

Symmetry	E (eV)	f	Assignment	%
	11.171	0.0000	$22t_2 \rightarrow 10t_1$	99.54
	11.316	0.0000	$7e \rightarrow 23t_2$	75.52
			$6t_1 \rightarrow 23t_2$	15.37
	11.320	0.0000	$6t_1 \rightarrow 23t_2$	74.34
			$19t_2 \rightarrow 23t_2$	13.34
	11.346	0.0000	$22t_2 \rightarrow 27t_2$	89.45

Importance of the relativistic effects and choice of the functional

Figure S1 shows the excitation spectra (oscillator strengths) calculated with four different methods at the SR-LDA/TZP ground state geometry. The comparison serves as demonstration how important is it to include the relativistic effects and to use a proper functional.

Relativistic TDDFT calculations at SR-SAOP/TZP level of theory are in excellent agreement with electron energy loss spectrum[5] and is discussed in the main text. The inclusion of spin-orbit coupling changes the spectrum only marginally, the reasons for this explained in the main text. Position of the excited states in NR calculations is shifted towards lower energies. Inclusion of relativistic effects is also important for the oscillator strengths – NR calculations are not able to reproduce correctly relative position of the highest intensity peak. Calculations using general gradient approximation, e.g. PW91, Fig. S1 are not able to reproduce high-energy excitations.

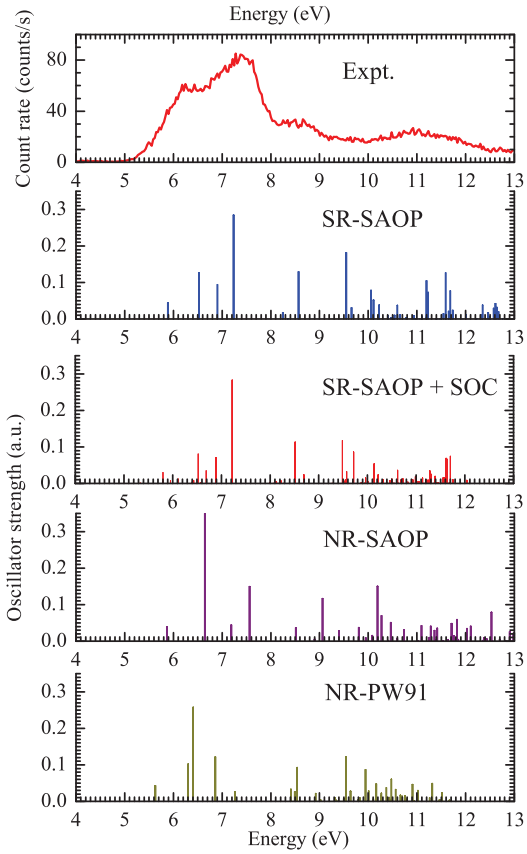

Figure S1: Top panel: Electron energy loss spectrum of $Pt(PF_3)_4$. Lower panels: TDDFT calculated transition energies at different levels of theory (SR-SAOP/TZP; the same with spin-orbit splitting included; NR-SAOP/TZP; NR-PW91); the heights of vertical lines indicate calculated oscillator strengths

Excited states at different Pt−P bond distances

Table S7 lists calculated excited states at SR-BHandHLYP/TZP//SR-B3LYP-D3/TZP level of theory at two different Pt−P bond lengths, at 2.266 Å (equilibrium distance in $Pt(PF_3)_4$ at SR-B3LYP-D3/TZP level of theory) and at 10.000 Å (PF_3 essentially dissociated). Symmetry labels of excited states in C_{3v} point group is given as well. These excited states correspond to those plotted in Fig. 2 in the main text.

The excited states from Table S7 are calculated at different level of theory than those listed in Table S4, as explained in the main text, and are shifted to higher energies for approx. 0.5 eV. All listed excited states at Pt−P bond length of 10.000 Å exactly correspond to those of $Pt(PF_3)_3$ in its ground state energy minimum that are listed in Table S7.

Table S7: TDDFT (SR-BHandHLYP/TZP//SR-B3LYP-D3/TZP) excitation energies (eV) of $Pt(PF_3)_4$ on different Pt−P bond distances and comparison to the excitation energies of $Pt(PF_3)_3$ and symmetry label of the states in C_{3v} point group

	Singlets			Triplets		
	$Pt(PF_3)_4$	$Pt(PF_3)_3{-}{-}PF_3$	$Pt(PF_3)_3$	$Pt(PF_3)_4$	$Pt(PF_3)_3{-}{-}PF_3$	$Pt(PF_3)_3$
Pt−P (Å)	2.266	10.000	–	2.266	10.000	–
A_1	6.3899	5.5861	5.5912	5.46119	4.5323	4.5365
	6.6648	8.0179	8.0219	5.64451	6.8357	6.8400
	7.0558	8.6682	8.6792	6.23193	7.8420	7.8518
	7.7879	8.7361	8.7465	7.15288	8.2036	8.2173
	8.1491	8.7758	8.7832	7.44466	8.4792	8.4858
A_2	6.0946	7.6079	7.6115	5.55630	6.9189	6.9218
	6.6925	8.3972	8.4073	6.49748	8.1073	8.1159
	7.8192	8.5985	8.6046	7.47542	8.4896	8.4964
	7.8363	8.7215	8.7207	7.83484	8.7117	8.7110
	8.4011	9.5425	9.5470	8.28981	9.5499	9.5546
E	6.0946	5.0003	5.0062	5.55630	4.5651	4.5698
	6.2780	6.3020	6.3098	5.64451	5.7272	5.7350
	6.3899	7.8224	7.8256	5.65921	6.9881	6.9915
	6.6925	8.0349	8.0392	6.23193	7.4442	7.4444
	7.0558	8.4355	8.4400	6.49748	7.6280	7.6320
	7.7879	8.5087	8.5182	7.15288	7.8906	7.9000
	7.8192	8.7714	8.7804	7.29160	8.0153	8.0260
	7.9490	8.8941	8.9010	7.44466	8.3955	8.4024
	8.1491	8.9364	8.9411	7.47542	8.6720	8.6820
	8.4011	8.9854	8.9966	8.11793	8.8854	8.8911

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